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SECTION IV

KEY NOTE LECTURES

LCA AS A USEFUL TOOL FOR SUPPORTING THE DEFINITION OF A SUSTAINABLE WASTEWATER TREATMENT PLANT

Almudena Hospido[*]

Group of Environmental Engineering and Bioprocesses, Department of Chemical Engineering, Institute of Technology, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.
*****: *almudena.hospido@usc.es.*

Introduction and study objectives

Water management has been part of human history since its very beginning, being wastewater management slightly more recent. The same happens with treatment, as water treatment also predates wastewater treatment. At the time the first modern water treatment plant was built (i.e. 1804), wastewater treatment was considered unnecessary due to the idea of self-purification. More than a century was need to change human minds and, in 1920, the first full-scale activated sludge started operating in Sheffield. As population increases, so the amount of wastewater and the level of pollution on it do, and, consequently, wastewater treatment plants (WWTPs) have been designed and implemented all over the world in the past two centuries, moving, as does our relationship with the environment, their raison d'être from pollution removal to resource recovery. In this present context, several methods are available to assess the environmental impacts and benefits of WWTPs and, among them, Life Cycle Assessment (LCA) can be considered the best practice, even when there is always room from improvement. Having said this, this keynote presentation will go through the evolution of LCA when applied to WWTPs, since the first studies from the 1990s to year 2017, with focus on the reasons for its application, on the main similarities and also the main differences, as well as its combined application with other environmental and/or economical tools.

Methodology

The speaker will use her own experience and research done on this topic in order to go through the evolution of the LCA as a useful tool for supporting the definition of a sustainable WWTPs. The presentation will be based also on the collaborative publications done in collaboration with researchers from the University of Santiago de Compostela as well as from other foreign institutions.

Particular focus will be paid on the analysis done and the conclusions achieved by:

1) The Working Group (WG) on Life Cycle Assessment of Water and Wastewater Treatment, which is a WG within the International Water Association (IWA) Modelling and Integrated Assessment (MIA) specialist group established in 2013 to facilitate the exchange of ideas and develop consensus regarding methodologies to promote better use of LCA in the anthropogenic water cycle. The seed for this discussion group was the review paper published in 2013 (http://dx.doi.org/10.1016/j.watres.2013.06.049) and nowadays is still active on Linked-In (https://www.linkedin.com/groups/4921250) with 322 members.
2) The Task Force (TF) Environmental Assessment within the WG3 Environmental and economic impact (http://www.water2020.eu/wg3-environmental-and-economic-impact) of the COST action Water2020. One of the main outputs of this TF has been the publication of a chapter "Assessing environmental impacts and benefits of wastewater treatment plants" included in the coming book entitled "Wastewater Treatment & Resource Recovery Technologies: Impacts on Energy, Economy and Environment" (ISBN: 9781780407869), which aims at presenting the basic steps of LCA as described in the ISO standards and at exemplifying, by means of four cases studies, its application and expected outcomes and usefulness.

Results and conclusions

The talk will come to an end with the identification of the still existing challenges that require further development to fully cover all relevant environmental aspects of the WWTP of the future.

Acknowledgment

The speaker is grateful to all the researchers that, from different approaches and with diverse objectives, believe LCA is a useful tool to assess the environmental performance of individual technologies and complete processes for wastewater treatment, as well as those that have contributed to the continuous development of the methodology.

"Coming together is a beginning, staying together is progress, and working together is success." – Henry Ford

NOVEL 2D COMPOSITE THIN LAYERS FOR SUSTAINABLE WASTEWATER TREATMENT

Anca Duta*, Ion Visa, Cristina Bogatu, Maria Covei,
Dana Perniu*

R&D Centre: Renewable Energy Systems and Recycling, Transilvania University of Brasov, Romania;29, Eroilor Bvd. 500036 Brasov, Romania,
**: a.duta@unitbv.ro*

Introduction and study objectives

According to the *Nature* report of Jan Eliasson (deputy UN General Secretary), by 2025 more than 1.8 billion people will experience water scarcity, while two thirds of the world population will face water shortage; these are related to common and emergent pollutants discharged in the environment at much higher levels than regulated, either as lack of proper treatment (or lack of any treatment at all) or due to the cumulative effect of long term discharge, allowed by the legal frame. While the first has legal remediation instruments, the latest poses a significant risk, as most of the pollutants in this situation were evidenced in water only in the past decade(s) as result of progresses in the analysis equipment, although the contaminants were intensively used in the 50 years. Not being watched at discharge but also in the water sanitation steps, these pollutants are actually part of our daily life and are responsible for significant (and negative) consequences. Therefore, the EU directive 2013/39/EU extended the list of priority substances along with new/updated environmental quality standards to be met by 2021 (updated values, e.g. for phenols) or 2027 (for new micro-pollutants); further on, in 2015 the EU watch list (EC Decision 495/2015) was extended with 10 new groups of substances, including pesticides, antibiotics and hormones.

Conventional WWTP are not fully prepared to mitigate the emergent organic contaminants (EOC) down to what we currently consider as acceptable discharge concentrations; on the other hand, membrane technologies can be efficient in micro-pollutants removal, but are energy intensive, use rather expensive equipment, and raise significant concerns on the concentrate that needs special disposal technologies.

Thus, the WWT concept should focus on mineralization to break EOCs in non-harmful components and advanced oxidation processes (AOPs) are well suited to fulfill this task. The main barriers in scaling up heterogeneous photocatalysis impose sustainability increase and reducing the cost of treated water. This asks for low cost activation energy and solar radiation is the most obvious candidate; thus photocatalysis needs Vis-active materials, obtained using low cost and environmental friendly precursors, through low-energy intensive, up-scalable technologies. An additional request for real technology transfer asks for simple WWT-AOP (thus films are preferred to suspensions), able to deal with large amounts of polluted water resulted from the conventional treatment processes (thus continuous flow processes). Last but not least, the energy consumed during these processes should be “green”, i.e. obtained from renewables.

This presentation touches all these points and presents a rather new concept of Vis-active 2D thin layers composites integrated in a continuous flow photoreactor, powered by a PV array.

The Design Prerequisites: Photovoltaics represent the well-known 2D composite structures activated by solar radiation. Therefore, an aqueous-stable photovoltaic cell should be a Vis(solar) active photocatalyst; this rules out the silicon-based n-p junctions but leaves room for the photovoltaics of the 3rd and 4th generation: 2D composites of n-type wide band gap semiconductors (MOx, M: Ti, W, Zn etc.) interconnected with p-type narrow band gap semiconductors. Considering the PVs development, the best suited candidates are the sulfides as $CuInS_2$ (to be avoided as In is a scarce/critical material), or Cu_xS (to be avoided due to photo-corrosion) or Cu_2ZnSnS_4 (CZTS).

The MOx/CZTS photocatalyst should be able to function 24/7, thus also during the night and in cloudy days. Therefore, highly efficient structures are required and these should be powered by renewables. In a fully circular concept, powering should come from PVs, (e.g. Si- based, CdTe, etc.).

Methodology

Novel 2D composite structures were obtained by an easily up-scalable technique (Spray Pyrolysis Deposition, SPD) and their photocatalytic efficiency proved to be very good in the phenol and imidacloprid removal. The tests at low Vis-irradiance values allowed kinetic modelling while tests on the solar-simulator (500 and 1000 W/m^2) allowed estimating the energy input supporting wastewater processing when solar radiation is not available. Based on, the PV array required for powering the system is estimated and the initial investment and operational costs can be calculated and benchmarked (e.g. with RO).

Results and discussions

One key issue governing the novel photocatalytic/photovoltaic structure is the interfacial control among the n and p-type layers in the FTO/TiO_2/CZTS 2D structure. The roles of crystallinity and morphology are of outmost importance, but there are some limits that can hardly be overstepped (the size and type of the crystalline cells in TiO_2 and CZTS, the significantly different morphology of the pristine layers, etc.). Therefore optimization results are presented considering CZTS doping and/or the use of a buffer layer, with the main role in increasing the interfacial compatibility. Imidacloprid (5ppm) removal reached efficiencies close to 90% after 6 hours of Vis-irradiation (9W/m^2), in a continuous flow thin film photoreactor, while phenol removal (as expected) runs with a slower TOC decrease. Based on these results, PV array preliminary calculations showed an average energy consumption of 1.44 Wh/L/m^2. Considering an average flow rate of 330 L/h of wastewater flowing over a 1m^2 of photocatalytic film, each day allows the treatment of 2,5 m^3; the average yearly energy demand can be met by a tracked PV array with 7 poly-crystalline PV modules. These values are fully up-scalable through batteries of plate-photoreactors and proportionally larger PV arrays.

Acknowledgement:

This work was supported by a grant of the Romanian Authority for Scientific Research and Innovation, CNCS/CCDI-UEFISCDI, project no. PN-III-P2-2.1-PED- 2016-0514, under PNCDI III.

SUSTAINABLE PRODUCTION OF MATERIALS, CHEMICALS AND ENERGY FROM BIOMASS AND BIOWASTE

Anton Friedl

TU-Wien, Institute of Chemical, Environmental and Biological Engineering
Getreidemarkt 9/166, 1060 Vienna, Austria
[*]: anton.friedl@tuwien.ac.at

Due to increasing uncertainties of fossil resources as basis for many products and energy supply new resources are under investigation. A valuable bio based resource are various types of biomass and assorted collected and pre-separated municipal organic waste has been recognized as a valuable resource for the sustainable production of material, chemicals and energy carriers. Within the European Community a goal has been defined to increase the recycling rate from municipal waste from 44% to 70%. Until 2030 the plane is that only 10% of the waste is needed to be deposited.

The application of a cascaded valorization process for utilizing these resources in form of biorefinery concepts is considered to be favorable both for ecologic and economic reasons. Therefore, it is suggested to firstly extract/produce high-priced material and chemicals followed by the production of fuels and energy carriers. Electric power and thermal heat can be generated in a final step. Residuals of this cascade will be converted to fertilizers.

The International Energy Agency (Task 42) defines a biorefinery as "The sustainable processing of biomass into a spectrum of marketable products". The target of a biorefinery is the conversion of various biomass in a cascaded use and integrated processing with the aim of using all substrate components and also valorization of waste and byproducts into competitive products. This can be a replacement of products which are identical in chemical composition to existing products, but based on renewable resources or a substitution of products which have a different chemical composition to existing products, but a similar functionality.

Already existing biorefineries are sugar and starch factories as well as bioethanol production with the products bioethanol and the byproduct DDGS (distiller dried grain and solubles) which is produce in the same amount that the main product.

For the development of new biorefinery concepts two principal ways are possible the bioproduct driven direction producing e.g. pulp&paper and lactic acid or the bioenergy driven way producing bioethanol via fermentation or Fischer-Tropsch biofuels via a gasification process.

Available treatment and separation processes are of mechanical, physical, chemical or thermochemical, biochemical as well as combinations thereof. As substrates can be used sugar, starch, lignocellulosic material consisting of cellulose, hemicellulose and lignin, plant oil and protein.

Bioproduct driven biorefineries can provide cellulosic fibers for clothes or paper, acetic acid, vanillin, lactic acid for the production of PLA and a very interesting product group can been derived from lignin which is focus af many research activities.

The US Department of Energy published 2004 the "TOP 10" biobased chemicals. In 2010 this list has been adapted from Sandén and Pettersson to following chemicals biohydrocarbons (e.g. isoprene), lactic acid, ethanol, succinic acid, furans (furfural, HMF, FDCA), hydroxypropionic acid/aldehyde, levulinic acid, glycerol and derivates, sorbitol and xylitol.

Bioenergy driven biorefineries have a focus on bioethanol produced via fermentation with sugar, starch or lignocellulosic substrates. Biodiesel can be produced from plant oil via transesterification with glycerol as byproduct. As an alternative route, the biological and thermal gasification processes are available with products like methane, hydrogen, methanol, dimethylether, Fischer-Tropsch diesel, mixed alcohols, aldehydes and isobutan.

The development of the so-called second-generation biofuels are intensively studied and large-scale installations are planned or already build. Details about these plants can be found on the IEA Bioenergy Task 39 webpage organized from bioenergy 2020.

An interesting route is the CO_2 conversion via algae process. Target products are higher value products like omega 3 fatty acids or algae oil that can be converted to biodiesel.

Important for the development of new biorefinery routes is the evaluation of the material use efficiency, the energy efficiency as well as the evaluation ecological impacts using life cycle analyses (LCA). Putting these results together will ensure the development of efficient and sustainable production of materials, chemicals and energy.

Literature:

http://demoplants.bioenergy2020.eu/
Sandén B., Pettersson K., SYSTEMS PERSPECTIVES ON BIOREFINERIES, 2013
Chalmers University of Technology ISBN 978-91-980973-2-0

PROCESS EVALUATION OF BIOLOGICAL PROCESSES BASED ON THE REMOVAL AND TRANSFORMATION OF EMERGING CONTAMINANTS

Thomas Ternes*, Arne Wick, Kevin Jewell, Gudrun Nuerenberg, Per Falas, Adriano Joss, Jörg Oehlmann

Federal Institute of Hydrology (BfG), Koblenz, Germany
: ternes@bafg.de

So called "emerging contaminants" are recently detected in wastewater and environmental matrices up to several µg/L, although they might already be present for decades. Innovative analytical instrumentation enables the identification and quantification of organic contaminants down to the lower nanogram per litre and nanogram per kg range. Prominent examples of emerging contaminants are pharmaceuticals, estrogens, ingredients of personal care products, biocides, flame retardants, benzothiazoles, benzotriazoles or perfluorinated compounds. In wastewater treatment plants (WWTPs), during soil passage and in surface waters many of these emerging contaminants are converted to appreciable portions into transformation products (TPs).

Thus, surface water and groundwater contain frequently a very complex mixture of contaminants and their TPs at the sub-mg/L range comprising an extreme high variety of different properties such as polarity, sorption affinity, biodegradability, chemical reactivity or UV-stability. It is even known that drinking water in some locations contains an appreciable number of emerging contaminants and TPs. Neither, the ecotoxicological impact nor the human health impacts of those mixtures are currently well understood.

Currently, it is very challenging to evaluate biological treatment processes using only a limited number of selected target compounds without considering the formation of stable transformation products and without considering the complexity of compounds present. Thus, a concept was developed combining target and non-target analysis of emerging compounds their transformation products as well as results of a set of in-vitro bioassays for evaluating biological processes.

Chemical target analysis of emerging micropollutants as well as newly developed non-target approaches considering thousands of potential micropollutants and TPs have been developed. A non-target analysis workflow enables the evaluation of different wastewater treatment processes. Moreover, the formation and the removal of TPs can be assessed. Individual TPs have been identified for more than 15 emerging micropollutants and were quantified with the target compounds in pilot plants as well as in full-scale WWTPs.

Results indicate that the compound composition in cascaded reactors change significantly, particularly for treatments at different redox conditions (i.e. aerobic pre-treatment followed by anoxic and anaerobic post-treatment) or including biofilm reactors. Thus, further degradation of wastewater-born compounds by the anaerobic post-treatment occurs and further supported the results from target analysis that the process combinations covering aerobic and strictly anaerobic conditions as well as biofilm reactors broaden the range of micropollutants being removed.

Diclofenac can be removed effectively in a cascaded hybrid moving bed biofilm reactor (hybrid-MBBR) achieving nitrification and denitrification. The degradation primarily occurred in the last compartment containing the carrier-attached biomass. In this study, a fast dissipation was observed but many TPs were formed which were further degraded. Due to the highly branched nature of the transformation pathway, these are mostly present at very low concentrations in the WWTP effluent

The presentation provides an overview about the transformation pathways of selected emerging compounds, the evaluation of different biological processes and the potential of biological processes to enable an overall removal of emerging compounds.

SUSTAINABILITY ASSESSMENT AND MANAGEMENT IN THE CONTEXT OF CIRCULAR ECONOMY

Adisa Azapagic

The University of Manchester, UK
adisa.azapagic@manchester.ac.uk

It is now widely accepted that sustainability performance should be assessed on a life cycle basis, taking into account environmental, economic and social aspects. With the drive towards the implementation of the circular economy concept, measuring and managing sustainability is becoming increasingly more important. However, it is not clear yet how this should be carried out and what methods and tools may be best suited to guide the development of a circular economy. In an attempt to stimulate a debate on this topic, this talk will discuss current practice in sustainability assessment and how it may need to be developed further in the context of circular economy.

WATER AND WASTEWATER CYCLES: TECHNOLOGIES, RECYCLING AND VALORIZATION

Francesco Fatone[1,*], Christian Loederer[2], Thomas Wintgens[3]

[1) Coordinator of the Horizon2020 "SMART-Plant", Department of Materials, Environmental and Urban Planning Science and Engineering, Faculty of Engineering, Polytechnic University of Marche, Ancona, Italy
[2) Coordinator of the Horizon2020 "POWERSTEP", Berlin Competence for Water, Germany;
[3) Coordinator of the Horizon2020 "AquaNES", University of Applied Sciences and Arts Northwestern Switzerland
[*]: f.fatone@univpm.it

Introduction and study objectives

According to the UN WATER (2017) "In the face of ever-growing demand, wastewater is gaining momentum as a reliable alternative source of water, shifting the paradigm of wastewater management from 'treatment and disposal' to 'reuse, recycle and resource recovery'. Wastewater can also be a cost-efficient and sustainable source of energy, nutrients, organic matter and other useful by-products. The potential benefits of extracting such resources from wastewater go well beyond human and environmental health, with implications on food and energy security as well as climate change mitigation". Several novel key enabling management options, technologies and potential value chains have been studied to comply with local frameworks and to maximize the multiple potential benefits

However, the technology readiness level of the investigated eco-innovative solutions was often not sufficient to demonstrate the economic, financial and environmental sustainability of new value chains and business models. On the other hand, for the water sector the transition to a circular economy presents an opportunity to accelerate and scale-up recent scientific and technological advances that support greater efficiency in the sector (IWA, 2017).

Methodology

Within Horizon2020 a number of Innovation Actions (e.g. SMART-Plant (www.smart-plant.eu), POWERSTEP (www.powerstep.eu), AquaNES (www.aquanes.eu)) are scaling-up in real environment eco-innovative solutions and related value chains, that are studied and assessed considering even the demand, regulation and policy and social aspects. These are paving three interrelated pathways, related to water, energy and materials, that can make the water utilities and industries the engines of the circular economy.

Results and conclusions

As far as the **materials pathway** is concerned, the Horizon2020 SMART-Plant proves the feasibility of circular management of urban wastewater and environmental sustainability of the systems and co-benefits of scaling-up water solutions through Life Cycle Assessment and Life Cycle Costing approaches. SMART-Plant is scaling-up in real environment eco-innovative and energy-efficient solutions to renovate existing wastewater treatment plants and close the circular value chain by applying low-carbon techniques to recover materials that are otherwise lost. 7+2 demo systems are being optimized for more than 2 years in real environment in 5 municipal water treatment plants, including also 2 post-processing facilities. The systems are automated with the aim of optimizing wastewater treatment, resource recovery, energy-efficiency and reduction of greenhouse emissions. A comprehensive SMART portfolio comprising biopolymers, cellulose, fertilizers and intermediates will be recovered and processed up to the final end-products. Therefore, opportunities of SMART-Plant are: (1) for providing state of the art innovative technology the water treatment landscape, as SMART-Plant will address needs of water utilities for reducing overall costs, while improving the quality of treatment and compliance to regulations; (2) for granting access to new feedstock sources to chemical and its downstream industry, as SMART-Plant will make available a full portfolio of products by in situ biochemical conversion of recovered resources.

As far as the **energy pathway** is concerned, the Horizon2020 POWERSTEP is proving the feasibility of energy positive municipal wastewater treatment plant. Thanks to 6 full-scale case studies located in 4 European countries POWERSTEP will merge treatment scheme modelling and design, global energy and heat management, carbon foot-printing, integrated design options. Beyond the definition and demonstration of new concepts, POWERSTEP is demonstrating the replicability of the approach in order to accelerate the market uptake.

As far as the **water pathway** is concerned, the Horizon2020 AquaNES is catalyzing innovations in water and wastewater treatment processes and management through improved combinations of natural and engineered components. The project focuses on 13 demonstration sites in Europe, India and Israel covering a representative range of regional, climatic, and hydro geological conditions. Among the demonstrated solutions are natural treatment processes such as bank filtration (BF), managed aquifer recharge (MAR) and constructed wetlands (CW) plus engineered pre- and post-treatment options.

The keynote presentation will critically review the advances of these relevant Horizon2020 innovation actions as state-of-the-art of the European R&D&I ready-to-market eco-innovative solutions. In addition, solutions to overcome the barriers to overcome the barriers to circular economy in the water sector will be presented with major focus to the Innovation Deal on water reuse.

Acknowledgments

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SECTION I

ENVIRONMENTAL BIOTECHNOLOGY IN THE CIRCULAR ECONOMY

SELECTION OF MARINE BACTERIA WITH POTENTIAL ABILITY TO PRODUCE POLYUNSATURATED FATTY ACIDS

**Noura Raddadi*, Roberta Romano, Lucia Giacomucci,
Fabio Fava**

Department of Civil, Chemical, Environmental and Materials Engineering (DICAM),
University of Bologna, Italy
via Terracini 28, 40131 Bologna, Italy.
**: noura.raddadi@unibo.it*

Introduction and study objectives

Marine environment constitutes one of the most promising resources for the discovery of new microbial species with the ability to produce compounds that could be of interest for industrial biotechnology. It has been reported that both microbial diversity as well as metabolic capabilities of marine-dwelling microorganis are still underexplored. Hence studies directed to unravelling the microbial diversity and discover new metabolic capabilities are very encouraged for a sustainable blue growth. Specifically, marine microbes and their products including enzymes, antimicrobial compounds as well as pigments and long-chain polyunsaturated fatty acids (LC-PUFAs) are getting increasing interest in the frame of the marie biotechnology sector.

LC-PUFAs are essential nutrients that have to be supplied by the diet and there is an increasing interest in their application in food and pharmaceutical industries as well as aquaculture feeds. Hence, the demand for LC-PUFAs continues to grow. Currently, fish oil is the main source of LC-PUFAs and it has been reported that more than 75 % of fish oil is used for aquaculture. Consequently, the sustainability of the aquaculture system necessitates of further available sources for the LC-PUFAs supply. Bacterial production of LC-PUFAs could be a promising alternative to fish oil. Currently, LC-PUFAs production by bacteria has frequently been reported from deep ocean habitats and cold marine environments by relatively low number of bacterial genera. To the best of our knowledge, investigation of LC-PUFAs production from Mediterranean sea has not performed yet. The aim of this study was to test the ability of 114 isolates obtained from marine sediments to produce LC-PUFAs.

Methodology

Isolation of the marine bacteria was performed from sediment samples collected from three sites located in the south of Italy by spreading serial dilutions of grinded sediment samples in sterile 3 % saline solution on agar plates of modified mineral salt medium (mMSM) containing 1 % (w/v) of glucose as the major carbon source. The plates were incubated at 20 °C or 30 °C and the bacterial isolates were purified after three successive streakings on the same medium.

A primary screening for LC-PUFAs production was performed on bacterial cells after growth in liquid modified mineral salt medium (mMSM). After 72 h of growth, 0.1 % (w/v) of the dye 2,3,5-triphenyltetrazolium chloride (TTC) was added to the growth broth and the samples were incubated at room temperature for 20 to 30 min. The formation of pink colour was scored as a positive result. Furthermore, several bacterial isolates among the collection were grown in seawater supplemented with glucose and yeast extract and their ability to reduce TTC was evaluated as described before.

Results and conclusions

A total of 114 bacterial isolates were obtained from marine sediments collected in three harbors in the Med sea, after several successive streaking on mMSM agar medium. The isolates were shown to grow in liquid medium and were screened for the LC-PUFAs production. Among these, 56 isolates including 26 grown at 20 °C and 30 at 30 °C are potentially LC-PUFAs producers based on their ability to produce the pink colour in the colorimetric assay. Further screening for LC-PUFAs production performed on 25 out of the 56 isolates resulted in the selection of fourteen of them able to grow in seawater and reduce the TCC. Additional studies aiming to confirm LC-PUFAs production and to characterize the produced fatty acids are in progress.

With regard to the isolates identity, partial 16S rRNA gene sequencing performed on most of the isolates revealed the bacteria to be mainly from the genera *Marinobacter, Thalassospira,* and *Halomonas*. Although there are reports on the production of LC-PUFAs from marine bacteria, to the best of our knowledge, there have been no reports on the investigation of these interesting biotechnological traits from the genera reported in this study.

SCREENING OF DIFFERENT ADSORBENT MATERIALS FOR BIO-BUTANOL SEPARATION

**Francesca Raganati[1], Alessandra Procentese[2],
Giuseppe Olivieri[1], Maria Elena Russo[2], Antonio Marzocchella[1]**

[1)] *Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale - Università degli Studi di Napoli Federico II, P.le V. Tecchio 80, 80125 Napoli, Italy*
[2)] *Istituto di Ricerche sulla Combustione– Consiglio Nazionale delle Ricerche, P.le V. Tecchio 80, 80125 Napoli, Italy*
**: francesca.raganati@unina.it*

Introduction and study objectives

The Acetone-Butanol-Ethanol (ABE) fermentation was a consolidate process to produce butanol during the first half of the last century but its modern industrial success is hindered by several issues. The selection of a technology for recovering low-concentration butanol from fermentation broth that is characterized by high recovery/selectivity performance and low energy request is a key issue for a successful bio-butanol production process. Several recovery processes were analysed in the literature and the adsorption was found to be very promising. This contribution reports on the butanol recovery by means of adsorption. The focus was on the selection of the adsorbent to maximize the butanol recovery. Three materials were characterized in terms of solvent adsorption capacity: Amberlite XAD7, Amberlite XAD4 and Zeolite Y.

Methodology

Batch liquid phase adsorption equilibrium tests were carried out in closed 50 mL vials.. The vials contained pre-set mass of butanol, acetone, ethanol, water and adsorbent. Typically, 0.5 g adsorbent were dispersed in 25 mL solution. The suspension was agitated by a shaker with agitation at 120 rpm under controlled temperature conditions. The tests were carried out at 25, 30, 37, and 45 °C to assess the effects of the temperature on the adsorption. The initial concentration of the adsorbed species ranged in a wide interval. The adsorption tests were carried out until equilibrium conditions was approached: typically within 24/48 h. The concentration q of a sorbate (i) for unit of mass of adsorbent (a) was calculated by means of the mass balance referred to the sorbate Eq. (1).

$$q_{e,i} = \frac{(c_{i,0} - c_{i,e}) \times V_0}{m_{a,0}} \qquad (1)$$

where qe,i is the mass of adsorbate per unit mass of adsorbent at the equilibrium, ci,0 the initial concentration of sorbate in the solution, ci,e the concentration of the adsorbate in the solution at the equilibrium, V0 the volume of solution in contact with adsorbent, and ma,0 the mass of the adsorbent.

Results and conclusions

Figure 1 reports the adsorption isotherms of butanol, acetone and ethanol assessed for binary solvent/water solutions for the three investigated adsorbent materials. The isotherms were measured at the investigated temperature: 25, 30, 37, and 45 °C. The investigated material adsorbed all the solvents. The butanol was characterized by the highest affinity among the investigated solvents for all the tested materials. Acetone and then ethanol were characterized by lower affinity than the butanol. The observed scale of affinity was expected and it may be rationalized in terms of the relative hydrophobicity of the adsorbates and the hydrophobic character of the adsorbent.

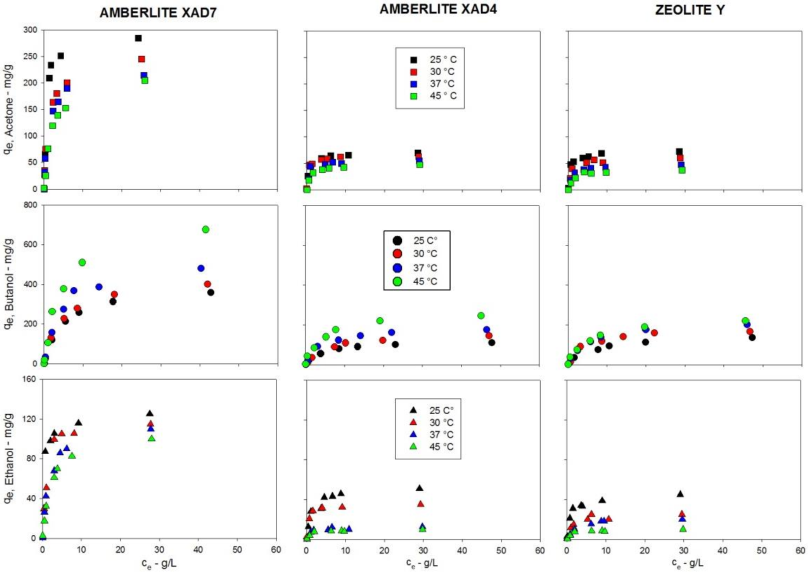

Figure 1: Amberlite XAD7, XAD4 and Zeolite Y adsorption isotherms.

The analysis of Figure 1 points out that the adsorption capacity of Amberlite XAD-4, Amberlite XAD-7 and Zeolite Y increased with the temperature for butanol and decreased with the temperature for acetone and ethanol. The observed phenomenon may be interpreted taking into account that the temperature affect not only the adsorption process but also the solubility of the adsorbate in the liquid solution. On one hand, the solubility of solvents as acetone and ethanol have positive temperature coefficients and the adsorption is progressively less promoted with the temperature. On the other hand, the solubility of butanol decreases with the temperature (negative ptemperature coefficient) and the adsorption capacity is progressivley more promoted with the temperature.

Acknowledgements

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EVALUATION OF THE BIODEGRADABILITY OF DIFFERENT PETROLEUM-DERIVED PLASTICS BY AEROBIC BACTERIA

Lucia Giacomucci, Noura Raddadi*, Michelina Soccio,
Nadia Lotti, Fabio Fava

Department of Civil, Chemical, Environmental and Materials Engineering (DICAM),
University of Bologna, Italy.
via Terracini 28, 40131 Bologna, Italy.
**: noura.raddadi@unibo.it*

Introduction and study objectives

In 2015, global and European plastic productions were 322 and 58 million tons, respectively. About 64% of the total European plastic demand is mainly for polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) and polystyrene (PS). Over one-third of plastics is used to produce disposable products, such as packaging, disposable bags, *etc*., with a lifespan of 3 years. The high amounts of plastics produced yearly resulted in their accumulation in the environment leading to esthetic and environmental concerns. In specific, plastics have been reported to be among the main components of marine litter, leading to further environmental and health issues following the fragmentation of macroplastics to microplastics that can exert toxic effect on marine biota and even enter the food chain. To date, little is known about microbial degradability of the petroleum-deriving polymers/plastics and most available literature reports are dealing with biodegradable plastics.

The aim of this study was to evaluate the ability of five culture collection bacterial strains to degrade PE, PP, PS and PVC films under aerobic conditions.

Methodology

Five culture strains, i.e. *Pseudomonas chlororaphis, Pseudomonas citronellolis, Bacillus subtilis, Bacillus flexus* and *Chelatococcus daeguensis,* were purchased from culture collection and screened for their ability to degrade PE, PP, PS and PVC films. In a primary screening, plastic films were cut into 3 cm x 3 cm pieces, sterilized by immersion in 70% ethanol for 30 min, dried and added as unique carbon source at a final concentration of 2 g/L. The experiments were performed in 100 mL shake flasks containing 30 mL of mineral salt medium and the bacterial incubation was performed on an orbital shaker (150 rpm) at 30°C for 3 months. A set of abiotic controls were also setup. Based on the results of the primary screening, PVC biodegradation process was scaled up to a final volume of 1 L using neat PVC with the two strains showing biodegradation abilities. Finally, further experiments were set up in order to evaluate the ability of the most active strain to grow and degrade sterilized as well as non-sterile waste PVC films recovered from fruits or vegetable packaging. Bacterial growth and adhesion on films surfaces were estimated by plate counting and by determining adhered protein concentration (Crystal violet or Lowry method). Chemical analyses including gravimetric weight loss; Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and gel permeation chromatography (GPC) were performed to detect physical/chemical changes in the plastic films.

Results and conclusions

In the first experiment, planktonic bacterial cell count, monitored for the whole duration of the experiment (3 months), showed a progressive decrease of the CFU/mL for all strains, suggesting bacterial adhesion on film surfaces. Biofilm formation was confirmed for two strains grown with PE and one with each of PP, PS and PVC according to crystal violet and Lowry assays. After 90 days of incubation, plastic films were subjected to washing for the removal of adhered bacterial cells followed by chemical analysis. The results showed that no microbial attack has occurred for PE, PP and PS. However, partial PVC films degradation was detected after incubation with *P. citronellolis* and *B. flexus* strains. Specifically, gravimetric weight losses of 8.17±1.00 % and 6.41±0.72 % were recorded for the films incubated with *P. citronellolis* and *B. flexus*, respectively; compared to 3.20±0.27 % in the case of abiotic control. Based on these results, the strain *P. citronellolis* was selected for biodegradation assays of PVC film at the end of its work life using PVC wastes subjected to two sterilization methods and without the sterilization step. The results showed that when incubated in the presence of PVC waste films, *P. citronellolis* exhibited even higher activity compared to that observed against neat PVC. Specifically, waste PVC films showed a gravimetric weight loss of up to 18.58±0.01% compared to neat PVC films which exhibited up to 13.90±6.84 %. TGA curves of PVC samples incubated with the bacterium move towards higher temperatures compared to that of non-incubated films, suggesting strain ability to reduce the additives amount in waste PVC.

In conclusion, this work presented the biodegradative abilities of *P. citronellolis* and *B. flexus* towards PVC film. Both strains were shown to apparently act against PVC additives.

Acknowledgements

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CHARACTERIZATION OF A LEAD-RESISTANT BACTERIAL STRAIN ISOLATED FROM POLLUTED SEDIMENTS OF SARNO RIVER MOUTH, CAMPANIA, ITALY, AND ITS POSSIBLE USE IN BIOREMEDIATION OF NATIVE SEDIMENTS

Milva Pepi[1,*], Cecilia Balestra[1], Stella Tamburrino[2], Mario Sprovieri[2], Maria Saggiomo[1], Marco Borra[1], Elio Biffali[1], Raffaella Casotti[1]

[1)] *Stazione Zoologica Anton Dohrn, Napoli, Italy;*
[2)] *Istituto per l'Ambiente Marino Costiero (IAMC)-CNR, Napoli-Campobello di Mazara, Trapani, Italy*
[*]*:* milva.pepi@szn.it

Introduction and study objectives

Lead (Pb) is one of the most diffused pollutants in the environment originating from industrial activities as production of ceramics and batteries. Lead can induce changes in the conformation of nucleic acids and proteins, inhibit enzyme activity, originate disorder in membrane functions and alter oxidative phosphorylation.

Despite the high toxicity of lead, many microorganisms have evolved mechanisms of lead-resistance including metal biosorption by extracellular polysaccharides, precipitation, cell exclusion, sequestration as insoluble phosphates, intracellular lead bioaccumulation, improved siderophore production and metal ion efflux out of the cells. Microbial extracellular polymeric substances, including biofilm, are very versatile structures enclosed within extracellular polymeric substances (EPS) secreted by microorganisms, and constitute central elements in heavy metal biosorption and bioremediation.

The Sarno River receives wastes from industrial areas it crosses, and buries high loads of heavy metals in sediments near its mouth, in the Gulf of Naples, Italy.

This study was finalized to the isolation of an autochthonous lead-resistant bacterial strain from polluted sediments at the mouth of the Sarno River, Campania, Italy, and its characterization, for possible bioremediation processes of native sediments.

Methodology

Sediment samples were collected in April 2014 by a VanVeen grab. Enrichment cultures were arranged for lead-resistant bacteria isolation. Resistance of the isolated bacterial strain to the presence of different heavy metals was evaluated by the minimum inhibitory concentration (MIC) tests.

Genomic DNA of isolate was extracted and 16S rRNA gene sequenced using the primers 27f and 1495r. The whole 16S rDNA gene was sequenced and compared with those retrieved from databases (GenBank and RDPII). Sequences were aligned with ClustalW included in the MEGA 6.1 software package.

Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) was performed using a JEOL JSM 6500-F (JEOL, Tokyo, Japan). The lead removal rate Re was obtained by the following equation: Re = (C_f-c - C_f-e)/ C_i × 100% where C_i = initial concentration, C_f-c = final concentration from control group, and C_f-e = final concentration from experimental group.

Results and conclusions

A Pb-resistant bacterial strain was isolated from enrichment cultures from sediments polluted by Pb, and named Pb15. Sequencing of 16S rRNA gene assigned the isolate to the genus *Bacillus* with nearest type strain *B. pumilus* SAFR-032 (NR_074977), an UV and H_2O_2 resistant strain, isolated from a sterility box. Spore-forming *Bacillus* species are commonly found in extreme environments, such as also the Sarno River mouth sediments, as responses to adaptive strategies to survive in these environments.

Minimum inhibitory concentrations (MICs) in the presence of Pb(II) was 4.82 mmol l^{-1} a much higher value than reported in the literature (from 1.4 mmol l^{-1} to 2.5 mmol l^{-1}), suggesting that this strain could experience frequent exposure to Pb in nature. Strain Pb15 also showed resistance to other toxic elements present in the same sampling site such as Ar, suggesting that autochthonous isolates are to be preferred for bioremediation purposes, being less exposed to other environmental toxicants than exogenous strains.

Pb biosorption was detected by ICP-AES, and removal rates (Re) of 31.02% in the presence of 100 µg ml^{-1} of Pb(II) and of 28.21% with Pb(II) 250 µg ml^{-1} were calculated. Controls, consisting in medium culture without bacteria added, in the presence the two concentrations of Pb(II) showed an almost full recovery of the inoculated Pb(II), with a removal rate (Re) of 3.45% and 0.6% in the presence of additions of 100 µg ml^{-1} and 250 µg ml^{-1}, respectively.

Elemental analysis by SEM-EDS showed presence of Pb in the precipitate of the cultures of Pb15, suggesting that this strain is able to take and accumulate the metal once added to the culture medium. A percentage of about 14% of original inoculated Pb was measured in the bacterial biofilm of Pb15 strain grown in the presence of 100 µg ml^{-1} Pb(II).

Bacterial extracellular polymeric substances (EPS) contain high molecular weight compounds with charged functional groups and possess both adsorptive and adhesive properties. Due to the presence of charged moieties, EPS preferably serve as natural ligand bases, providing binding sites for other charged particles/molecules including metals.

This study provides evidence that the isolated strain *Bacillus* sp. Pb15 is resistant to Pb(II), and to a lesser extent to other heavy metals, and shows potentials for being used for Pb removal from contaminated sediments from the Sarno River, based on its biofilm properties and growth and Pb removal rates. For the first time a bacterial strain resistant to heavy metals was isolated from this polluted area. Further studies are in progress to explore the potential of the isolate.

BIODEGRADATION AND DETOXIFICATION OF BASIC BLUE 41 BY *PICHIA KUDRIAVZEVII* ISOLATED FROM TEXTILE DYE EFFLUENT

Crăița Maria Roșu[1,*], Mihaela Avădanei[2], Daniela Gherghel[1], Cosmin Mihai[1,3], Marius Mihășan[4], Gabriela Vochița[1]

[1]Department of Experimental and Applied Biology, Institute of Biological Research Iasi, 700107, Romania
[2] Department of Physics of Polymers and Polymeric Materials, "P. Poni" Institute of Macromolecular Chemistry, Iasi, 700487, Romania
[3]Interdisciplinary Research Department – Field Science, "Al. I. Cuza" University of Iasi, 700506, Romania
[4]Department of Biology, "Al. I. Cuza" University of Iasi, 700506, Romania
[*]: craita2002@yahoo.com

Introduction and study objectives

Dye containing effluents from textile, paper, cosmetics and food industries constitute a relevant problem of environmental pollution related to the high level of toxicity of textile dyes and their biodegradation products. Azo dyes are the most common group of synthetic dyes and represent 60 – 70% of 10,000 dyes and pigments used in textile industry. The major concern related to their presence in aqueous ecosystems is coming from their colour, which affects water transparency and gas solubility, diminishing photosynthetic activity and finally causing toxic effects on aquatic flora and fauna. Also, due to the presence of azo bond (N=N) bearing aromatic rings and of sulfonate groups (some of them) they are highly recalcitrant to biodegradative processes. Many azo dyes and/or their degradation metabolites have been proven to be mutagens or carcinogens to humans. In the last decades, efforts in efficient removing of textile dyes from aqueous effluents have been made. One of the most promising bioremediation technologies, environmental friendly, involves biotreatment of wastewater with yeast cells. The purpose of the research was to characterize the efficiency of biodegradation and detoxification of textile azo dye Basic Blue 41 by ascomycetous yeast *Pichia kudriavzevii* CR-Y103.

Methodology

The ascomycete yeast was isolated from a local textile dyeing wastewater treatment plant (Iasi, Romania) and identified according with 26S rDNA partial gene sequence, using colony – PCR technique. The cationic azo textile dye C.I. Basic Blue 41 (Sigma Aldrich; dye content ca. 40%) at 1 g L^{-1} stock solution, filter sterilized, was used. The effects of different parameters on dye decolorization were studied in semi – synthetic medium, in the presence of various concentration of glucose, yeast extract, $(NH_4)_2SO_4$, pH value and initial dye concentration. The decolorization experiments were performed under shaking conditions at 30°C and 120 rpm.

Analytical procedures: The decolorization of dye was determined by measuring the absorbance of culture supernatant at λ_{max} = 600 nm, using a UV–vis spectrophotometer (Beckman Coulter DU 730) and the percentage of decolorization at different time intervals was calculated. Also, the dye biodegradation was evaluated by UV–vis analysis (200 – 800 nm) of the cell free supernatants once complete decolorization was achieved. The ethyl acetate extracted metabolites produced after complete decolorization of BB41 were characterized by UV–vis spectral analysis, high performance liquid chromatography (HPLC) and Fourier transform infrared spectroscopy (FTIR).

Ecotoxicological evaluation: phytotoxicity tests of dye and degradation products thereof were monitored by seed germination and plant growth bioassay (Monocots and Dicots species). *In vitro* cytotoxicity studies were performed using Vero cells isolated from the kidney of African Chlorocebus monkey, by MTT assay.

Results and conclusions

The new yeast strain, identified as *Pichia kudriavzevii* CR – Y 103, was able to decolorize 99.75% of BB41 dye (50 ppm) at pH 6 - 8, in the presence of 10 g L^{-1} glucose, 1 g L^{-1} $(NH_4)_2SO_4$ and 0.2 g L^{-1} yeast extract, within 6 hours of incubation at 30°C and under shaken conditions (120 rpm). Ammonium sulphate (6 g L^{-1}) or yeast extract (1 g L^{-1}), as sole nitrogen sources, increased decolorization efficiency to 99% in the first 4 h of incubation. Increasing or decreasing glucose concentration lowered the decolorization efficiency. The same observation was made when decreasing pH value. The maximal decolorization efficiency (%) with respect to the highest initial concentrations of the dye was obtained after 12 h (more than 99% at 100 ppm BB41) and 48 h (maximum 90% at 200 ppm BB41). The biodegradation product analysis revealed that the major peak of BB41 in the visible region at 600 nm and also, in UV spectra at 300 nm, disappeared completely at the end of the process. The HPLC analysis confirmed the complete degradation of the dye by the new yeast strain. Disappearance or reduction of the main vibrations of the dye BB41 in FTIR spectrum of the resulting metabolites, indicates that BB41 undergone some major chemical changes. The bands of frequency of vibration observed at 1598, 1484 and 1404 cm^{-1}, characteristic of aromatic rings, noticeably decreased to a large extent; also, the signals specific to thiazole ring at 1536, 1483 cm^{-1} and 860 cm^{-1} and also azo-aromatic, at 1520 cm^{-1} and 1426 cm^{-1} almost disappeared. The phytotoxicity study, using *Triticum aestivum* and *Trifolium pratense* plant test, revealed the non toxic nature of the biodegradation products of BB 41 (500 ppm), seed germination, root and shoot length being relatively similar to control (distilled water). Also, the MTT test confirmed the detoxification of the BB41; the established IC_{50} of the resulted metabolites in Vero cells being (315 ppm), compared with IC_{50} of the BB41 (16 ppm).

Based on the experiment, we can conclude that our strain is a good candidate for effective decolorization and detoxification of azo dye Basic Blue 41.

Acknowledgements:

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MULTIPLE DEHALOGENATING CAPABILITIES IN MARINE OHRB AND IDENTIFICATION OF RDASE GENES

Marco Rocca, Andrea Nuzzo, Maria Elena Antinori,
Fabio Fava, Giulio Zanaroli

Department of Civil, Chemical, Environmental and Materials Engineering (DICAM),
University of Bologna, via Terracini 28, 40131 Bologna, Italy

Introduction and study objectives

Organohalide-respiring bacteria (OHRB) are the main responsible for the bioremediation of halogenated pollutants in anaerobic layers: they can remove halogen atoms from organic pollutants through reductive dehalogenation. Reductive dehalogenase enzyme (RDase) are central to this process. Most of the knowledge on OHRB, RDase genes and enzyme characterized so far comes from freshwater environments, whereas less is known about marine OHRB. The aim of this study was to determine the susbtrate specificity of known PCB-dechlorinating marine OHRB enriched from the Venice Lagoon towards different organochlorides and to identify their RDase genes. The organohalides tested were hexachlorobenzene (HCBe), 1,2,3,5-tetrachlorobenzene (TeCBe), pentachlorophenol (PCP), 2,3,5-trichlorophenol (TCP) trichloroethene (TCE), Aroclor 1254 PCBs and 1,2,3,4-tetrachloro-*p*-dioxin (TeCDD).

Methodology

A PCB-dechlorinating sediment culture, enriched in OHRB VLD-1 and VLD-2, belonging to the non-*Dehalococcoides Dehalococcoidia* subclass, was transferred at 5% v/v in slurries of autoclave-sterilized sediment and filter-sterilized water of the Venice lagoon, under anaerobic conditions. HCBe, TeCBe, PCP, TCP and TCE were spiked at final concentration of 20 mg/l of slurry, PCBs at a total 500 mg/kgdw and TeCDD at 50 mg/kgdw. TCE-spiked cultures were then subcultured at 5% v/v in sterile synthetic marine water with no sediment, amended with vitamin solution and different electron donors (formate, acetate, lactate or pyruvate) at 20 mM, and spiked further with TCE. Chlorobenzenes and PCBs were analyzed via batch extraction with 3 volumes of hexane:acetone mixture (9:1) and analyzed via GC-ECD; chlorophenols were analyzed via preliminary separation of water and sediment phase, extraction from sediment with 2 volumes of ethanol and injection of both aqueous phases in HPLC-UV/DAD; chloroethenes were monitored by headspace analysis in GC-ECD and GC-FID using Henry's constant to infer concentrations in the liquid phase; TeCDD were monitored via extraction with 5 volumes of toluene:acetone 1:1 and GC-ECD analysis. OHRB were monitored via PCR-DGGE of the 16S rRNA gene of *Chloroflexi* bacteria. RDase genes were PCR-amplified from the sediment-free cultures using a set of degenerate primers designed on the *Dehalococcoidia*-class known dehalogenases; PCR products were cloned using PCR-TOPO™ vectors and sequenced.

Results and conclusions

No dechlorination was detected in any of the sterile controls (data not shown). On the other hand, all organohalides were effectively dehalogenated, often to non-chlorinated products, with no lag phase. Chlorobenzene dehalogenation was directed preferentially against double-flanked *ortho* and *para* positions, leading to the accumulation of mainly 1,3,5-TCBe both from HCBe and TeCBe, then further dehalogenated to 1,3-DCBe; benzene was not monitored but molar balances suggest that the dehalogenation activities removed all halides from spiked chlorobenzens. The two spiked chlorophenols were dehalogenated differently: PCP was dehalogenated preferentially in *meta* position, with the conversion of more than 90% of the spiked molecule into 2,4,6-TCP, not further dechlorinated, while remaining quantities of 2,3,5,6-TeCP were further dehalogenated to 3,5-DCP and then to phenol at the end of incubation. On the other hand, TCP was dehalogenated mainly in *ortho* positions, but the accumulated 3,5-DCP was not further dehalogenated to phenol. Multiple TCE spikes showed that dehalogenation activities were very fast (2-4 weeks) and lead to equimolar accumulation of *cis*- and *trans*-DCE. PCB dechlorination activities led to the accumulation of di- to tri-chlorinated-CBs and the decrease of the average chlorine substitution per byphenil molecule from 5.1 to 3.8 in 24 weeks; these data were coherent to the activities detected in the original Venice lagoon sediment culture used as inoculum for the whole set. Notably, also TeCDD was dehalogenated in *peri* position, leading to the accumulation of 1,2,4-TCDD, which was not further dehalogenated.

The Chloroflexi community showed that both OHRB inoculated, VLD-1 and VLD-2, were present in all the dechlorinating cultures except PCP-dechlorinating cultures, which enriched only VLD-1, and TCE-dechlorinating cultures, which enriched only VLD-2. Overall, the data confirm that the two OHRB enriched from Venice lagoon sediment cultures might dehalogenate several compounds and this is a relevant information to design further bioaugmentation/bioremediation approaches in the area.

Provided that TCE dechlorination activities were fast and that apparently TCE allowed the selection for VLD-2 phylotype over VLD-1, TCE-dechlorinating cultures were subcultured in synthetic sterile marine water (sediment-free) amended with electron donors to favor the growth of VLD-2. Lactate-amended subcultures exhibited the fastest activities and shorter lag phase, and were thus selected for RDase gene investigation. At least 5 different RDases were detected with degenerated primers B1R/RRF2, targeting the *RdhA/RdhB* complex in *Dehalococcoides*. The sequences obtained had 50% to 70% amino-acid identity with known *D. mccartyi* RDases. The presence of RDases orthologous to the cluster of known *Dehalococcoidia* RDases is currently being investigated. Further experiments will investigate the expression of selected RDase genes in relation to the spiking of differet organohalides to obtain indications on the substrate specificity of the different RDases.

Acknowledgements:

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EFFECT OF POLYMER-ENCAPSULATED SOPHOROLIPIDS AND CYCLODEXTRINS ON THE BIOAVAILABILITY AND ANAEROBIC BIODEGRADATION OF CRUDE OIL HYDROCARBONS IN MARINE SEDIMENTS

Antonella Rosato[1,*], Giulio Zanaroli[1], Laura Sisti[1],
Paola Fabbri[1], Annamaria Celli[1], Danny Reible[2], Fabio Fava[1]

[1] Department of Civil, Chemical, Environmental and Material Engineering (DICAM), University of Bologna, Bologna, Italy
[2] Department of Civil and Environmental Engineering, Texas Tech University, Lubbock, TX, United States
[*]: antonella.rosato2@unibo.it

Introduction and study objectives

Marine sediments are the final sink for weathered petroleum hydrocarbons: they tend to adsorb strongly onto the organic matter of the sediment, thus their biodegradation rate is very limited due to their low bioavailability. Previous studies revealed that sophorolipids and hydroxypropyl-β- cyclodextrin (HPB-CD) were able to enhance remarkably the anaerobic microbial biodegradation of *n*-alkanes in an oil-contaminated marine sediment. Moreover, investigations of surfactant releasing formulations for the deployment of these agents to the sediments showed that HPB-CD could be efficiently encapsulated in agar hydrogels, while sophorolipids in polybutylene succinate (PBS) microspheres. The release rate in oil-contaminated slurry microcosms were similar for both encapsulation formulations (approximately 86% release in 65 days). The aim of this work was to assess the effectiveness of polymer-encapsulated sophorolipids and cyclodextrins in enhancing the bioavailability and anaerobic biodegradation of crude oil hydrocarbons in marine sediments.

Methodology

Two sets of sterile slurry microcosms of crude oil-contaminated sand (5 g/kg_{sand}) suspended in synthetic marine water (20% w/v) were set up to investigate the effect of encapsulated surfactants on hydrocarbons bioavailability: a "freshly spiked" set, used immediately after contamination, and "weathered" set, used 40 days after contamination in order to allow the adsorption of the oil contaminants to the sand. For each set, PBS-encapsulated sophorolipids and agar-encapsulated HPB-CD were added at the final concentration of 0.2 and 1 g/L, respectively; un-amended controls and microcosms supplemented with the same concentration of not encapsulated sophorolipids and cyclodextrins were also set up. The evaluation of hydrocarbons bioavailability was investigated via the measurement of *n*-alkanes concentration in the porewater through passive sampling with polydimethylsiloxane (PDMS) fibers. The microcosms were incubated at 20 °C, 150 rpm and the fibers replaced every 20 days to sample water-dissolved hydrocarbons. An additional, identical set of weathered slurry microcosms was set up and inoculated (10% v/v) with an hydrocarbon-degrading marine microbial community previously enriched from Gela harbor (Italy), in order to investigate the effect of encapsulated biosurfactants on hydrocarbons biodegradation under anaerobic conditions (N_2:CO_2 70:30 headspace gas). These slurries were incubated statically at 20 °C for 32 weeks and periodically sampled. The hydrocarbons concentration was monitored via GC-FID analysis of *n*-alkanes.

Results and conclusions

After 20 days of incubation, porewater concentration of *n*-alkanes in "freshly spiked" slurries was comparable in all conditions (ranging from 320 to 470 ng/L). After 60 days, it decreased in the un-amended control (80 ng/L), indicating that adsorption of spiked hydrocarbons to the sand had taken place. A comparable increase of *n*-alkanes porewater concentration was observed after 60 days in the presence of free and encapsulated HPB-CD (1600 n/g L). The increase of porewater concentration in the presence of PBS-encapsulated sophorolipids (500 ng/L) was instead about 50% of that observed with free sophorolipids. Both encapsulated surfactants were thus able to reduce remarkably hydrocarbons adsorption to sand thus increasing their bioavailability. In "weathered spiked" slurries, the porewater concentration of *n*-alkanes in unamended control was constant over time, confirming that hydrocarbons adsorption to sand was completed during the 40-day weathering period. Porewater concentrations higher than the unamended control were observed in the presence of free sophorolipids (about 1000 ng/L) and of both free and encapsulated cyclodextrins (about 1500 ng/L), while no significant effect was observed with encapsulated sophorolipids. In case of weathered contaminated sands, therefore, only encapsulated HPB-CD are able to desorb *n*-alkanes and increase their bioavailability.

During 32 weeks of incubation, *n*-alkanes biodegradation was absent in un-amended sterile and biotic controls, and approximately 63% and 40% in the presence of not-encapsulated sophorolipids and HPB-CD, respectively. The encapsulation of sophorolipids in PBS reduced the *n*-alkanes anaerobic biodegradation to approximately 14%, which is consistent with its low/negligible effect on hydrocarbons bioavailability observed on weathered contaminated sand. Conversely, *n*-alkanes removal in the presence of agar-encapsulated HPB-CD was comparable than that of the free cyclodextrins, in line with their ability to increase the hydrocarbons porewater concentration. Redox potential was positive in both un-amended sterile and biotic controls, whereas it decreased to -100/-250 mV after 6 weeks in the cultures amended with all surfactants, suggesting that the addition of biodegradable surfactants and polymers stimulated the activity of indigenous anaerobic microorganisms. Sulfate reduction was absent in un-amended sterile and biotic controls, and it was stimulated by the supplementation of sophorolipids (either encapsulated or not) and encapsulated HPB-CD. Therefore, the extent of sulfate reduction was apparently not correlated to the hydrocarbons biodegradation. Agar-encapsulated HPB-CD are a promising solution for the enhancement of both hydrocarbons (bio)availability and anaerobic biodegradation in contaminated marine sediments.

Acknowledgements:

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INNOVATIVE TECHNOLOGIES FOR FERTILIZATION AND IRRIGATION IN PROTECTED SPACES, IN ORDER TO DIMINISH SOIL POLLUTION

Ioan Ţenu*, Oana Corduneanu, Radu Roşca, Vasile Stoleru,
Petru Cârlescu, Gheorghe Şovăială

University of Agricultural Sciences and Veterinary Medicine "Ion Ionescu de la Brad" in Iaşi, Sadoveanu 3, Iasi, 700490, Romania;
**: itenu@uaiasi.ro*

Introduction and objectives of the study

Worldwide studies show that 60% of the soils have very low or low fertility, 29% are moderately fertile and only 11% are highly fertile. In order to increase the agricultural potential, the present plant growing technologies are based on modern agro-technical methods, which are synonym with the progress and development, such as: mechanization, irrigation, chemical fertilization etc. Because of these interventions the agricultural ecosystems are continuously modified at a much faster rate than natural ecosystems. For example, there is a complex impact when applying mineral fertilizers: the environment is acidified or alkalinized; the agro-chemical and physical properties of the soil are improved or deteriorated; there is metabolic absorption or desorption of ions in/from the soil solution; the chemical absorption of cations is slowed down; soil humus is either mineralized or synthesized; the nutritional elements in soil are either mobilized or immobilized.

The present paper investigates the improvement of the operating process of a drip irrigation and fertilization system for vegetable crops grown in protected spaces. The aim of the research was to evaluate the effect of the fertilization method for different types of fertilizers:

- chemical fertilizers, spread on the terrain surface;
- micro-organisms based fertilizers, spread on the terrain surface;
- hydro-soluble fertilizers, applied using a drip irrigation and fertilization system.

These variants were compared with an unfertilized control variant.

The use of a drip irrigation and fertilization system has a potentially conservative effect because of the following: reduction of water consumption; increased water storage capacity of the root system; significant reduction of soil erosion; reduced pollution through the leakage of chemical substances into the water reserve; reduced multiplication of pests and diseases, leading to a lower number of chemical treatments. Moreover, the nutrients can be applied at a specific moment, in the desired quantity and with lower costs.

Methodology

The experimental tests presented in this paper were performed in a semicircular type greenhouse, with an area of 270 m2, located at the "V. Adamachi" farm of USAMV Iasi.

Pepper plants belonging to the cultivar Brillant F1 and Minaret F1 tomatoes were studied; the plants were grouped in four experimental variants. The plants were grown in strips - 80 cm between strips, 60 cm between the rows of each strip, 45 cm between plants; this resulted in a density of 31740 plants/ha. A dripping line was used in order to irrigate the plants (16 mm diameter; 10 cm between emitters). The irrigation was performed every second day, between 8 and 10 a.m. or between 7 and 9 a.m., depending on the ambient temperature.

A dripping and fertilizing system was built; the system consisted of: water tank (capacity: 20 tons); tank for the preparation of the fertilizer solution; filter; automated irrigation timing system.

In variant V1 the plants were fertilized in the same time with the drip irrigation, twice a week, in the morning. For variant V2 chemical fertilizers were spread over the area surrounding each plant; microorganisms based fertilizers were used for variant V3. Only drip irrigation was applied (no fertilization) to the plants in variant V4.

Biometrical measurements were performed at specified moments, in order to evaluate the growth dynamics: plant height, the number of flowers and inflorescences, the number of leaves and the number of fruits were evaluated. The mass, length, width and diameter of the fruits were also measured.

Results and conclusions

During one fertilization cycle 2 grams of fertilizer per plant were administered (200 g for 100 plants). The classic chemical fertilization was performed using 11g of substance per plant (1100 g for 100 plants); in the microorganisms fertilization variant an amount of 3.25 g/plant was used (325 g for 100 plants). Over the entire vegetation cycle, for the 270 m^2 area an overall amount of water of 5600 m^3 was used for the irrigation (20.7 m^3 per 1 m^2).

The tomatoes production was comprised between 69651 kg/ha for the control sample and 92076 kg/ha for variant V_1; the 22425 kg/ha difference was considered to be very significant. The pepper production was comprised between 55.870 kg/ha for the witness variant and 85.850 kg/ha for variant V_1.

The experimental results led to the conclusion that the best spatial and time distribution of the fertilizer was achieved when fertilization was applied in the same time with the irrigation; water and fertilizer consumption were reduced due to the use of localized irrigation (plant root area). Soil erosion, pests and diseases were significantly reduced, while the chemical treatments were kept at minimum.

Acknowledgments:

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IMPACT OF FISH FARMING ACTIVITY ON THE POPULATION OF HETEROTROPHIC BACTERIA IN THE WATER COLUMN AND POND SEDIMENT

Isabelle Metaxa*, Aida Vasile, Petrea Ștefan Mihai,
Alina Mogodan, Săndița Plăcintă

"Dunărea de Jos"University of Galați, Domnească, 47, Galați – 800008, Romania,
**: Imetaxa@ugal.ro*

Introduction and study objectives

In fish ponds the bacterioplankton includes the pelagic microbial population such as: photoautotrophs, chemoautotrophs and heterotrophs with little or no ability to control their horizontal location. The benthic microbial community is numerical higher and activity much higher than in the plankton. The structure of microbial communities is sensitive to changes of environmental parameters, particularly to changes connected with the introduction of nutrients. The organic matter accumulation on the bottom of the aquatic ecosystem determines the increase of bacterial activity and the lowering of oxygen levels, producing anaerobic conditions. The bacterial degradation in the sedimented organic particles is responsible for oxygen depletion resulting in mortality among large fish.

We studied the distribution of some microbial indicators both in water column and sediment, in relation to physical, chemical and biological parameters to evaluate the bacterial response to the disturbance induced by fish pond bio-deposition in different areas of a Romanian cyprinid fish farm located in the NE Moldavian region of the country.

Methodology

The surface water and the sediment samples were collected from the two ponds of a fish farm located in Iaşi district, Romania, with an area of 0.45 ha each and an average water depth of 1.5 m. The water source of the farm is represented by Jijia River. The water inlet and outlet from the ponds were made gravitationally, by using „monk" type hydraulic constructions.

The water samplings were collected monthly during the end of summer season of year 2016 from nine stations divided as: one common station ponds inlet, five stations in pond P1 and three stations in pond P2. The pond P1 was divided from technological point of view in two sections: one for carp monoculture and the other for other cyprinid polyculture (bighead carp, silver carp, grass carp).

Heterotrophic bacteria count was performed by the pour-plate method on agar using successive dilutions, method provided by the Romanian Standard STAS 3001-91. Bacteria density was expressed as Colony Forming Units (CFU) per grams of dry weight for sediment and CFU per millilitre for water samples.

Measurements of the physical and chemical parameters, such as pH, temperature, oxygen were also performed by the probe.

Results were statistically analysed by Pearson correlation coefficient and ANOVA by Office XP software per Windows.

Results and conclusions

In the water column as in the sediment, we checked if there were variations between the different sampling points. Results of water and sediment analysis showed a different distribution of heterotrophic bacteria. A distinct increase in the number of heterotrophic bacteria was observed in the sediment compared with the column of water as it is mentioned in Figure 1 and Figure 2.

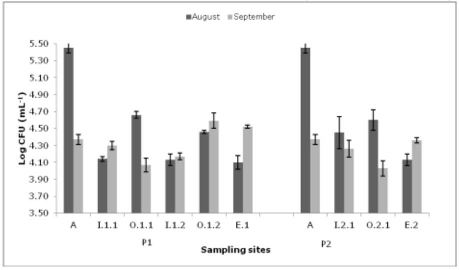

Figure 1: Heterotrophic bacteria spatio-temporal variations in water column, expressed in CFU/ml of water

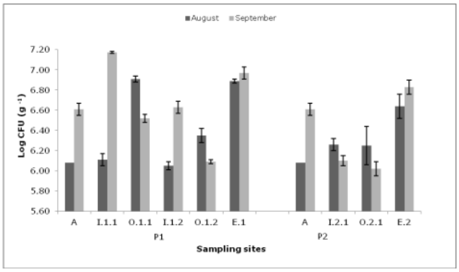

Figure 2: Heterotrophic bacteria spatio-temporal variations in ponds sediment, expressed in CFU/ml of sediment

In August, the number of heterotrophic bacteria from the water sampling points of the both ponds (P1 and P2) ranged between 4.10 log CFU / mL and 5.45 log CFU / mL. The maximum value of CFU was registered into the water supply of the both ponds, which was encoded (A) in both figures.

According to figures, in September there were recorded values between 4.03 log CFU / mL and 4.59 log CFU / mL in the sampling points of ponds. Bacterial number in the analysed water from P1 and P2 ponds were in the range of 4 log CFU mL^{-1}. These results were lower than the values recorded by Ntengwe & Edema (2008) in the order of 6 log CFU mL^{-1} from fish culture pond water, but higher than those observed by Ahmed & Naim (2003) in the tilapia pond culture (3 and 4 log CFU mL^{-1}).

The heterotrophic bacteria in the sediment were collected from the same sampling points as in the water column. The number of heterotrophic bacteria in the sediment ranged between 6.05 and 6.89 log CFU / g (dry weight) of sediment in August. Also, it ranged between 6.02 and 7.17 log CFU / g (dry weight) of sediment in September.

After identification of variation in number of heterotrophic bacteria in August and September, it can be concluded that in the pond (P1), where it is practiced integrated multitrophic aquaculture, there is an evident variation of heterotrophs, both in water and in sediment, comparing with the variation identified in the pond (P2) where it is practiced a traditional fishculture. The impact of fish farming and the physical and chemical changes of the environment determined changes in abundance of heterotrophic bacteria and consequently modified the benthic food chain.

MICROBIAL FUEL CELL BIOSENSORS BASED ON ENVIRONMENTAL ELECTROACTIVE CONSORTIA FOR FRESHWATER QUALITY MONITORING

V. Agostino[1,2,*], V. Margaria[1], G. Massaglia [1,2], M. Gerosa [1,2,] ,
G. Saracco[1], M. Quaglio[1]

[1)] Center For Sustainable Future Technologies @Polito, Istituto Italiano Di Tecnologia,
Corso Trento 21, 10129 Torino, Italy
[2)] Department of Applied Science and Technology, Politecnico di Torino, 10129 Torino,
Corso Duca Degli Abruzzi 24, 10129 Torino, Italy
[:] valeria.agostino@iit.it;*

Introduction and study objectives

The Microbial Fuel Cells (MFC) represent a promising biotechnological approach able to convert directly the chemical energy stored in organic matters into electricity, through reactions catalysed by electroactive microorganisms. Wastewater treatment with simultaneous energy recovery was the first application of this technology. More recently, increasing attention has been paid to the potential use of MFCs as sensors for in-situ water quality monitoring. The current generated by MFC directly reflects the metabolic activity of the anodophilic electroactive bacteria. Thus, the presence of a toxicant in the electrolyte can affect the microbial metabolism with consequent changes in the current production. In particular, in MFC-based biosensor the sensing element does not need a physical transducer to obtain a readable signal. Moreover, MFC-based biosensor is a fast response early detector, it is simple in operation and can be highly cost effective. These unique characteristics perfectly meet the requirement for long-term in-situ sensing application.

The majority of studies about MFC-based biosensors for water quality monitoring made use of pure culture bacteria (*Geobacter sulfurreducens* and *Shewanella oneidensis*) or mixed consortia taken from long-term operated MFCs, not considering the importance of the origin of the inoculum source. Moreover, simulated toxic events were usually tested in controlled laboratory conditions, without taking into consideration the environmental variation of such important parameters (i.e temperature) that affect the microbial activity and thus the current generation.

Focusing on the development of a freshwater quality monitoring system, the aim of this study is to investigate the biosensing capability of a mixed community biofilm directly coming from river sediment, in not controlled temperature conditions.

Methodology

A river sediment sample from Valle d'Aosta was used as inoculum source. Anodic biofilm acclimation was performed with a low external resistance (47Ω), resulted in a positive anode potential polarization. The consortia sensitivity towards a general toxic compound, glutaraldehyde (0.0005 to 0.1%), and towards different types of heavy metals, nickel(II) and chromium(III) (2, 20, 60 mg/L), was tested in a squared small membrane-less single-chamber MFC. 1 kΩ external load was chosen as control mechanism for the MFC-based biosensor toxicity tests. The toxic events were performed in a semi-continuous mode: the MFCs were fed 4 hours per day, with an hydraulic retention time of 1 hour. This operation modality was chosen mimicking a sensor networks where each single MFC represents a sensor node which works at defined interval time during the day. The biosensors performance was evaluated in terms of inhibition ratio, linearity of the response and recovery. Experiments were conducted in duplicate.

Results and conclusions

Before starting the toxicants tests, the MFCs were trained with several cycles carried out with non-toxic influent at a fixed concentration of acetate (1 g/L). The different non-toxic cycles showed a high level of reproducibility (99% comparing the cycle of the same MFC in term of current profile, current density production after 4 hours of feeding and total coulombic yield). Even the smallest percentage of glutaraldehyde (0.0005%) affected the normal trend curve observed in non-toxic condition. In particular, a linear response of the MFC-based biosensor was detected after the end of feeding period (4 hours). Moreover, in contrast with several studies, the anodic microbial activity was recovered even after the highest concentration of glutaraldehyde.

The anodic consortium shown to be tolerant to the lowest concentration of nickel(II) while demonstrated a linear sensitivity towards higher concentrations, if considering the current time point after 4 hours or the total coulombic yield.

The trivalent chromium was selected as a model for heavy metal with a low degree of toxicity. No response was shown with 2 mg/L of chromium(III). When the concentration was increased to 20 mg/L a peculiar current density profile was observed: in contrast with the data obtained for glutaraldehyde and nickel(II), a very small current density change occurred after 4 hours of feeding but a steep decrease was visible after few hours of batch condition. This particular response underlined a different modality of chromium (III) bioaccumulation and toxic action towards the anodic consortium, compared to nickel. Looking at these results, it is clear that, even if non-specific, the MFC-based biosensor could reveal some information about the modality of action of the single toxic substance used.

This study provide preliminary information about the application of environmental electroactive consortia in MFC-based biosensors. In particular for the first time the biosensing capability of a mixed-community consortium originated from a river sediment sample was demonstrated in not controlled temperature conditions. A bioanode in equilibrium with the natural microbial composition of the environment to monitor is necessary for real application of MFC biosensor as freshwater quality monitoring device.

THE INFLUENCE OF STORAGE CONDITION ON SOME BIOACTIVE COMPOUNDS AND HEALTH PROMOTING PROPERTIES OF FRUIT BERRY

Otilia Murariu[1], **Alin C. Dîrțu**[4], **Dragoș Robu**[2,*], **Liviu Irimia**[3], **Florin Murariu**[2], **Teodor Robu**[1]

[1] Department of Plant Science, Faculty of Agriculture, "Ion Ionescu de la Brad" University of Agriculture Science and Veterinary Medicine, 3 M. Sadoveanu Alley, Iași
[2] Department of Agroeconomy, Faculty of Agriculture, USAMV, 3 M. Sadoveanu Alley, Iași
[3] Department of Horticulture Technologies, Faculty of Horticulture, USAMV, Iași
[4] Laboratory of Analytical Chemistry, Department of Chemistry, "Al. I. Cuza" University of Iași
**: robu_dragos@yahoo.com*

Introduction and study objectives

This study aims on characterizing the presence of some biologically active compounds contained by berry fruits, including pH and non-nutritive compounds such us acids, as well as nutritive compounds such as vitamin C and soluble dry matter. The main criteria underlying this research consist in assessing the influence of the principal storage technologies on the content of some bioactive compounds contained by berry fruits.

To balance fluctuations in product supply and market demand, fresh berry fruits often require short- or long-term storage in order to extend the supply of the berry fruits beyond the end of the harvest season. Understanding the interaction between the fruits and the environment is crucial for obtaining the most suitable conditions for extending shelf life.

Berry fruits consumption play an important role in balancing the human diet, mainly because the composition of fruit differs markedly from other food items of plant and animal origin. This type of fruit is particularly rich in antioxidants such as ascorbic acid and anthocyans.

Previous literature in this field have shown that ascorbic acid of natural origin is superior when compared to the synthetic product, due to the presence of certain flavonoid compounds in those fruits which influence the blood circulation, increasing the permeability and the elasticity of the capillary vessels. Portions of 250 g of strawberries, cranberries, gooseberries, blackberries or raspberries contain considerably more than the minimum daily requirement of vitamin C, while most of the other fruit can provide more than half the daily requirement of 60-100 mg for romanian adult people and 35-65 mg for children. In order to freeze the berries fruits, generally no pretreatments are applied and therefore no changes in nutritive values occur during storage if proper packaging are used. During thawing, however, losses may occur.

Methodology

To characterize the influence of some preservation technologies applied and the potential health benefit of the berries, quality and physico-chemical parameters along with the vitamin C content, were evaluated for three fixed time points of refrigerated storage condition at 2^0C, and also after different freezing condition (-18^0C).

The biological material studied was represented by 4 types of berries, as follows: cranberries (*Vaccinium myrtillius*), gooseberry (*Ribes rubrum*), blackberries (*Rubus fructicosus*) and raspberry (*Rubus idaeus*) which were assessed in terms of quality in fresh condition (T_0 – moment), after 3, respectively 7 days of refrigerate storage condition as well as after 6 month of freezing (in bulk and packaged in polyethylene bags).The vitamin C content was determined using the extraction method with oxalic acid and titration with 2,6 – dichlorophenol – indophenols. The pH values were determined by direct potentiometric method using Hanna Instruments. The soluble dry matter was read using the portable refractometer Zeiss.

Results and conclusions

The soluble dry matter substances content was noticed to decrease in refrigerated storage condition between T_1 and T_2 time points ($p<0.001$) for all analyzed parameters. Instead storage on freezing condition highlights a decrease only for cranberries and raspberries ($p<0.001$), the gooseberries barely decrease and blueberries content highlight a slight increase (0.1 – 0.2 U.N. $p<0.05$).

As concerning the differences in vitamin C content between fruits storage in bulk and packaged with polyethylene film were revealed significantly higher values ($p<0.001$) for all analyzed species that were packaged also in refrigerated and freezing storage conditions. When compared to the other fruits tested, the red gooseberries (43,5 mg/100 g), followed by raspberries (35,6 mg/100g) were evidenced by their high vitamin C content.

Although independently of the preservation technique applied (refrigeration or freezing) the Vitamin C content of the tested fruits was noticed to significantly decrease, it could be evidenced that it's concentrations were measured at still high values: 27.8 mg/100 g for gooseberries and 24.3 mg/100 g for raspberries even after 7 days of storage at 2^0C. Regarding the type of packaging used, it is noted that all products purchased from retail packaged in closed polyethylene recorded higher values of the bioactive compounds analyzed in all time points considered (T_0, T_1, T_2 and after freezing).

Our research suggest that preservation technique as well as packaging materials used for such fruits storage is of a high importance when addressing the minimal degradation of bioactive compounds responsible for a series of high benefits to human health. However, future research should properly test for other conditions to be applied for such fruits preservation including controlled atmosphere or refrigerated storage as well as freezing in vacuum conditions.

A CRITICAL ASSESSMENTS OF SOME MACROALGAE BIOMASS FOR MINE POLLUTED WATER REMEDIATION

Gabriela Ungureanu[1], Sílvia Santos [1], Irina Volf [2,*],
Cidália Botelho [1]

[1)] *LSRE-Laboratory of Separation and Reaction Engineering, Associate Laboratory LSRE/LCM,*
Faculdade de Engenharia da Universidade do Porto, Portugal
[2)] *"Gheorghe Asachi" Technical University, Faculty of Chemical Engineering and*
Environmental Protection, 73 Prof.dr.docent D.Mangeron Street, 700050 Iasi, Romania,
[*]:iwolf@ch.tuiasi.ro

Introduction and study objectives

The removal of contaminants from mining-influenced water has becoming more demanding, with stricter discharge limits imposed on various contaminants, like arsenic, antimony and selenium. Mining activity is one of the greatest pollution causes by these metalloids, generating contaminated waters in many countries around the world. As and Sb have chemical and toxicological similarities, and pollution from both commonly co-occurs. Se is quite different, its toxicity being related to its chemical similarity to sulphur. Different species, with different charges and oxidation states, can be present in aqueous solution, depending on the pH and redox potential, which makes the chemistry of these metalloids to be complex. There are several methods to remove As, Sb and Se from contaminated waters, but biosorption has been viewed as a valuable technology for toxic metals and metalloids removal from wastewater, because of low requirements in chemicals and energy, efficiency and the low cost of the adsorbents. The purpose of the present work is to expose an alternative methodology for As, Sb and Se removal from aqueous solutions, using dead marine seaweeds as biosorbents.

Methodology

The brown macroalgae tested in this study, *Ascophyllum nodosum* and *Sargassum muticum,* were collected at Viana do Castelo beaches (Portugal) and the green algae, *Cladophora sericea* and *Ulva rigida,* were harvested on Romanian coast of Black Sea. The seaweeds were used after washing, milling and drying. In order to characterize the surface functional groups of the algae, infrared spectra and potentiometric titrations were performed; scanning electron microscope (SEM) images were obtained. The experiments were performed in batch-mode to sequester As(III), As(V), Sb(III), Sb(V), Se(IV) and Se(VI) from synthetic solutions. The effect of pH (range 2-8) and competing ions was evaluated using initial oxyanions concentrations of 25 mg L^{-1} and adsorbent dosage of 10 g L^{-1}. Biosorption kinetics (at the most favorable pH value after preliminary pH tests, different initial adsorbate concentrations and algae dosages) and equilibrium isotherms were determined. Metalloid concentrations in liquid phase were analyzed by flame or graphite furnace atomic absorption spectroscopy. To clarify if any redox reaction involving Sb occurs during assays, certain solutions were analyzed by DPASV (Differential Pulse Anodic Stripping Voltammetry). In order to improve the sorption capacity of the algae surface, different chemical pre-treatments were tested (iron pre-treatment, protonation, treatment with HDTMA and ammonium pre-treatment). These simple chemical modifications were evaluated in order to have, as much as possible, an economically feasible process. Additionally, continuous-mode experiments were carried out in fixed-bed adsorbers of *S. muticum* using different Sb(III) inlet concentrations (1 mg L^{-1} and 25 mg L^{-1}) and flowrates (4 and 10 mL min^{-1}). Breakthrough curves were obtained and mathematically modeled. Tests with real mine effluent from Rosia Montana mine (Romania) and also from Penedono gold mine (Portugal) were performed to study the performance of algae adsorption capacity in a real matrix water.

Results and conclusions

Infrared spectra of studied algae evidenced the presence of amine, carboxyl and hydroxyl groups. A continuous model based on Langmuir isotherm and Sips distribution was fitted to potentiometric titration data and acid groups (assigned to carboxyl) and basic groups (hydroxyl) were quantified in both algae. Based on the results of screening tests, *S. muticum* and *C. sericea* were selected for further experiments. pH influence on the amount of adsorbed metalloid is revealed in fig.1

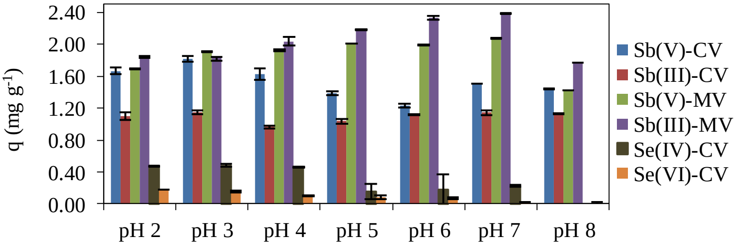

Figure: 1. Effect of pH on the biosorption of Sb(III), Sb(V), Se(IV) and Se(VI) by virgin *Cladophora sericea* (CV) or virgin *Sargassum muticum* (MV) (initial adsorbate concentration 25 mg L^{-1}, 10 g L^{-1} of algae, temperature of 23±1°C).

Voltammetric measurements results evidenced no significant oxidation/reduction reaction. Sb and Se removal is not or moderately affected by the presence of possible coexisting competing ions. Adsorption kinetics were fast (equilibrium reached in approx. 2 h). The main adsorption capacities obtained in batch-mode are 4±1 mg g^{-1} for Sb(III) removal on *S. muticum*, 3.1±0.4 mg g^{-1} and 2.1±0.3 mg g^{-1} for Sb(III) and Sb(V) adsorption on *C. sericea* and 0.5±0.06 mg g^{-1} of adsorbed Se(IV) on *C. sericea*. Moreover, the maximum biosorbed amount determined experimentally in packed-bed flow operation of 3.8 mg g^{-1} for Sb(III) removal on *S. muticum* is very close to the capacity obtained in batch mode which is a very good indicator for a possible use in real operating conditions.

In conclusion, brown and green seaweeds, in natural form, showed good perspectives to be applied for Sb uptake from aqueous solution. In contrast, a limited capacity was found for Se, and a completely null efficiency was observed to As removal from aqueous solutions. Also, considering the environmental and economic aspects related to the adsorbent pre-treatments and the limited improvement experienced, it was determined that brown and green seaweeds in raw form offer better perspectives to be used as adsorbents on the uptake of antimony and selenium from aqueous solutions.

GREEN ALTERNATIVES IN BIOREFINING PROCESS FOR SPRUCE BARK WASTE VALORISATION

Oana-Alexandra Pătrăuţanu[1], Gabriela Ungureanu[2],
Mihai Brebu[3], Valentin I. Popa[1], Irina Volf [1,*]

[1)] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 73 Prof. dr. docent D. Mangeron Street, 700050, Iasi, Romania
[2)] "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, 3, Mihail Sadoveanu Alley, 700490, Iasi, Romania
[3)] "Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania
[*]:iwolf@ch.tuiasi.ro

Introduction and study objectives

Biorefining aims at a complete valorisation of biomass by performing processes with a minimum mass and energy consumption and a maximal value of the production chain. It consist of an efficient fractionation of biomass into various value-added products and energy using physical separation processes in combination with bio-chemical and thermo-chemical conversion steps. The bark from forest species, resulted as a solid waste in wood processing, represents an important biomass feedstock that is currently considered as an under valorised resource. This abundant biomass is commonly used to produce heat and electrical energy, biofuels (12 million m^3 of biofuel in Europe) but in recent decades, there has been a growing interest in converting it into value added products.

The bark from forest species are rich in fine chemicals that could be used in a variety of fields, from pharmaceutical and bioactive compounds to green polymers and bio-based materials. It is clear that a valorisation of bark will lead to a more efficient use of resources with environmental and economic benefits.

The paper addresses green alternatives for valorise the spruce bark in a two steps biorefining process. The first phase consists pretreatment in chemical characterization of the feedstock and a green extraction and separation of extractives (especially polyphenols). In this primary biorefining step an ultrasonic assisted extraction (UAE) was performed. The secondary biorefinery continue with the conversion of biomass. In this stage two also green processes were applied: an enzymatic hydrolysis processes and also pyrolysis in order to obtain a solid charcoal-like material (biochar) and bio-oil, (biocrude or pyrolysis oil).

Methodology

All the methods applied for chemical characterization of biomass were performed after NREL Laboratory Analytical Procedures for standard biomass analysis.

The ultrasound assisted extraction followed the protocol described by Lazar et al., 2016. The pyrolysis was conducted according to Tao et al., 2016.

Results and conclusions

The characterization of biomass (table 1 and table 2) reveals a valuable composition suitable for a biorefinery approach.

Table 1: Characterization of biomass

	Humidity	Ash content	Extractives (ethyl alcohol)	Extractives (alcohol-toluen 1:2)	Hemicellulose	Cellulose	Lignin
Percentage (%)	8.84	1.84	8.70	7.06	39.29	29.30	42.45

Table 2: The pseudo-total concentration of several metals

Metal	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Selenium	Zinc
Concentration (ppm)	ND	0.125	ND	0.120	1.735	ND	ND	ND

A biorefinery flow sheet was elaborated (fig.1) in order to present the sequence of operations needed for an integral and complex processing of spruce bark. The technology implies two distinct stages: extraction/separation (extraction of the specific compounds, extraction of the secondary compounds) and conversion (with biochemical and thermochemical processes).

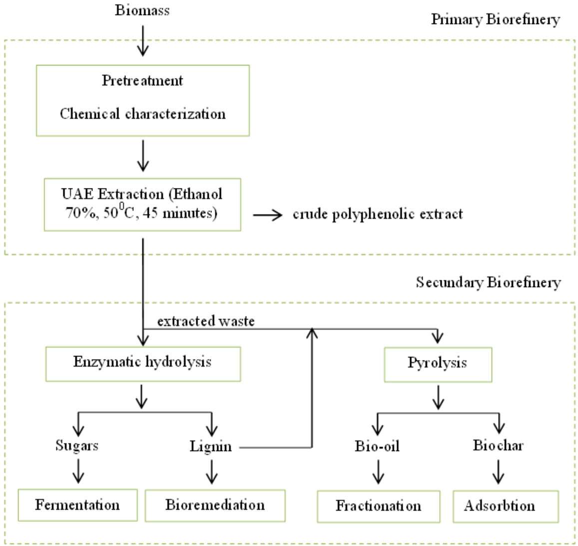

Figure 1: Flow sheet of integrated and complex processing of spruce bark biomass

All the obtained bioproducts (crude polyphenols extract, sugars, lignin, biochar and bio-oil) were characterized and innovative applications are proposed for each.

THE MYCOREMEDIATION APPROACH TO RESTORE AN HOSTORICALLY CONTAMINATED DREDGED SEDIMENTS: BIORESNOVA PROJECT

Giovanna Siracusa[1, *], **Simone Becarelli**[1,2], **Ilaria Chicca**[1], **Salvatore La China**[1], **Monica Ruffini Castiglione**[1], **Roberto Lorenzi**[1], **Giulio Petroni**[1], **Alessandro Gentini**[3], **Gualtiero Masini**[3], **Simona Di Gregorio**[1]

(1) Department of Biology, University of Pisa; Via Luca Ghini 13, 56124 Pisa (PI), Italy,
(2) BD, Biodigressioni srl, Pisa
(3) Teseco Spa, Pisa
**: giovanna.siracusa@biologia.unipi.it.*

Introduction and study objectives

The mycoremediation is a biotechnological approaches in which fungi (ascomycetes and/or basidiomycetes) are applied in combination to chemico-physical treatments to remove salinity and metal contamination from solid matrices. A new fungal strain was isolated from contaminated dredged sediments, massively grown and re-inoculated in the original matrix to remove Total Petroleum Hydrocarbon contamination (TPH). TPH, the main contaminant present in sediments affected by hydrocarbon contamination, are partially soluble, volatile and toxic compounds and are one of the main pollutants that cause a serious risk for the public/human health (Andreoni and Gianfreda, 2007). TPHs contain an "unresolved complex mixture" (UCM). The term UCM describes hump-shaped chromatograms that are often observed in gas chromatograms of extracts from environmental matrices contaminated by crude oil and petroleum derivates (Gough et al., 1990; Booth et al., 2008). The interest in environmental samples containing hydrocarbons is often motivated by the potentially toxic nature of these UCM contaminants (Golon, 2012). *Vicia faba*, a higher plant, was exploited as indicator of the quality of the treated sediments and used for the evaluation of the eco-safety of the final product.

In this study, the ability to deplete the contamination associated to UCM was studied in a meso-scale experimentation. The experimentation was conducted to evaluate the capacity of an ascomycetes strain isolated from the dredged sediment to deplete the UCM associated to the profile contamination of the polluted sediments. The goal of this work was the removal of TPHs contamination from sediments, being mainly focused on the reduction of the UCM toxicity, in order to restore the safe status of the matrix.

Methodology

Depletion of TPHs

Each sample was analysed in triplicate by GC-MS following the protocol of Klein et al. (2012).

Mesocosm experimentation set up

The mesocosm scale trial was set up according the following steps: mixing sediments with lignocellulosic matrix (30% w/w) used as bulking agent (BA); sand (30% w/w); macronutrients content adjustment. The experimentation has provided the preparation of 6 mesocosms in triplicate, to test different thesis.

Monitoring the fungal biomass

The ergosterol was used as molecular marker of the fungal activity, as described by Giubilei et al. (2008).

Vicia faba bioassay

The test was conducted on sediment sample and elutriates. Petri capsules with seeds were prepared according to ISTISAN protocol.

Results and conclusions

Results obtained show that the ascomycetes microF is able to deplete more than 86% of TPH present in the dredged sediments, on meso-scale experimentation (Figure 1).

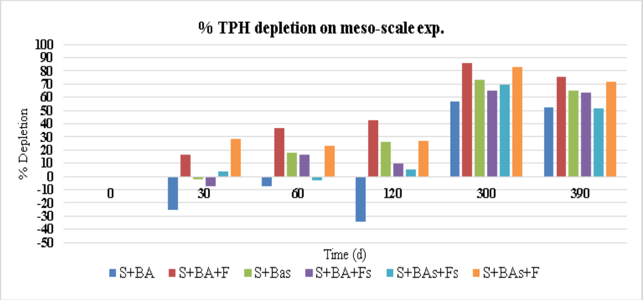

Figure 1: Percentage of TPH depletion during the one-year experimentation. P<0.001

Despite a high TPH removal, a detoxification of the treated matrix was not recorded. *Vicia faba* system model showed any germination of the seeds for each time of analysis, probably related to the high TPH residual concentration. The ergosterol data indicates that microF survived for 60 days in the meso-scale test and, to improve the TPH removal, a second bioaugmentation was necessary.

In conclusion:

- The bioaugmentation processes using microF, isolated from the dredged sediment, represent a good instrument to decrease contamination by TPH and the UCM fraction, in a period of time compatible with a real scale pilot system;
- The high decontamination of the matrices in meso-scale experiment, doesn't match with the detoxification of the matrix, which still displayed high toxicity after 1 year of incubation.

Acknowledgments

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INFLUENCE OF GROWTH CONDITIONS ON MICROALGAE CULTIVATION SYSTEMS FOR BIOFUELS

Alexandra Tucaliuc [1], Alexandra Cristina Blaga [1], Lenuta Kloetzer [1], Dan Cascaval[1,*], Anca Irina Galaction[2,*]

[1) Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Organic, Biochemical and Food Engineering, Iasi, Romania
[2) Biomedical Science Department, Grigore T. Popa" University of Medicine and Pharmacy, Faculty of Medical Bioengineering, 9-13 M. Kogalniceanu Street, 700454 Iasi, Romania
[*]: dancasca@ch.tuiasi.ro; anca.galaction@bioinginerie.ro

Introduction and study objectives

The increase in fossil fuel prices and global energy consumption, cumulated with the environmental effects of greenhouse gas emissions have led to an overwhelming interest among researchers to develop economically viable processes for the production of alternative fuels.

The algal biomass offers great potential as a sustainable feedstock which can be processed for bioethanol and biodiesel production, due to its many advantages: rapid growth rate, the ability to accumulate important amounts of carbohydrates, all the materials produced are nontoxic and biodegradable. However, in order to produce high concentrations of ethanol, it is necessary to convert all specific carbohydrate components of microalgae: glucan, sulfated polysaccharides, mannitol, alginate, agar, and carrageenan.

The algal biomass production worldwide is about 12 million tonnes for macroalgae and 9200 tonnes for microalgae (dry weight), mostly grown in open ponds, but also in enclosed photo-bioreactor. Since 1950s photobioreactor technology has evolved, different designs being developed and investigated to improve control strategies for long-term stability and reliability of operations. In order to choose the most appropriate, one must consider not only the yield, the increase in photosynthetic efficiency and enhancement of gas exchange rate, but also the capital investment and operating costs, to prove that it can be commercially feasible. Many challenges are still to be overcome in developing models for radiative transfer mechanism, hydrodynamics, but also for photosynthetic and growth kinetics. Microalgae are prokaryotic or eukaryotic photosynthetic microorganisms that are incredibly diverse in natural environment (typically in fresh water and marine systems). Microalgae strain selected, as the first and important step of algae-based biodiesel industry, determine the corresponding nutrients and cultivation unit available for their growth.

Methodology

The experimental equipment that can be used for algae cultivation consisted in two types of photo-bioreactors (PBR): bubble column (a) and flat (b) (Fig.1.), where algae are cultivated in suspension in a closed system, and offers advantages in terms of yield and control: high productivity, low contamination, continuous operation and controlled growth conditions, but with some limitations regarding low light penetration and sophisticated construction.

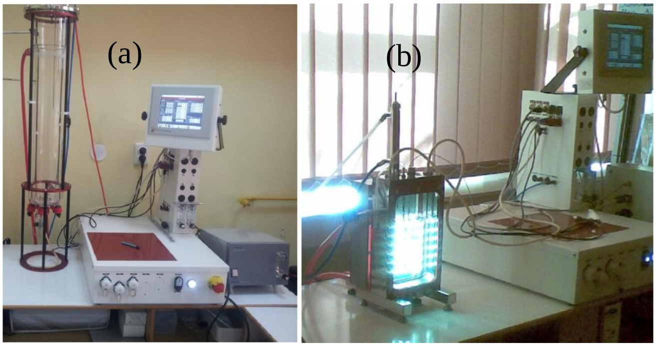

Figure 1: Photo-bioreactors

PBR system is a controllable environment in which the algae can be cultivated, and where the supply of light, nutrients, carbon dioxide, air, and temperature can be controlled and regulated.

Results and conclusions

Microalgae are able to grow and develop in very different conditions, but in order to obtain high productivity and the consistency of the structure and composition of the bioactive compounds, it is important to have a very good control of the process. Microalgae cultivation is extremely important for the production of lipids (used for biodiesel) or carbohydrates (used for bioethanol), due to an extremely important effect on productivity of the environmental conditions. The main parameters that need to be investigated for achieving high growth are: medium composition (e.g. Modified Zarrouks medium, artificial sea water, BG 11 medium, SOT medium), temperature, intensity and quality of light, pH, CO_2 availability, and residence time. Nutrient limitation (nitrogen, sulphate, calcium or phosphorous starvation) can be used to accumulate large amounts of bioactive compounds, but this determine a negative effect on cell growth and since for most of these products, synthesis occurs along with growth phase: during all growth phases, or just exponential or stationary, research needs to be focused on maximizing different conditions of the culture medium such as: irradiance, carbon dioxide supply, pH and temperature to increase productivity.

Acknowledgments:

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NEW MICROALGAE AND PROCESSES FOR A CIRCULAR BIOECONOMY

Spiros N. Agathos[1,2], Borhane Samir Grama[3],
Clayton Jeffryes[4]

1) Université Catholique de Louvain, 1348 Louvain-la-Neuve, Belgium
2) Yachay Tech University, 100119 San Miguel de Urcuquí, Ecuador
3) Université Larbi Ben M'hidi, Oum El Bouaghi, Algeria
4) Lamar University, Beaumont, TX 77710, USA

Phototrophs such as algae and cyanobacteria are generating a significant portion of the Earth's primary biomass by utilising solar energy and carbon dioxide. In this way they can contribute to the bioeconomy for the sustainable production of biofuels and value-added chemicals, while at the same time being a major environmental cleanup agent. Our current work with novel extremophilic microalgal strains seeks to exploit their metabolic features and to devise innovative bioprocessing through the rational design of scalable and energy-efficient photobioreactor systems. Photoheterotrophy conditions with the addition of glycerol, a side product of biodiesel manufacture, to the new microalgal strain **Dactylococcus dissociatus** MT1 can simultaneously increase biomass production and reduce or eliminate the need for gas sparging. This behaviour is modelled mechanistically by linking the oxygen exchange between the cells and the culture medium as a function of glycerol concentration, cellular chlorophyll content, and photosynthetic efficiency to biomass productivity. The latter is greatest when the photosynthetic and respiratory pathways are nearly balanced. This implies that an intracellular recycling of O_2 and CO_2 increases biomass production efficiency and that a process set-point can be reached which eliminates the need to provide supplementary O_2 or CO_2. In the same strain, environmental stressors can induce the production of the valuable carotenoids canthaxanthin, adonixanthin and astaxanthin. Light intensity has a positive influence on the accumulation of the major carotenoid, canthaxanthin, similarly to salinity stress, while nitrate deprivation has more of an effect on lipid production, an additional product stream. Nitrate depletion and salinity stress in combination increase both lipid and carotenoid accumulation. The growth and carotenogenesis phases can be initiated, reversed and repeated at regular intervals, thus opening the way to a scalable and sustainable bioprocess that is fully compatible with a circular bioeconomy.

ECOTOXICOLOGICAL EVALUATION OF ORGANIC CONTAMINANTS FOR PLANT-ASSOCIATED MICROORGANISMS

Laura Carmen Apostol[1,2,*], Maria Gavrilescu[2,3]

1) "Stefan cel Mare" University of Suceava, Faculty of Food Engineering,
13 Universitatii Street, 720229 Suceava, Romania
2) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof.dr.docent D. Mangeron Street, 700050 Iasi, Romania
3) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
**: laura.apostol@fia.usv.ro*

Pollution of environmental compartments such us water and soil with organic contaminants has generated a need for remediation. A lot of organic species are biodegradable, and in this case bioremediation is often a viable approach for active and passive decontamination.

The present investigation focuses on remediation with particular interest on the interactions between plant and the associated microorganisms to restore organic contaminated sites. The plant microbiome is a key determinant of plant health and productivity and has received substantial attention in recent years. The use of plant microbiome has the potential to increase agricultural production, reduce the incidence of plant disease, the chemical inputs and emissions of greenhouse gases, resulting in more sustainable agricultural practices.

The cooperation between plant-associated microorganisms allows greater plant survivability and treatment outcomes in contaminated sites. In water or soil impacted by organic contamination, microbial bioremediation generally relies on the addition of high-energy electron acceptors (e.g., oxygen) and fertilization to supply limiting nutrients (e.g., nitrogen, phosphorous, potassium) in the face of excess carbon source. Plant-associated microorganisms improve plant growth by reducing soil toxicity through contaminant removal, producing plant growth promoting metabolites, liberating sequestered plant nutrients from soil, fixing nitrogen, and more generally establishing the foundations of soil nutrient cycling. On the other site the ability to evaluate the role of plant-associated microorganisms in the fate of the pollutants in the ecosystems is a major challenge for ecotoxicological point of view. In study, evidence from traditional and modern technologies are discussed to provide a framework for plant–microbe interactions during organic pollutants remediation sites.

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WHY AND HOW TO WRITE ERC PROPOSALS

Rainer U. Meckenstock[*]

University of Duisburg-Essen
Biofilm Centre, Universitätsstr. 5, 45414 Essen, Germany,
[*]: rainer.meckenstock@uni-due.de

Abstract

The European Research Council funds three different categories of grants: Starting grants (up to 6 years after PhD), Consolidator grants (up to 12 years after PhD), and Advanced grants (after 12 years). All grants have a duration of 5 years and are funded with 1.5, 2.0, and 2.5 Mill € respectively. The ERC grant is an award to an individual person and considers both the personal achievements and the scientific proposal with 50% each. Besides providing excellent funding, ERC grants are the most prestigious funding tool in Europe today and universities or research institutions respect their laureates as a performance parameter.

In the presentation, I will point out the most important requirements and aspects of an ERC proposal and give recommendations how to write a proposal. Special respect will be given to environmental microbiology and how ERC proposals could look like in this field. A short summery on the ecology of life in oil will be presented as an example.

SECTION II

WATER AND WASTEWATER CYCLES: TECHNOLOGIES, RECYCLING AND VALORISATION

DISCOVER THE MECHANISM OF SULFONAMIDE BIODEGRADATION IN WASTEWATER TREATMENT PLANTS, IN SITU AND ON A MOLECULAR LEVEL

Kevin Kroll[1,*], Alexander Timm[2], Rafael Peschke[2], Marius Majewsky[2, 3], Hans-Peter E. Kohler[4], Boris A. Kolvenbach[1], Philippe F.X. Corvini[1]

[1] University of Applied Sciences Northwestern Switzerland, Switzerland, Gruendenstrasse 40, 4132 Muttenz, Basel,
[2] Karlsruhe Institute of Technology (KIT), Germany
[3] University of Heidelberg, Germany
[3] Eawag, Switzerland
[*]: kevin.kroll@fhnw.ch

Introduction and study objectives

The application of sulfonamide antibiotics is common in the treatment of various kinds of infection. Due to constant prescription and an insufficient removal in wastewater treatment plants (WWTP) a concentration of up to 1 µg per liter in surface and groundwaters can be detected. Hence, sulfonamide antibiotics are be categorized as micropollutants. Although the environmental concentrations are too low to be bacteriostatic they can have an immense effect on the environment and there human population. Even at these low concentrations they were shown to foster the propagation of resistance genes in different environmental compartments, potentially culminating in the evolution of multiresistant pathogens. In *Microbacterium* sp. strain BR1, which had been isolated from activated sludge, the ability to biodegrade sulfonamides and use them sources of carbon and energy was discovered. This strain was further investigated to understand the biochemical and molecular biological mechanisms of this process. The degradation of sulfonamides was found to occur via a typical ipso-substitution degradation pathway. Several genes were found to be involved in the biodegradation homologues of which could also be identified by DNA sequence analyses in other degrading strains. We applied this knowledge on the specific pathway, genes and metabolites to expand our view from the *Microbacterium* sp. BR1 to the system of biological WWTP. There we scrutinized sulfonamide degradation by means of a multifactorial investigation encompassing chemical, biochemical and molecular biological analyses.

Methodology

The main focus of our research is the investigation of sulfonamide degradation in five different WWTP, two in Germany and three in Switzerland. These WWTP were sampled over the course of one year on a biweekly time interval. In the influent and effluent samples, we quantified 21 compounds, both sulfonamide antibiotic and potential metabolites by HPLC-MS to assess removal performances. We also looked into the ability of the different activated sludges to degrade sulfonamides by an assay in lab scale format using radiolabelled sulfamethoxazole. In addition, the abundance of the known resistance genes *sul1* and *sul2* were determined by real-time PCR. Further analysis carried out an NGS-based community analysis for sludge samples to complement the research.

Results and conclusions

Analysis of the parent compounds and respective metabolites indicates that the sulfonamide degradation pathway elucidated for *Microbacterium* sp. BR1 is contributing to sulfonamide degradation in the WWTP. Throughout the campaign, the sulfonamide removal efficiencies of the WWTPs showed a characteristic pattern for each WWTP. This pattern deviates from the generally accepted conception that the removal of micropollutants correlates with nitrogen removal processes implemented in WWTP. Interestingly, the removal performances in the WWTP deviated from results obtained for samples of the respective sludges in benchmark degradation assays. The apparent significance of the *ipso*-pathway could be deduced from detecting the specific metabolite 3-amino-5-methylisoxazole. Additionally, preliminary data from principal component analyses of the microbial communities (based on 16S rDNA) showed clusters similar those obtained after performing the mineralization benchmark assays for the different sludges. Applying a multifactorial approach consisting of chemical analyses, biochemical assays with radiolabeled substrates, quantitative PCR and Next Generation Sequencing, we could contribute to a better understanding of the removal of sulfonamide traces during the wastewater treatment process.

PHOTOCATALYTIC ACTIVITIES OF PURE ANATASE AND BROOKITE TIO_2 NANOPARTICLES IN 4-CHLOROPHENOL OXIDATION

Petru Apopei[1,*], **Carmen Teodosiu**[1], **Daniela Fighir**[1],
Cezar Catrinescu[1],**Sébastien Royer**[2]

[1)] Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73 Prof.dr.docent Dimitrie Mangeron Street, 700050 Iasi , Romania,
[2)] Univ. Lille, CNRS, ENSCL, Centrale Lille, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et de Chimie du Solide, F-59000 Lille, France,
[*]: petruapopei@ch.tuiasi.ro

Introduction and study objectives

Among the advanced oxidation processes (AOPs), heterogeneous photocatalysis was proved to be a viable method for the degradation of priority organic pollutants from wastewaters, with the ability to transform them into harmless products, such as CO_2 and H_2O.

Photocatalytic processes take place in the presence of photocatalysts (usually semiconductors), sources of light irradiation (the UV and/or visible) and oxidizing agents. Among many candidates for photocatalysts, TiO_2 (present in three crystalline forms: anatase, rutile and brookite) is the most used semiconductor, because of its high oxidative potential, chemical stability and lack of toxicity.

A particular group of priority organic pollutants is represented by phenols and their halogenated derivatives, which are characterized by high toxicity, persistence and resistance to biodegradation. In this study, the research focused on 4-chlorophenol, considered as model-pollutant, due to its carcinogenic and toxic effects.

Starting from information reported in literature, according to which anatase is the most active form of TiO_2 and considering that brookite is the least studied form of TiO_2, the main objective of this study was to obtain these two TiO_2 polymorph forms and to compare their photocatalytic activity in 4-chlorophenol oxidation from synthetic wastewater.

Methodology

The two TiO_2 photocatalyst were obtained by hydrothermal methods. All phases were characterized by physico-chemical techniques such as: DR UV-VIS spectroscopy, Raman Spectroscopy, X-Ray Diffraction (XRD), Nitrogen adsorption-desorption isotherms and Transmission Electron Microscopy (TEM-HRTEM). To evaluate the photocatalytic performance of the studied photocatalysts, there have been performed photocatalytic tests for 4-chlorophenol removal from synthetic wastewater. The concentration of 4-chlorophenol was analyzed by the 4-aminoantypirine standard method.

Results and conclusions

The nature of the crystalline phases was identified by X-ray diffraction. The XRD patterns registered for TiO_2 powders are according to the specific Joint Committee on Powder Diffraction Standards (JCPDS) reference, indicating that anatase and brookite TiO_2 phases were successfully synthesized. These results are confirmed by Raman spectroscopy that clearly describes the presence of frequency bands specific for each TiO_2 phase. The band gap energy for each photocatalyst was calculated on the basis of Tauc graphs and 1^{st} order derivates of the DR UV-VIS spectra, registered in the reflectance mode. The values of band gap energy calculated for the TiO_2 nanoparticles are in the same range as the ones reported in the literature: 3,23-3,59 eV for anatase and 3.40-3.45 eV for brookite.

Textural properties of TiO_2 nanoparticles were described by using nitrogen physisorption. The adsorption/desorption isotherms registered are specific to mesoporous materials, type IV. Transmission electron microscopy (TEM-HRTEM) is used to describe the morphological properties of each synthesized TiO_2 nano-powder. The anatase samples are characterized by the presence of round shaped, uniform particles, a very well-defined crystalline structure, with average size of around 10 nm. The Brookite sample present 40-60 nm sized aggregates, formed of 5-7 nm round shape particles. The results are consistent with the ones reported in the literature.

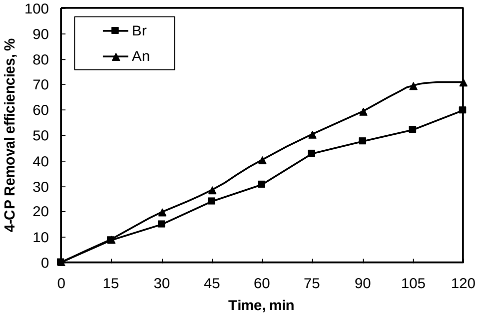

Figure 1: 4-chlorophenol removal efficiencies for anatase and brookite TiO_2 nanoparticles, conditions: T = 25 ºC, V = 0.5 L, 500 rpm, pH=5, C_{4CP} = 20 mg L^{-1}; C_{TiO2} = 200 mg L^{-}

The photocatalytic activity, expressed as the removal efficiency of 4-chlorophenol, for anatase and brookite samples is presented in Figure 1. Our data show that anatase performs better (70% efficiency in 4-chlorophenol removal) than brookite (60% efficiency in 4-chlorophenol removal), which confirms the information reported in the literature, that the most active form of TiO_2 is anatase.

Acknowledgements

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HOW MUCH IS SUSTAINABLE PRODUCING LOW-COST ADSORBENTS FOR WASTEWATER TREATMENT? A COMPARATIVE EVALUATION

Sabino De Gisi*, **Michele Notarnicola**

Department of Civil, Environmental, Land, Building Engineering and Chemistry (DICATECh),Technical University of Bari, Via E. Orabona n. 4, 70125 Bari (ITALY),
**: sabino.degisi@poliba.it*

Introduction and study objectives

The number of scientific articles concerning production and testing of low-cost adsorbents for water and wastewater treatment has increased significantly in recent years. However, the number of studies related to the comparison of the performance of low-cost adsorbents both in terms of pollutants removal both in terms of sustainability of their production cycle is limited. In this regard, Gautam *et al.* (2014), highlight the need to compare such performance in a systematic way in order to obtain results useful for directing future research. The intent is to avoid the production of new adsorbents that although highly performing in terms of pollutants removal, are then unsustainable in terms of production. With the intent to fill this gap, the aim of the study was to define and apply a novel methodology that, based on the use of a composite indicator, was able to assess the sustainability of the production supply chain of low-cost adsorbents. For the purpose, agriculture and household low-cost adsorbents tested in literature for the removal of heavy metals from wastewater were considered.

Methodology

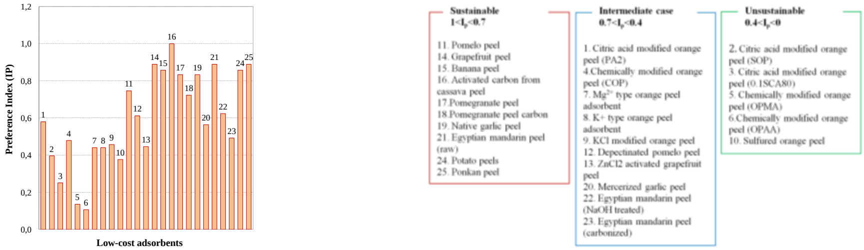
Since there are no direct references in literature, a novel homemade methodology has been defined according to the following two main phases: (1) Study of literature and identification of the main production supply chains; (2) Assessment of the sustainability of each production supply chain (Output 2). The latter included the construction of a composite indicator whose main steps were the following: (i) Identification of the goal; (ii) Definition of appropriate evaluation criteria; (iii) Determination of criteria weighs; (iv) Construction of the composite indicator (indicated as IP) by means of the linear aggregation method. Furthermore, the following criteria priorities have been considered: $I_2 > I_1 > I_3$. Further information on the indicator construction is given in Table 1.

Results and conclusions

Low-cost adsorbents such as pomelo peel, grape fruit peel, banana peel, pomegranate peel, potato peel, peel ponkan, are the most "sustainable" (1.0 <IP <0.7) since they need only few production processes, generally simple and of mechanical type (See Fig. 1). Instead the adsorbents subject to chemical treatments fall for the most part in the category "average sustainable" (0.7 <IP <0.4) because they need few chemical treatments and/or small quantities of reagents. Finally, the "not sustainable" sorbents (0.4 <IP <0.0) are the following: citric acid modified orange peel, chemically modified orange peel, Chemically modified orange peel and sulfured orange peel. In fact, these sorbents are characterized by a high number of chemical treatments, an increase in the reagents consumption as well as a large number of unit production processes.

Table 1: Evalutation criteria and main rules for the composite indicator contruction

N.	**Evaluation criterion**	**Unit**	**Description and response classes**
I_1	Unit processes in the production cycle	Positive integer	The criterion measures the number of processes that make up the production cycle of the low-cost adsorbent so as reported in the investigated literature. The lower the number of unit processes, the greater the value attributed to the I_1 criterion. To MINIMIZE in respect of IP (MIN).
I_2	Degree of complexity of the production cycle	Class 1 = 0.9 (best condition); Class 2 = 0.7; Class 3 = 0.5; Class 4 = 0.3; Class 5 = 0.1 (worst condition)	The criterion measures the degree of complexity of the low-cost adsorbent production cycle. Starting from the surveying of the production chains, the following classes were defined: • Class 1: The implemented supply chain is represented by the basic configuration; • Class 2: The implemented supply chain provides at least one chemical treatment (for example, with citric acid or sodium hydroxide); • Class 3: The implemented supply chain provides at least two chemical treatments. • Class 4: The implemented supply chain provides at least three chemical treatments. • Class 5: The implemented supply chain provides a number of more than 4 chemical treatments. To each class, a score is assigned as following reported: • Class 1 = 0.9 (best condition); • Class 2 = 0.7; • Class 3 = 0.5; • Class 4 = 0.3; • Class 5 = 0.1 (worst condition). The lower the degree of complexity of the production cycle, the greater the value to be attributed to the criterion I_2. To MAXIMIXE in respect of IP (MAX).
I_3	Consumption of liquid reagents	mL/g of obtained adsorbent	The criterion measures the consumption of liquid reagents used in the production cycle low-cost adsorbent. For example, the required millilitres of Na (OH) for the chemical treatment of a gram of raw adsorbent. In case of use of more reactive, the criterion is the sum of the quantities consumed. The lower the consumption of liquid reagents, the higher the value attributed to the I_3 criterion. To MINIMIZE in respect of IP (MIN).
Construction of the composite indicator (IP) adopted in our investigation			
Method: Linear aggregation			
$IP_i = (w_1 \cdot a_{i,1} + w_2 \cdot a_{i,1} + w_3 \cdot a_{i,3})$ where: i = i-th alternative to be compared (in our case, the alternative = low-cost adsorbent); a_{ij} = performance of the i-th alternative in respect of the j-th criterion (j = 1, 2, 3); (w_1, w_2, w_3) = weight vector of the 3 comparison criteria evaluated by means of the PCT method.			



(a) (b)

Figure 1: Results related to the application of the „sustainability methodology" developed to quantify the sustainability of the lw-cost production chain: (a) Performance comparison in terms of IP; (b) Effert to divide the low-cost adsorbents investigated in class on the basis of the value of IP

SEQUENCING BATCH BIOSORPTION OF MICROPOLLUTANTS FROM AQUEOUS EFFLUENTS: EQUILIBRIUM AND OPTIMIZATION STUDIES

Irina Morosanu, Carmen Teodosiu*, Carmen Paduraru, Corina Petronela Musteret

Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection,"Gheorghe Asachi" Technical University of Iasi, 73 Prof. Dr. D. Mangeron Street, 700050, Iasi, Romania,
*: cteo@ch.tuiasi.ro

Introduction and study objectives

Water is a finite and shared natural resource, which underpins the societal and economic progress. In order to achieve the Sustainable Development Goals, an integrated approach of the water resources management is essential for maintaining good water quality status under the pressures of urban, industrial and agricultural pollution, climate change events or reduced water availability for users. Recycling/reusing of the reclaimed water is a prerequisite for closing the loop in the water-systems. In this sense, the tertiary (advanced) treatment of the wastewater must ensure a high quality effluent by targeting the priority micropollutants that could not be removed in the conventional wastewater treatment stages. Heavy metals and dyes are recurrent micropollutants of industrial effluents, with significant impact upon the environment.

Many industries, including textile, rubber, plastics, paper and cosmetics, use dyes in the manufacturing process and consume large volumes of water. The major concern about dye-containing effluents is related to the color and turbidity of the wastewater. Dye molecules are refractory to biological aerobic treatment and present high stability in the presence of conventional oxidizing agents, some dyes having mutagenic and carcinogenic effects. Pollution caused by toxic metals is a major global concern because they can be found in the wastewater discharges of industries, such as electrochemical, leather and tanning, metallurgical, textile, steel and aluminum, mining etc. Many toxic metals, like cadmium, lead, zinc, chromium, copper etc., are considered priority pollutants, due to significant effects of toxicity, mutagenicity and carcinogenicity on human health and environment.

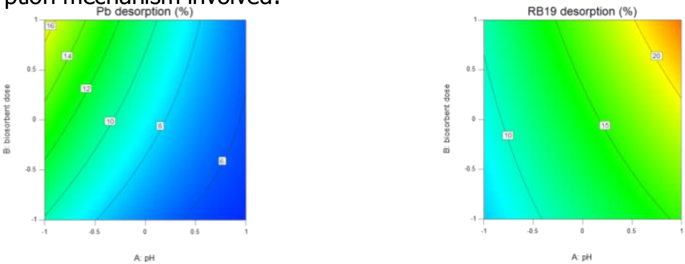
Biological, membrane separation, chemical, electrochemical and sorption processes have been used in order to remove toxic metals and dyes from wastewaters. These techniques all have advantages and disadvantages. Among them, sorption processes have proved to be an efficient wastewater treatment process, targeting various categories of pollutants, although entailing some high costs because of activated carbon acquisition and regeneration. In recent years, utilization of different types of biomaterials (microorganisms, algae, vegetal materials) as sorbents in the biosorption processes has gained a particular attention. The valorization of wastes through biosorption process using lignocellulosic wastes for wastewater treatment, constitutes an opportunity that considers also the circular economy principles. However, the work regarding the removal of toxic metals and dyes in binary systems is ongoing. This study presents the sequential biosorption of lead ions, Pb(II), and Reactive Blue 19 (RB19) dye from aqueous solutions by using rapeseed waste (RS).

Methodology

The rapeseed waste was obtained after the oil extraction in biodiesel production and was used in the biosorption process after washing, drying and grounding (0.1-0.2 mm). Sequencing batch experiments were conducted by first equilibrating the biosorbent with one of the pollutants (C_0: 100 mg Pb(II)/L or 100 mg RB19/L), separating the solid by centrifugation and drying at room temperature overnight. The enriched biosorbent was then used to investigate the removal of the other pollutant left by varying the initial concentration and contact time. The general experimental conditions were those already optimised from the single component biosorption studies, namely biosorbent dose: 10 g/L, pH: 5-5.6, T: 20°C. After sequential biosorption, batch desorption tests of the used biosorbent (containing both lead and RB19 dye) were performed by varying the pH of the eluent (ultrapure water), in the same conditions as the sequencing biosorption tests. The Central Composite Design (CCD) in the Response Surface Methodology (RSM) by *Design-Expert*$^{@}$ Ver. 10.0.1 (Stat Ease, USA) was used to analyze and optimize: (i) the sequencing biosorption process by varying three factors: pH, initial concentration and biosorbent dose, and (ii) the desorption process by varying two factors: pH and biosorbent dose.

Results and conclusions

In the case of the sequencing batch biosorption of lead on the sytem rapeseed-RB19 (RS-RB19), the Langmuir isotherm model and the pseudo-second order kinetic model were found to be the best fitted models for the process under study. The optimum conditions for maximum Pb(II) biosorption capacity given by the RSM model were: pH 4.67, C_0 75 mg/L and RS-RB19 dose 5 g/L. RSM analysis revealed that pH, used biosorbent dose and their interaction are significant to the desorption of Pb(II) ions and RB19 dye (Fig. 1). The experimental data in the case of the sequencing batch biosorption of RB19 dye on the system rapeseed-lead (RS-Pb) was well correlated with both Langmuir and Freundlich isotherm models. The kinetics of the sequential biosorption followed the pseudo-second order model. RSM analysis indicated the significant effect of dye initial concentration and RS-Pb dose on the biosorption process. Insignificant desorption efficiencies for RB19 and small desorption efficiencies for Pb(II) ions were obtained due to the chemisorption mechanism involved.



a. **b.**

Figure 1: Response surface contour plot of interactive effect of pH and used biosorbent dose in the case of Pb(II) desorption(a) and RB19 dye desorption (b)

BIOSORPTION OF METANIL YELLOW DYE FROM AQUEOUS SOLUTIONS BY THE ENTIRE WATER HYACINTH PLANT (*EICHHORNIA CRASSIPES*) AND ITS VEGETATIVE ORGANS

Imelda Guerrero-Coronilla, Eliseo Cristiani-Urbina*

Instituto Politécnico Nacional, Escuela Nacional de Ciencias Biológicas, Departamento de Ingeniería Bioquímica. Avenida Wilfrido Massieu s/n. Unidad Profesional Adolfo López Mateos. Ciudad de México, 07738, México.
* *: ecristianiu@yahoo.com.mx*

Introduction and study objective

Azo dyes are one of the main sources of water pollution because they are used widely in industry for coloring foods, drinks, drugs, cosmetics, textiles, leather, paper, wood, plastics, etc. The rise in the number of industries worldwide has led to increased pollution of natural water resources and soil by azo dyes and their biodegradation intermediates. This is of great concern because of potential health hazards associated with their toxic, allergenic, mutagenic, carcinogenic and genotoxic properties.

Metanil yellow dye (Acid Yellow 36) is a sulfonated monoazo compound, which is used mainly in developing countries for coloring foodstuffs. However, metanil yellow causes serious health hazards, such as insufficient oxygen supply to skin and mucous membranes, degenerative changes to the stomach, liver, kidney, abdomen and testes, as well as cyanosis, methaemoglobinaemia, reproductive effects, neurotoxicity, mutagenicity and carcinogenicity.

The removal of azo dye compounds from water and wastewater by conventional physicochemical and biological methods is extremely problematic because they are highly soluble in water, stable to light, heat and oxidizing agents and recalcitrant to biodegradation due to their complex chemical structures and xenobiotic nature. Biosorption is among the biotechnological processes that have proven effective and cost-effective for the treatment of dye-contaminated water and industrial wastewater.

The water hyacinth (*Eichhornia crassipes*) is a free-floating aquatic plant with worldwide distribution that can reproduce both sexually and asexually under different environmental conditions and has an accelerated growth rate. Its presence in water bodies inhibits navigation, causes nutrient depletion, and reduces light penetration and oxygen transfer within water bodies. However, its ability to remove different pollutants from wastewater has been demonstrated.

In the present work, we studied the kinetics of metanil yellow biosorption onto the vegetative organs (root, stem, and leaf) and the entire *E. crassipes* plant.

Fourier transform infrared (FTIR) spectroscopy was also employed to identify the key functional groups involved in metanil yellow biosorption.

Methodology

Water hyacinth plants were collected from the water channels in Xochimilco, Mexico City and washed thoroughly with distilled water. The roots, stems and leaves were cut off from some plants; while others were kept intact. All vegetative organs and the entire plants were oven-dried, milled and sieved. Batch kinetic biosorption experiments were performed under the following conditions: pH of solution = 2; initial metanil yellow dye concentration = 50 mg L-1; initial biosorbent concentration = 1 g L-1; particle size = 0.15-0.3 mm; temperature = 25 °C; and agitation speed = 120 rpm. Metanil yellow dye concentrations were determined spectrophotometrically at 434 nm. The kinetics of metanil yellow biosorption were analyzed using the pseudo-first-order, pseudo-second-order, Elovich, and fractional power models. Finally, to identify the functional groups involved in the metanil yellow biosorption process, the chemical composition of the surface of each biosorbent was characterized by FTIR, before and after saturation with the dye.

Results and conclusions

The biosorption kinetics of metanil yellow dye indicated that the leaves, stems and roots, as well as the whole water hyacinth plant are capable of removing the azo dye from aqueous solution. Regardless of the biosorbent tested, rapid metanil yellow biosorption was observed initially, with the rate gradually diminishing until the metanil yellow capacity reached maximum constant values corresponding to the equilibrium biosorption capacity. The biosorption capacities at equilibrium were as follows: 42.87, 34.29, 29.66, and 25.5 mg g-1 for the leaves, whole plant, roots and stems, respectively.

Kinetic modeling of metanil yellow biosorption by all the vegetative organs and the entire water hyacinth plant showed that experimental data concurred well with the pseudo-second-order model, suggesting that the rate-limiting step in the metanil yellow biosorption process may be chemical in nature.

FTIR results indicate that chemical interactions between the biosorbents amide I and amide II functional groups and the metanil yellow dye molecules were involved in dye biosorption. These functional groups are constituents of the proteins present in the biosorbents.

Based on the above results, it can be concluded that water hyacinth leaves manifested optimum performance for biosorbing metanil yellow dye from aqueous solutions, that the kinetic mechanism followed a pseudo-second order model and that proteins play a key and relevant role in the dye biosorption process. Thus, water hyacinth leaves exhibit remarkable potential for application in detoxification of metanil yellow-contaminated aqueous solutions.

FATE OF ANTIBIOTIC RESISTANCE GENES IN BIOLOGICAL NUTRIENT REMOVAL WASTEWATER TREATMENT PLANTS

Serkan Kucukunsal, Bulent Icgen*

Department of Environmental Engineering,
Middle East Technical University 06800, Ankara, Turkey,
**: bicgen@metu.edu.tr*

Introduction and study objectives

Antibiotic resistance genes (ARGs) have been detected in groundwater, wetlands, sediments and surface waters. High concentration of multi-drug resistant bacteria has also been detected in hospital wastewater, drainage from livestock feeding operations and domestic sewage. Therefore, wastewater treatment plants (WWTPs) play a crucial role in minimizing or even complete removal of many water pollutants, including pathogens and antibiotics. On the other hand, WWTPs also act both as collection points for resistant microorganisms, antimicrobials and potential point sources for of ARGs. The biological treatment units of WWTPs not only promote bacterial growth but also provide genetic exchange of ARGs which might lead to further ARG proliferation. Although there are various studies about the role of WWTPs on the dissemination of antibiotic resistance bacteria, the studies about the dissemination of ARGs are scarce. Therefore, in this study, dissemination of ARGs including β-lactams, sulfonamides, tetracyclines, aminoglycosides, macrolides, lincosamides, quinolones, fluoroquinolones and vancomycins was investigated in biological nutrient removal (BNR) type WWTP.

Methodology

Samples from influent and effluent water were collected from BNR type WWTP throughout four seasons. The WWTP serves 160,000 people and it receives an average daily flow of 42,000 m^3 made up by domestic wastewater. Sampling locations and processes of the WWTP can be seen in figure 1.

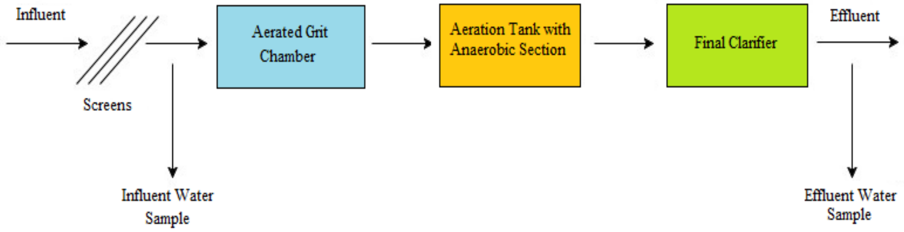


Figure 1. Sampling locations and processes of the WWTP

After collection, samples were immediately transported to laboratory within 2 hours. 50 mL of each sample was centrifuged at 13000 rpm for 20 min to collect the pellets. The pellets were then fixed in 50% ethanol-water solution. All samples were preserved in 20ºC before DNA extraction. DNA extractions were done manually by 50% phenol-chloroform solution for purification and 70% ethanol-water solution for precipitation. Purity of extractions then checked with both microvolume uv-vis spectrophotometer and gel electrophoresis to minimize PCR inhibition. Real time PCR amplifications were performed with specific primers targeting; blaCTX-M, sul1, tetA, aadA, ermB, qnrS, vanA and 16s rRNA genes. For real time PCR standards, purified PCR products of bacterial genes that have resistant to β-lactams, sulfonamides, tetracyclines, aminoglycosides, macrolides, lincosamides, quinolones, fluoroquinolones and vancomycins were used. Calibration standard curves for positive controls were generated by performing serial dilutions. Negative controls contained all PCR mixture components without DNA template. Finally, resulting data of real time PCR were processed.

Results and conclusions

Water samples for the seasons summer, autumn, winter have been collected so far. After being fixed, DNA extractions were done. DNA was visualized with gel electrophoresis (Figure 2) and quantifications were done with microvolume uv-vis spectrophotometer (Figure 3). Real time PCR analyses of the antibiotic specific genes are under progress.

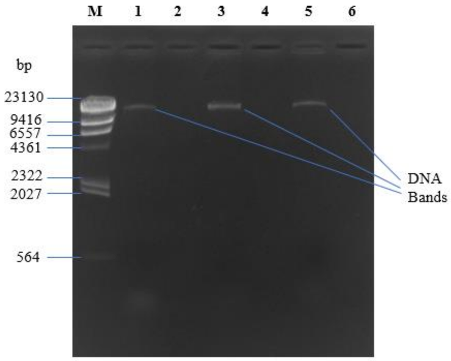


Figure 2: DNA extractions from BNR WWTPs': influents and effluents for summer (lane 1-2), autumn (lane 3-4), winter (lane 5-6), respectively. Marker (M).

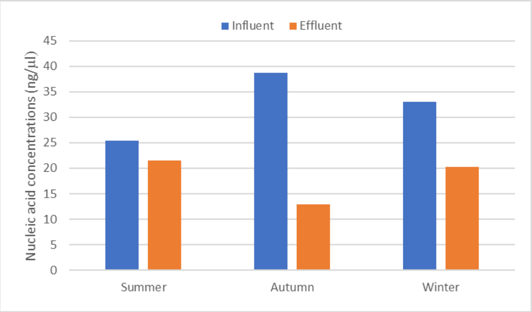


Figure 3: Nucleic acid concentrations of water samples collected in 2016 - 2017

EFFICIENT DEGRADATION OF A PERSITENT PHARMACEUTIC COMPOUND THROUGH AN ADVANCED OXIDATION PROCESS VIA A STATISTICAL OPTIMIZATION APPROACH

Lidia Favier[1,*], Andrei Ionut Simion[2*], Lacramioara Rusu[2], Cristina-Gabriela Grigoras[2], Yassine Kadmi[3], Raluca Hlihor[4,5], Dominique Wolbert[1]

[1]Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226,
11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France
[2]"Vasile Alecsandri" University of Bacau, Faculty of Engineering, Department of Chemical and Food Engineering, 157 Calea Marasesti, 600115 Bacau, Romania
[3]Université d'Artois, Institut Régional en Agroalimentaire et Biotechnologie Charles Viollette, Equipe Qualité et Sécurité des Aliments (QSA), Arras, France
[4]"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
[5]"Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania
[*]: lidia.favier@ensc-rennes.fr; asimion@ub.ro

Introduction and study objectives

In the past decade pharmaceutically active compounds and their metabolites have been reported as one of the diverse chemical classes of aquatic contaminants. Among them, clofibric acid (CA) is one of the most frequently detected in surface water and even more in drinking water. The biological effects of this lipid regulator drug are not completely elucidated but it has been associated with endocrine disruption through interference with cholesterol synthesis.

The major concern related to this molecule arises from its environmental persistence, stability (more than 20 years) and it is amplified by its resistance to water treatment technologies. Several studies demonstrated that this substance is not completely removed by the current techniques used for the wastewater treatment. Hence, the wastewater treatment plants and hospital effluents are the main sources of dispersion of this molecule to the aquatic environment. Thus, nowadays research efforts are focused on the development of efficient techniques for achieving their total elimination.

In recent years, various techniques were assessed with regard to their removing potential of pharmaceuticals. Among them, advanced oxidation processes (AOPs) received an increasing attention. Indeed, such techniques mainly generate highly reactive, unselective and short-lived hydroxyl radicals and further promote the organic compounds oxidation. Some works demonstrated that ozonation and Fenton oxidation improve total organic carbon removal but leads to the production of toxic reaction by-products that require special treatments. Adsorption with activated carbon was reported as effective for the removal of some pharmaceuticals, but in the case of clofibric acid the process was rather difficult. Other studies have reported the effectiveness of heterogeneous photocatalysis, one example of AOPs, for the complete oxidation of inorganic or organic pollutants.

This work explores the potential of photocatalysis on the removal of clofibric acid in aqueous titanium dioxide (TiO_2) suspensions. The influence of some critical operating parameters were investigated and optimized by central composite design (CCD) based of response surface methodology (RSM) to determine the optimal degradation and mineralization conditions. In addition, the general photocatalytic mechanism of CA was discussed based on the identified intermediates determined by HPLC/MS/MS.

Methodology

Degradation studies were conducted at laboratory scale in a cylindrical batch reactor (working volume of 2L), mechanically stirred equipped with two UV lamps under aerobic conditions. The lamp position is adjustable in order to vary the incident light flux intensity. All experiments were carried out in aqueous solution at natural pH = 4.2 (given by dissolved clofibric acid), at room temperature (22 ± 0.5°C) and with TiO2 PC 500 as photocatalyst. In order to determine the CA degradation kinetics, samples were collected according to the experimental algorithm and the concentration of the target compound was monitored by high performance liquid chromatography (HPLC) using a WATERS® system equipped with a C18 packed column (Symmetry WATERS®; 250 mm x 4.6 mm, 5 µm) and a diode array detector (DAD). Total organic content (TOC) was measured with a Shimadzu system operated in NPOC mode and equipped with an ASI-V autosampler.

Response Surface Methodology (RSM) was employed to evaluate the effects and the interactions between the key operating parameters over degradation process and to determine the optimal conditions of CA elimination. Considered input data were: for initial pollutant concentration between 0.5 and 15 mg.L-1, for catalyst load between 0.1 to 2 g.L-1 and 0 to 190 min for exposure time at 95.22, 20.92 and 7.9 W.m-2 UV light intensity. As response functions the residual CA concentration and mineralization yield were examined.

Results and conclusions

The results indicated that the removal rate of the target pollutant is strongly influenced by its initial concentration. The effect of the TiO2 concentration on the degradation kinetics was significant. This is due to the positive influence of the increased number of TiO2 active sites on the process kinetics. After exploring the interaction effects by (CCD) experiments the optimal amount of catalyst for the degradation of CA was determined to be 1.2 g.L-1. Complete removal of the target compound was achieved at low concentrations in pollutant. The photocatalytic process shows high elimination efficiency even at higher pollutant concentrations after employing RSM optimized amounts of catalyst in reduced irradiation time and UV intensity.

In conclusion, we note that the results obtained in this work for the photocatalytic elimination of clofibric acid are very promising, given the refractory nature of this compound. Moreover, they can provide basic information to understand the oxidative degradation of this pollutant and process design.

DEGRADATION OF PARABENS BY HETEROGENEOUS ELECTRO-FENTON PROCESS

Ciprian Sandu[1,2], Marius Popescu[1,2], Emilio Rosales[1], Marta Pazos[1], Gabriel Lazar[2], María Angeles Sanroman[1,*]

1) Department of Chemical Engineering, University of Vigo, Isaac Newton Building, Campus As Lagoas, Marcosende 36310, Vigo, Spain
2) Faculty of Engineering, "Vasile Alecsandri" University of Bacau, Calea Marasesti 157 600115, Bacau, Romania
**: sanroman@uvigo.es*

Introduction and study objectives

Parabens are man-made chemicals often used in many personal care products that contain a significant proportion of water, such as shampoos, commercial moisturizers, conditioners, lotions, topical/parenteral pharmaceuticals, spray tanning solution, makeup, and toothpaste. Since these chemicals may cause severe damages to health, the development of highly effective removal methods is receiving a great deal of attention in the last years.

Advanced Oxidation Processes (AOPs) appear as an attractive alternative to treat this kind of pollutants. Among them, electro-Fenton which is able to produce a strong oxidant as hydroxyl radicals is considered a promising technology. In the literature is reported that the generation of H_2O_2 is one of the key parameters of this technology and several studies concluded that the selection of cathodic material is vital to increase its concentration in the bulk media. In addition, to treat a high volume of wastewater is necessary the operation in continuous flow system by use of heterogeneous system in which the iron is fixed on a solid matrix. One alternative option is the iron fixation on the cathode surface to permit the treatment by electro-Fenton process in continuous flow.

Therefore, the main goal of this study is to evaluate the ability of electro-Fenton technology to degrade a model paraben such as methyl 4-hydroxybenzoate and to enhance the process to operate in flow systems by fixation of iron on the surface of the cathode, permitting the self-regulation of iron and facilitating the operation in continuous mode.

Methodology

Experimental procedure: Anodic oxidation and electro-Fenton experiments were performed in an undivided and cylindrical reactor with working volume of 150 mL of methyl 4-hydroxybenzoate (100 mg/L). An external direct-current power supply was connected to two electrodes. Boron-Doped Diamond (BDD) electrode was used as anode and different modified carbon felt electrodes were tested as cathode. The assays were performed applying a constant current of 100 mA.

Iron cathode: Carbon felt was previously cleaned with absolute ethanol to remove the impurities from their surface for 1 hour and dried at room temperature for

24 h. The fixation of iron on carbon felt was performed by two different methods. CF-M1: Cleaned carbon felt was immersed in an ethanol solution of $\mathrm{FeCl3{\cdot}6H2O}$ at a concentration of Fe/C 30% (w/w). After a contact time of 24 h, the electrode was removed and air dried at room temperature for 48 hours. Afterwards, it was washed with distilled water several times and treated with ethanol in an ultrasonic bath in order to remove the weakly adsorbed iron. Finally, the electrode was air dried for 48 h and it was ready for further use. CF-M2: Cleaned carbon felt was immersed in 400 mL solution of $\mathrm{FeCl3{\cdot}6H2O}$ (28mM) and $\mathrm{FeSO4{\cdot}7H2O}$ (14 mM) with vigorous stirring at 70ºC. Then, NaOH solution (5 M) was added dropwise to precipitate the iron oxides and the suspension was mixed on a magnetic stirrer at 80ºC for 1h. Modified carbon felt was then dried in an oven at 100 ºC for 3 h. Finally, the obtained material was washed with distilled water (5 times) and then air dried for further use.

Analytical procedure: The degradation of methyl 4-hydroxybenzoate was monitored by HPLC with an XDB-C8 reverse-phase column. Identification and quantification of degradation intermediates was performed using HPLC and GC-MS.

Results and conclusions

The physical characterization of both prepared cathodes by scanning electron microscopy equipped with an energy dispersive spectrometric confirmed the fixation and homogeneous distribution of iron on the cathodes surface. Cyclic voltamperimetry was performed confirming the generation of $\mathrm{H2O2}$ and reduction reactions related to Fe presence in the prepared electrodes.

The initial results revealed that the methyl 4-hydroxybenzoate degradation followed pseudo-first order kinetics, also showing a clear advantage of electro-Fenton using CF-M1 or CF-M2 over anodic oxidation. There were no differences between the degradation levels achieved operating with both cathodes (nearly complete after 45 min). However, the reduction of total organic content was lower when CF-M1 was used. In addition, was confirmed that CF-M2 kept the iron fixed on the carbon felt in successive treatment cycles, which is indicative of the potential to apply this cathode to operate in flow systems. These results also confirmed that CF-M2 cathode could be a good alternative to the current cathodes permitting the electrogeneration of high concentration of hydrogen peroxide and the iron fixation, favouring the rapid reaction between both of reagents that increases the degradation rate of the organic pollutants present into solution. The degradation and mineralisation of the pollutant was verified by identification of several intermediate products (carboxylic acids and phenolic compounds) by GC-MS that permitted to propose a plausible degradation pathway for the methyl 4-hydroxybenzoate.

Acknowledgments:

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3D PRINTING OF ANAMMOX BIOFILMS

Damian Hausherr*, **Boris Alexander Kolvenbach,**
Patrick Shahgaldian, Philippe F.-X. Corvini

FHNW, Institute of Ecopreneurship
Hard 35, 8408 Winterthur, CH,
**: damian.hausherr@fhnw.ch*

Introduction and study objectives

Since the first observation of nitrogen gas accumulation in a wastewater treatment plant (WWTP) in the 1990s and the subsequent enrichment of the first anammox bacteria, considerable effort has been devoted to elucidate the anammox process. It provides both a positive energy balance, compared to energy consumption of the typical nitrification-denitrification treatment and a reduction of added carbon sources by 100%. This process relies on the anaerobic ammonium oxidation (Anammox), using nitrite (NO_2^-) as an electron acceptor and ammonium (NH_4^+) to generate N_2.

Since most wastewater amenable to anammox is very high in NH_4^+ but not NO_2^- the process is coupled to partial nitritation, which converts approximately half of NH_4^+ into NO_2^-, albeit in the presence of oxygen. These two interconnected processes lead to a complex biofilm formation involving the species responsible for each reaction. Most often the anaerobic anammox bacteria occupy deeper strata of a biofilm, whereas the AOB and AOA (ammonium oxidizing bacteria and ammonium oxidizing archaea, respectively) reside in the medium and oxygen exposed layer. This approach works well, demonstrated by over 200 full-scale facilities around the world, if certain conditions are met. The temperature is optimally between 28-35°C, oxygen concentration very low (0.5-1.5 mg) and chemical oxygen demand (COD) and biological oxygen demand (BOD) low (1-3 times N load). Problems may arise from competing bacteria, especially nitrite oxidizing bacteria (NOB), and if the biofilm is formed in a granular manner, the granules can break apart, exposing the anammox bacteria to oxygen and thus reducing process efficiency. One further constraint is the slow doubling rate of anammox bacteria ranging between 3-10 days, making them susceptible to be washed out of the reactor.

To alleviate these complications, we propose encapsulating the involved bacteria and construct a 3D scaffold to precisely position the bacteria containing beads. As has been previously shown, encapsulation confers tolerance to pH and COD stress and impedes washout of anammox bacteria. But so far, no studies have encapsulated AOB and anammox together nor subsequently designed biofilm formation on a scaffold. This work will advance our understanding of the anammox process and its interactions with other bacteria and further its applicability to diverse types of wastewater. So far initial studies on the encapsulation process have been completed and viability assays performed.

Methodology

The anammox bacteria are obtained from a WWTP in Zürich with a PNAA (partial nitritation annamox) reactor or the Swiss federal aquatic research centre EAWAG. The bacteria are mixed with an alginate solution to be added dropwise to a hardening solution, resulting alginate beads may be further coated with a chitosan layer before liquefying the alginate core to allow bacterial growth. Alternatively, alginate beads may also be applied directly to the bioprinting process. These beads are then placed within a scaffold that provides structural stability while only posing a minor obstacle to mass transfer. The loaded scaffolds will be tested into 1L reactors, fed by synthetic wastewater and the growth and composition of the biofilms as well as nitrogen removal is monitored.

Results and conclusions

Initial results show good viability of encapsulated cells (*E. coli*) after performing liquification of the core. Additionally, incubating these cells in appropriate medium leads to growing cells to fill the cavity. Initial attempts to crosslink chitosan beads with glutaraldehyde drastically reduced viability while failing to lead to a stable construct of beads. Yet embedding the alginate-chitosan beads into a colloidal silicon dioxide with activated TEOS showed promising results.

Building on these results we envision to further develop this new approach, promising a more stable and reproducible anammox process (as biofilms are produced as opposed to waiting for natural growth) and widening the scope of possible parameters for a streamlined WWTP process. This technique will allow us to control biofilm composition and structure to enhance the role of anammox process in nitrogen removal in wastewater. These artificial biofilms may also be applied to a plethora of other suitable tasks where precise architecture is needed.

THE MANAGMENT OF TPH CONTAMINATED LEACHATES: AN INNOVATIVE BIOTECHNOLOGICAL STRATEGY USING FUNGI

Giovanna Siracusa[1,*], Simone Becarelli[1,2], Ilaria Chicca[1], Salvatore La China[1], Alessandra Bardi[1], Roberto Lorenzi[1], Qiuyan Youan[3], Giulio Munz[4], Alessandro Gentini[5], Gualtiero Masini[4], Simona Di Gregorio[1]

[1)] Department of Biology, University of Pisa; Via Luca Ghini 13, 56124 Pisa (PI), Italy
[2)] BD, Biodigressioni srl, Pisa
[3)] Dep. Of Environmental And Civil Engineering, University Of Manitoba, Gillson Street 15, Manitoba, Canada
[4)] Dep. Of Environmental And Civil Engineering, University Of Florence, Via Santa Marta 3, 50139 Firenze, Italy
[5)] Teseco Spa, Pisa
[*]: giovanna.siracusa@biologia.unipi.it.

Introduction and study objectives

Soils and sediments are often contaminated by heavy hydrocarbons pollutants due to human activities, such as spills and industrial processes related to petroleum refining. Among them, the Total Petroleum Hydrocarbons (TPH) are composed of structures with different biodegradability. The volume of dredged sediments in Europe, to be disposed off, is around 200 millions cubic meters per year and the 60% of the total is contaminated mainly by Total Petroleum Hydrocarbons (TPH) [1]. TPH contains tens of different polyaromatic hydrocarbons (PAHs) and hundreds of different hydrocarbon compounds [2]. Today, the management of dredged sediments contaminated by TPH, is associated exclusively to landfilling. However, the long-term disposal strategy such as natural attenuation, can be associated to significant risks for the community, because of possible contaminant leakages and the consequent deterioration of the surrounding environment. The vehicle for contaminant leakage are mainly leachates, strongly polluted wastewaters [3]. The acceleration of the decontamination and the fast and safe reallocation of decontaminated sediments are actually a priority for the protection of the environment and for the reduction of the volume of contaminated leachates, that has to be treated as industrial wastewaters.

The fungal strain microF, isolated from marine dredged sediment, was tested as an allochthonous specimen for the treatment of two different leachates: one deriving from an urban landfill in Winnipeg (Canada), with a TPH contamination (1850 ppm) and a chloride concentration of 2240 mg/l; the second one, synthetic, containing tannic acid (1g/l), a chemical additive in tannery. The goal of this work is the treatment of TPH and tannic acid contaminated leachates for a real scale bioreactor set up.

Methodology

Leachate: The leachate was collected at Brady Road landfill, Winnipeg, Canada. The synthetic leachate was prepared according to the UK Environmental Agency 2009.

Immobilization of fungal biomass: The fungal biomass was grown in 2L Erlenmeyer flask with 50 sterile PUFs and 1.2 L of MEB. 40 ml of fungal biomass homogenate were added. The culture was maintained at 100 rpm, at room temperature for 7 days.

COD Removal: The COD was measured following the laboratory methods according to the Standard Methods [4].

Enzymatic assays: The enzymatic assays are: Manganese peroxidase (MnP) [5], laccase (Lac) [6;7], lignin peroxidases (LiP) [8] and tannase (Tan) assays [9].

Results

The trend of COD depletion in the row leachate experiment is showed in Figure 1. A progressive depletion of the COD was observed during the 14 days of incubation with a reduction of the COD of the 71% at the end of the incubation. No COD removal was observed in the control. Any enzymatic activity was recorded.

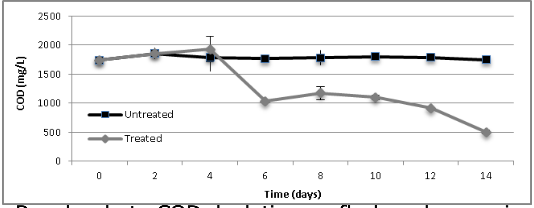

Figure 1: Row leachate COD depletion on flask scale experiment with microF (suspended). The control is without any addition of fungal biomass

A second flask scale experiment with the synthetic leachate and the fungal biomass inoculated as plug from maintenance MEA Petri dish, was conducted. The 40% of the COD depletion was recorded after 12 days of incubation. In the synthetic leachate (tannic acid) batch experiment, the microF is able to produce tannase during all the treatment. The peak of 157U/l of enzyme was recorded after 14 days of incubation. Any enzymatic tannase activity was recorded in the control.

Discussion and conclusion

The biological treatment of wastewater and landfill leachates was mostly investigated by the use of white-rot fungi [10; 11; 12]. The use of ascomyteces in biological treatment for the deletion of COD in landfill leachates is widely not investigated. In this study, the microF, isolated from a TPH polluted dredged sediment demonstrated to be able to reduce more than 70% of COD of landfill leachate without any addition of carbon source. This result is extremely promising for the scale-up of batch scale reactor for the treatment of raw leachate. The microF was also able to reduce the COD related to a different polluted matrix. In particular, the microF depleted the 40% of COD related to a synthetic leachate with tannic acid as chemical target. In this context, the capability to reduce the COD matched with the possibility to record the presence of enzymes involved in the pathway of degradation of tannic acid.

In conclusion: the fungal candidate was able to deplete the 73% of COD of landfill leachate after 14 days of batch scale experimentation and the 40% of COD related to tannic acid after 14 days of incubation. The presence of enzymatic battery putatively involved in the pattern of depletion of the chemical targets was tested. The microF, demonstrated to be able to deplete the COD related to tannic acid and to have an enzymatic battery related to tannases, during the flask scale experimentation.

Acknowledgments

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FUNCTIONING AND CONTROL OF A.S. WWTPS UNDER INFLOW VARIATIONS DUE TO A COMBINED DRAINAGE SYSTEM

Maurizio Mancini[*], **Carmine Fiorentino**[*]

Department of Civil, Chemical, Environmental and Materials Engineering–DICAM-
University of Bologna, Via Risorgimento,2-Bologna
[*]: maurizio.mancini@unibo.it

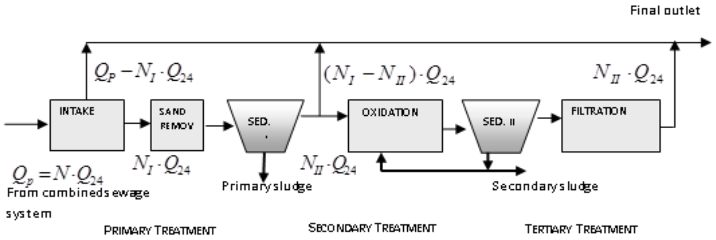
Introduction and study objectives

Wastewater collection in drainage system and secondary treatment for all Italian residential built-up areas are provided by Dlgs.152/2006 which defines parameter limits for discharges. During rainy conditions, in the existing combined city drainage system, a few Italian regional laws have recently classed each one in categories with reference to the flowrate which can cross the section before the start of discharge by the constrained mouths. In wastewater treatment plants (WWTPs), receiving both sewage and rain water, the respect of law limits requires an accurate management of catching work and primary treatment phases are forced to receive in rainy weather conditions a large amount of water volumes. Mathematic description and numerical simulations about active sludge WWTP performances in function of incoming and bypass fluxes (Bragadin & Mancini, 2008) indicate that, in a flow scheme based on the mixing of all plant bypasses flows with the final effluent, it must be received by primary settling a peak flow included between 4 to 5 times the mean dry weather hourly flowrate together with a 2 times permitted to the secondary. The two flow bypass exceeding limits are regularized by mixing with final effluent from secondary biological phases which require for this purpose the maintenance of an high level of purification also during the arrival of sewage diluted by rain. Three years experimental data available from Bologna WWTP made possible to verify behavior of BOD removal and nitrification efficiency in aeration and secondary settling phases during full scale functioning in different rainy conditions. Assumed as indicators the registered values of ammonium (Mancini et al., 2014) data permits to investigate plant performances under stress dilution due to flowrate variations varying between 1 and 3 times the mean daily flowrate in dry conditions.

Methodology

Efficiency calculation scheme - In order to provide treatment for the entire discharge arriving by the terminal sewer pipe, it has been adopted the flow distribution scheme proposed by Bragadin 2008, where is fixed in 2·Q24 the greater flowrate admissible to secondary treatment, and it's defined the input flow ratio deriving to primary and consequently the discharge fraction from the first bypass.

In rainy conditions incoming flowrate could be much bigger than medium daily discharge (Q24) in dry weather conditions. The flow rate scheme provides mixing of the entire water flux outgoing from tertiary phase with the head plant bypassed fluxes before discharge to the receiver.

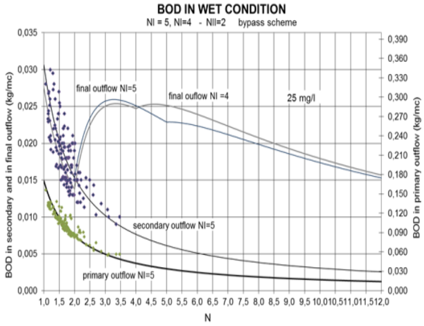


WWTP monitoring - Our study is based on daily data collected during a measurement campaign carried out for three years in the WWTP of Bologna (IDAR) in Italy. The influent is raw sewage from a combined sewer system serving about 500,000 PE from the city of Bologna and hinterland. The process is a traditional A.S. treatment without denitrification. The data come from four sections of the plant were measured in accordance with APAT-IRSA methods (IRSA CNR, 2003)

Plant section	Section	Measured parameters
Influent sewage lifted to WWTP	1	Q, BOD, COD, pH, SSS, TSS, N-NH4+, TKN, N-NO2-, TP , Surfactant
Input primary settling tanks after grid and sand removal	2	BOD, COD, pH, SS, TSS, N-NH4+, TKN, TP, Surfactants
Input aeration tanks	3	BOD, COD, pH, SS, TSS, N-NH4+, TKN, TP, Surfactants
Output from secondary settling tanks	4	BOD, COD, pH, SS, TSS, N-NH4+, TKN, N-NO3-, N-NO2-, TP, Surfactants

Results and conclusions

The following graph represents the final concentration of BOD in outfall as the result of the proposed scheme. Calculations carried out in accordance with measured efficiencies (primary = 26.5 % secondary= 82.1 %) permit to verify the performance of the scheme during N=1 to N=3 wet conditions.



It's interesting to note that NI=4 and NI=5 design choice obtains more or less the same result in term of respect of law limits. Right now similar conclusions cannot be drown within N = 3 – N = 4 because of registered efficiency decreases and scarcity of data representing the upper limit of dilution range.

CARBOXYLATES AND BIOGAS PRODUCTION FROM OLIVE MILL WASTEWATER: KINETIC STUDIES

Gonzalo Martinez, Sarah Notarfrancesco, Salvatore Puccio, Lorenzo Bertin, Davide Pinelli, Dario Frascari[*]

Department of Civil, Environmental and Materials engineering (DICAM),
University of Bologna
[*]*:* dario.frascari@unibo.it

Introduction and study objectives

Olive mill wastewater (OMW) is generated during the olive oil production, at a rate of 5-8 L_{OMW} kg_{Oil}^{-1} (3-phases extraction process). 3.3 Mt_{OMW} year^{-1} are generated in Italy. OMW is considered an environmental harmful waste because of its typical acidity (pH 3–6), high organic content (40–200 gCOD L^{-1}), occurrence of polyphenolic compounds (1–20 g L^{-1}), and seasonality. The development of integrated OMW valorisation schemes allow combining OMW treatment to the obtainment of added value products, namely: polyphenols, volatile fatty acids (VFAs) and biogas. Polyphenols are natural antioxidants and exert antimicrobial activity: both properties can be exploited in several industrial fields. VFAs can be employed in the carboxylate platform, i.e. in the production of ketones, aldehydes, esters, alcohols and alkanes. Biogas production would be useful for the proposed biorefinery energy requirements. The main goal of the present work was to study the production of carboxylates and biogas from the solid fraction of OMW. The specific aims were to study the kinetic of OMW solid anaerobic digestion and to determine possible matrix and/or substrate inhibitions.

Methodology

The OMW was kindly supplied by the "Société Huilerie Mnihla" Tunisian olive mill. Experiments were carried out using the OMW solid fraction (OMW_{Solid}) obtained by centrifugation (8000 rpm, 6 ºC, 25 min); it contained 27 ± 1 % of total solids (TS) and a 86.8 ± 0.4% ratio of volatile solids (VS) to TS. The inoculum provided from a commercial biogas production plant (Emilia Romagna, Italy) was exhausted in terms of actual substrates before using it and finally characterized (4.60 ± 0.03 % TS and 63 ± 3 % VS/TS). Acidogenic and methanogenic experiments were carried out in 100 mL Pyrex bottle microcosms

(53 mL of working volume) tightly closed with a modified Pyrex-cap that allowed gas and liquid sampling.

For the anaerobic fermentation (carboxylates production) the OMWSolid tested concentration rage was 12-127 g_{VS} L^{-1} and the inoculum to substrate ratio (ISR) range was 0.1-1.7. The incubation conditions were pH 7, 50 °C and 150 rpm. In the biogas production tests lower OMW solid concentrations were tested (0.47-36 g_{VS} L^{-1}) and the ISR range was 3-0.7. The incubation conditions were the same indicated above, except for pH (7.5). Both experiments were carried out in triplicate and blank control groups were set up by filling microcosms with water and inoculum, in order to determine the effective acids/biogas production. Microcosms were monitored every 1–3 days for biogas and carboxylates production. pH control was performed by adding drops of NaOH or H_2SO_4 (10M).

Results and discussion

The results for VFAs and biogas production experiments are shown in Figure 1. Maximal specific production rates (r_{max}) were calculated for each OMW_{Solid} concentration condition, in both experiments. VFA production follows a Monod type kinetic (Fig. 1-I), whereas the biogas rate production presents a more complex trend (Figure 1-II). More studies are being conducted to identify a kinetic model that includes inhibition from intermediates metabolites such as VFAs.

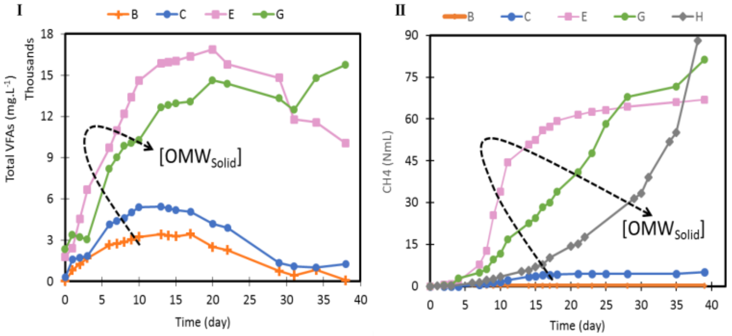


Figure 1: Carboxylates (I) and biomethane (II) production at different OMW_{Solid} concentrations. Black arrows indicate the increasing concentration conditions, from B onwards.

Acknowledgment

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BIOSORPTION OF NICKEL (II) AND ZINC (II) IONS FROM SINGLE AND BINARY METAL SOLUTIONS BY EUCALYPTUS (*EUCALYPTUS CAMALDULENSIS*) BARK

Marcos López-Nuñez, Gabriela Pineda-Camacho,
Eliseo Cristiani-Urbina*

Instituto Politécnico Nacional, Escuela Nacional de Ciencias Biológicas, Departamento de Ingeniería Bioquímica. Avenida Wilfrido Massieu s/n. Unidad Profesional Adolfo López Mateos. Ciudad de México, 07738, México.
**: ecristianiu@yahoo.com.mx*

Introduction and study objective

Heavy metal contamination of the environment is a major worldwide concern because of the potential threat to human health, caused by high toxicity, non-biodegradable nature, and the increasing discharge, persistence and ubiquitous occurrence of these metals. Divalent nickel [Ni(II)] and zinc [Zn(II)] are heavy metals usually found in industrial effluents, discharged from mineral processing, non-ferrous metal production, paint formulation, galvanization, and battery manufacture. High Ni(II) and Zn(II) concentrations cause serious acute and chronic health disorders.

Due to the deleterious effects of these heavy metals on human and environmental health, it has become essential to remove them from industrial wastewater and from surface and ground water streams. Conventional waste management strategies for heavy metal removal pose several technical and economic constraints. Biosorption provides an efficacious alternative for the detoxification of Ni(II) and Zn(II)-polluted water and wastewater and offers potential advantages over conventional heavy metal-removing technologies.

As single toxic metallic species rarely exist in natural and industrial wastewaters, any approach that attempts to remove heavy metals from multicomponent systems using biosorbents would be more realistic. However, although much information related to single-metal biosorption is available in the specialized literature, much less focuses on the biosorption of multi-metal ion systems. Two-metal biosorption studies are thus crucial for assessing and understanding the interference and competition between metal ions for biosorption sites.

The main aim of this work was to assess the performance of eucalyptus (*Eucalyptus camaldulensis*) bark for the biosorption of Ni(II) and Zn(II) ions from single and binary metal solutions, as well as for modeling the single and binary equilibrium of biosorption of Ni(II) and Zn(II) onto *E. camaldulensis* bark.

Methodology

E. camaldulensis bark samples were washed exhaustively and then oven-dried at 60º C until they reached constant dry weight. Dried samples were milled, and the resulting particles were screened using ASTM standard sieves. Particles ranging in size between 0.3 and 0.5 mm were used in the biosorption experiments conducted in this work.

Monometal and bimetal biosorption experiments were conducted at a pH of solution of 6.0, temperature of 28 °C, bark concentration of 1 g L^{-1}, and agitation rate of 180 rpm. We varied the initial metal ion concentrations of Ni(II) and Zn(II) within a range of 0.2-10 mM for equilibrium studies of a single-metal system. Then we conducted a series of tests at a constant concentration of the first metal within the range of 0.2-10 mM, and a varying concentration of the second one (within the same range) for the two-metal systems. Ni(II) and Zn(II) concentrations were determined spectrophotometrically by the dimethylglyoxime and zincon methods, respectively.

Results and conclusions

E. camaldulensis bark exhibited great capacity for removing Ni(II) and Zn(II) ions from single and binary metal solutions. In single metal solutions, the highest *E. camaldulensis* bark biosorption capacity of Ni(II) and Zn(II) was 0.96 mmol g^{-1} and 1.06 mmol g^{-1}, respectively. Among the eleven isotherm models tested, the Langmuir, Sips and Redlich-Peterson isotherm models fitted best to the experimental equilibrium biosorption data of Ni(II) and Zn(II).

Biosorption data in binary systems showed that the biosorbed amount of one metal decreased as the concentration of the other competitive metal simultaneously present in the solution increased. This effect was substantial for Ni(II) biosorption that was strongly inhibited by increasing Zn(II) concentration in solution. The competitive Langmuir model gave the optimum prediction for competitive biosorption of Zn(II) and Ni(II) ions, among the eight multicomponent isotherm models tested.

It is an interesting study of monometal and bimetal biosorption experiments. *E. camaldulensis* bark samples are used in their natural state, and results indicate that eucalyptus bark may represent a potential low-cost biosorbent.

EFFICIENCY OF LIVING *BACILLUS MEGATERIUM* IN CADMIUM REMOVAL FROM AQUEOUS SOLUTIONS

Mihaela Rosca[1,2*], Raluca Maria Hlihor[1,3*], Mariana Diaconu[1], Teresa Tavares[2], Maria Gavrilescu[1,4]

[1)] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
[2)] University of Minho, CEB – Centre of Biological Engineering, Campus de Gualtar, 4710-057 Braga, Portugal
[3)] "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania
[4)] Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
[*]: m.rosca@ch.tuiasi.ro, raluca.hlihor@ch.tuiasi.ro

Heavy metals presence in the environment represents a high risk for human health due to their persistence and bioaccumulation potential in the food chain. In certain concentrations, some heavy metals are carcinogenic or potential carcinogenic for humans and animals. The removal of these pollutants from environmental media is usually performed by applying physico-chemical processes like precipitation, ion exchange, membrane filtration, or electrochemical methods, which are regarded as expensive processes and economically feasible only for concentrations higher than 100 mg/L. On the other hand, eco-friendly and low-cost biotechnological processes such as biosorption and bioaccumulation can be applied with good results for the removal of different heavy metals from aqueous effluents, even for concentration lower than 100 mg/L. Cadmium is a heavy metal classified as carcinogenic for humans by the International Agency for Research on Cancer (IARC), being included in Group 1 of pollutants that proved "sufficient evidence in humans or sufficient evidence in animals and strong mechanistic data in humans", together with arsenic, benzene, chromium, formaldehyde etc. Therefore, cadmium must be removed from any environmental compartment. The main goal of this paper was to examine the capacity of living *Bacillus magaterium* bacterium applied as biosorbent for Cd(II) removal from aqueous solutions and to establish the optimal set of parameters (e.g. pH, contact time, initial concentration of heavy metal in solution) for future applications in bioreactors at laboratory, pilot and, on the long term, at industrial scale.

At this stage, the ability of living biomass of *B. megaterium* for Cd(II) removal from aqueous solutions was studied in batch system. The reagents used in experiments were: $Cd(NO_3)_2 \cdot 4H_2O$ for the preparation of cadmium stock solution of 10 g/L; H_2SO_4 1M or NaOH 1M for pH adjustments; HNO_3 69% for samples acidification (2%) before the determination of Cd(II) concentrations. Bacteria were grown in a medium containing 10 g of tryptone, 5 g NaCl and 5 g yeast extract (per 1 L of growth medium) at 30±2°C, for 24 hours and 150 rpm (inoculum preparation). All experiments were carried out in duplicate in 250 mL Erlenmeyer flasks with 95 mL sterile growth medium, 5 mL of inoculum containing $4 \cdot 10^9$ cfu/mL *B. megaterium* and 0.25-1mL solution of 10 g/L

Cd(II) (for initial concentrations between 25 mg/L and 100 mg/L). The flasks were shaken using Shel-Lab SSI3 Shaking Incubator at 130 rpm and 30^{0}C during 72 hours, for the experiments addressing pH influence, and 80 hours for studies concerning the influence of contact time, respectively on cadmium removal efficiency. The concentration of Cd(II) in solution was analyzed using Inductively Coupled Plasma Spectrometer (Optima 8000 ICP-OES model).

During the experiments, pH values varied between 4 and 7. We found that, when working with an initial concentration of 50 mg/L Cd(II), the maximum efficiency was achieved at pH 6 (42.13%) after 72 hours of contact time (Fig. 1a). As shown in Fig. 1b, Cd(II) removal by living biomass exhibits a maximum efficiency - between 50.76% (for 25 mg/L Cd(II) in solution) and 20.43% (for 100mg/L Cd(II) in solution), at a contact time of 75 hours. To understand the mechanisms involved in Cd(II) ions removal from aqueous solutions by living biomass, samples taken before and after the start of the removal process were further examined using SEM-EDX (Fig. 2) and FTIR techniques. The data collected during this set of experiments demonstrated the ability of *B. megaterium* both to cope with Cd(II) toxicity and retain the ion by biosorption and bioaccumulation. Based on these results, the living biomass of *B. megaterium* selected for Cd(II) ions removal from aqueous solutions will be further used in experiments developed in different contacting devices, such as in fixed bed, stirred tank and airlift in order to gain the bases for process modelling, scaling up and design.

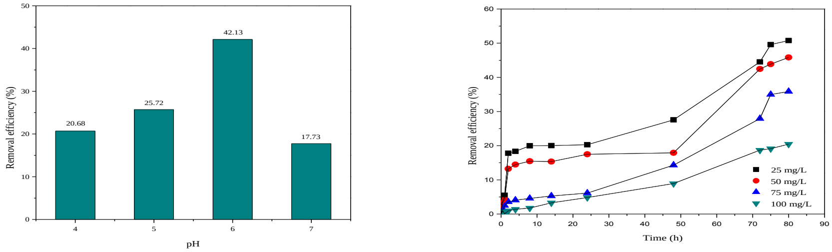

Figure 1: a) Influence of pH and b) contact time on Cd(II) bioaccumulation by *B. megaterium*

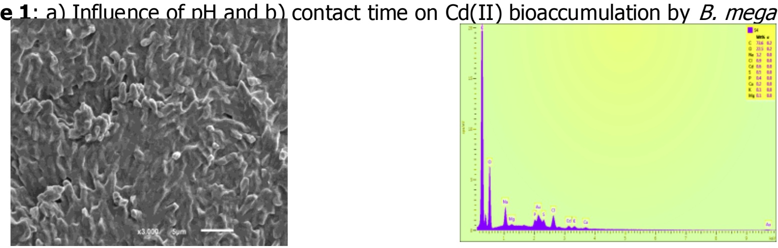

Figure 2: SEM- EDX analysis of *B. megaterium* after Cd(II) removal

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This work has been elaborated based on the collaboration between "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Romania and University of Minho, Center of Biological Engineering, Braga, Portugal. The Portuguese team input was performed under the scope of the strategic funding of UID/BIO/04469/2013 unit and COMPETE 2020 (POCI-01-0145-FEDER-006684) and BioTecNorte operation (NORTE-01-0145-FEDER-000004) funded by the European Regional Development Fund under the scope of Norte2020 Programa Operacional Regional do Norte.

CONVENIENCE OF FENTON-BASED TECHNOLOGIES FOR THE REMOVAL OF POLLUTANTS FROM DIFFERENT ENVIRONMENTS

Marta M. Pazos, Emilio Rosales, Mª Asunción Longo, María A. Sanromán*

Department of Chemical Engineering, University of Vigo, Isaac Newton Building, Campus As Lagoas, Marcosende 36310, Vigo, Spain
**: sanroman@uvigo.es*

Introduction and study objectives

In the last decades, Fenton's reagent has demonstrated to be a suitable oxidant agent for a wide variety of organic compounds. By Fenton's reaction (Eq.1) a strong oxidant as hydroxyl radical is produced by reaction of H_2O_2 and ferrous ion, which are highly reactive radical species that are known for their ability to mineralize a wide range of organic compounds (Eq.2). Among the multiple benefits of this technology, it is highlighted that the main reagents (iron and hydrogen peroxide) are relatively cheap and the process is technologically simple. However, several studies have demonstrated that some of the most important drawbacks of Fenton's treatment relies on the instability of H_2O_2 when it gets in touch with chemical species that are naturally in the environment and iron ions precipitation at pH higher than 4, reducing the degradation efficiency as well as difficulty post-treatment of iron sludge after the reaction. To overcome these problems, some research groups have reported that by combination with electrochemical technology is possible a stable generation of H_2O_2 and the continuous regeneration of ferrous ions into the bulk medium avoiding the iron precipitation. This hybrid technology is called as electro-Fenton process, when it is applied to aquatic environment. In electro-Fenton process, the electrical current induces the reduction on the cathode of ferric ions to form ferrous ions (Eq.3) and H_2O_2 is continuously electrogenerated on the cathode via two electrons O_2 reduction reaction (Eq.4).

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + \bullet OH \qquad \text{(Eq.1)}$$

$$R + \bullet OH \rightarrow CO_2 + H_2O \qquad \text{(Eq.2)}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad \text{(Eq.3)}$$

$$O_2 + 2H^+ + 2\,e^- \rightarrow H_2O_2 \qquad \text{(Eq.4)}$$

Although this technology was mainly focused on the removal of pollutants in wastewaters, the use of Fenton's reagents in the remediation of soils contaminated by organic compounds has gained prominence. Iron or iron complexes naturally exist in most soils; therefore, the injection of H_2O_2 in the soil is enough to produce the hydroxyl radicals without artificial iron addition. For the homogeneous distribution of the reagents through soil of low permeability the combination with electrokinetic treatment could be a good alternative. By application of electrokinetic-Fenton technology to soils the reagents are transported along the soils and the degradation of the organic pollutants takes place *in situ*.

This study describes the removal of emerging organic compounds, in wastewater and soil, by Fenton-based technologies. For this purpose, the effect of key variables of each methodology on its efficiency has been evaluated. In addition, several of these variables such as iron concentration, intensity, pH, were optimized.

Methodology

Electro-Fenton: Experiments were performed in an undivided and cylindrical reactor with working volume of 150 mL of polluted solution. An external direct-current power supply was connected to two electrodes: Boron-Doped Diamond (BDD) and Carbon felt used as anode and cathode, respectively. Continuous saturation of air was ensured by bubbling compressed air near the cathode at about 1 L/min.

Electrokinetic-Fenton: Experiments were carried out at laboratory scale in electrokinetic cells with a central tube (100 mm in length and 32 mm internal diameter) and two electrode chambers (0.3 L) were placed at each end of the sample compartment. The electrode chambers were filled with the desired H2O2 solution and Na2SO4 (0.1 M) as electrolyte. In enhanced experiments complexing agents were added to improve the process. A constant potential difference (3 V/cm) was applied by two graphite electrodes with a power supply.

Results and conclusions

The presence of emerging pollutants in the environment is a new global water quality challenge with potentially-serious threats to human health and ecosystems. In this study, the feasibility of the electro-Fenton process was evaluated for different new and emerging pollutants. In all cases, it has been pointed out that the iron concentration, pH and applied current intensity are key parameters affecting the performance of the electro-Fenton process. The degradation rate is higher operating in an acidic medium and the generation rate of radical •OH depends on the availability of iron in the system and the applied current intensity for H2O2 production.

On the other hand, the results, obtained when soil was treated using electrokinetic-Fenton, revealed that highest degradation rate was reached when a solution of H2O2 at around 10% was used, and slight influence of iron soil concentration was detected at the range of concentrations used in these experiments. In all cases, citric acid was added in order to solubilize the iron as Fe-citrate complex and to keep the pH in acid environment favouring that the Fenton's reactions take place into the soil.

This study has clearly demonstrated the success and efficacy of the combination of electrochemical process and Fenton's reagents for removal of emerging pollutants.

Acknowledgments:

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PARTICULATE MATTER IN WASTEWATERS: SIZE DISTRIBUTION AND TYPES, ADVANCED SOLID/WATER SEPARATION TECHNIQUES AND ITS ESTIMATED IMPACT ON TREATABILITY

Carmen Zaharia

'Gheorghe Asachi' Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management,
73 Prof.Dr.docent D.Mangeron, 700050-Iasi, Romania;
**: czah@tuiasi.ro or czaharia2003@yahoo.com*

Different types of particulate contaminants are presented in wastewaters or formed during a few sewage treatment processes (e.g. chemical precipitation, coagulation flocculation, biological processes, etc.). The first step in wastewater treatment is always associated with solids separation from wastewater (S/WW separation) under the prevailing hydraulic conditions, a mechanical treatment stage being indispensible in the preliminary/primary, or even secondary WW treatment for both municipal and industrial applications. The main goal of a preliminary or primary treatment stage is usually to completely separate floating, settling and suspended solids, and remove the particulate matter from flow into a container or special tank in order to increase the capacity of biological or advanced treatment stage. Operating reliability, efficiency and hygienic operations are important factors for an optimal S/WW separation by mechanical treatment steps, combining screening, washing, transport, compaction and dewatering in a single or multiple separation units sometimes associated with additional complex chemical and biological transformations.

Depending on size of particulate contaminants from different types of wastewaters (industrial, domestic or agro-zoo-technical ones), there were selected the bar spacing (>0.5 mm) or perforation (> 3 mm), screen size (up to 700 mm screen basket diameter) in a way which allows the individual adjustment to specific size requirements, together with continuous sludge/sediment thickening by mechanical-physical and chemical treatments. In actual times, there were adopted advanced S/WW separation techniques by using micro-screeners that can be installed either directly in the channel or in a separate tank for screening of flow rates from 15 to 300 m^3/h, and also multilayers-based filters or special designed centrifugation systems, settlement tanks or lagoons. For economy, operating reliability and maintenance of high performance S/WW separation equipment, there were designed different installations or specific equipments for assuring full and comprehensive services for long times at low operating costs which results in low whole life costs.

The wastewater services are now able to offer a full range of products and equipments for the complete wastewater treatment sector and worldwide market: (*i*) very fine screens for separation of finer particles; (*ii*) sedimentation (clarifiers), filtration (sand-based or multilayers-based filtration); (*iii*) new type of membrane bioreactors within the market with improved performance in order to separate of fibrous material to allow the membrane process to function effectively and to reduce the COD/BOD concentrations of the wastewater discharged into the receiving watercourse; (*iv*) grit separation of digestible organic materials and other mineral materials (aprox. 60 L/1000 m^3 of WW); (*v*) sludge treatment (screening-thickening-dewatering-drying from one source), etc. For further improvement of the efficiency of screens, settlers or filters, precipitation and coagulation agents are also added, all having a solids' agglomeration effect. Thus, dissolved and very fine particles from wastewater are converted into ease separable agglomerates to enable the filtreable solids to be reduced by up to 95%, COD/BOD by 65% and phosphorus by 60%.

In many regions within the world with no wastewater treatment plants, or insufficient wastewater treatment plants, fine screening can be a first and quick step in this right direction of S/WW separation. Quantification of solids and organic content derived from applied membrane separation methods for wastewaters permits to exam the particulate contaminants in WW in terms of size distributions and biological treatability. Usually, no more than 70-75% of the COD/TOD was found to be insoluble, and also the soluble organic matter smaller than 1 µm could be biochemically degraded at a much more rapid rate than organic particles larger than 1 µm.

The utility of particle size information (interest range in size from less than 0.001 µm to well over 100 µm, or more) for treatment design and process evaluation is discussed particularly for municipal and industrial WW treatment and reuse. Often the effluents from food-processing industries contain 40-70% of the total COD associated with the suspended solids, and also other contaminants such as metals, bacteria and viruses (size range of 0.01-10 µm), organic micropollutants (PCBs, PAH) are associated with particulate matter or particles. Therefore, one important goal of this work is to demonstrate that a very significant part of contaminants in wastewaters is associated with particles, and consequently that significant reductions of polluting species may be expected as results of direct simple and/or advanced S/WW separation in optimized conditions. Incorporation of treatment processes prior to biological treatment such as microscreening, primary direct filtration, sedimentation, or chemical coagulation/flocculation, flotation, activated carbon adsorption or membrane processes (microfiltration, ultrafiltration, reverse osmosis) and ion exchange has resulted in increased capacity of biological treatment units and improved WW treatment performance. Consequently, presentation of the most used S/WW separation equipments, processes and operations in different treatment systems and also different disposal methods is of high importance in this work.

An other important goal of this work is to present the techniques used to characterize the separated particles in wastewater, especially analysis of suspended solids by using advanced tech-niques for measurement of particle sizes and distribution of organic matter in wastewater.

The impact of particulated matter (existing/new formed) on treatability of different wastewaters, associated more or less with percentage of reduction of treatment performance for some species is also presented, considering mainly the technological criteria and removals, but it is not neglected a few economical, environmental and social aspects exposed in an integrative manner.

All separation processes may be used in any stage of a sewage treatment system, but nature of raw sewage limits each S/WW separation associated with cleaning regime adopted in treatment plant.

ISOTHERM MODELS AND KINETICS OF ZINC ADSORPTION BY USING GELLAN-GUM/GRAPHENE OXIDE BEADS

Cristina Modrogan[1], Pandele Andreea Madalina[1,*],
Dancila Madelene[1], Orbuleț Oanamari Daniela[1],
Orbeci Cristina[1], Constantin Bobirica[1]

[1]Analitycal Chemistry and Environmental Engineering Department, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest,
str. Polizu, no.1-7, Bucharest Romania,
**: pandele.m.a@gmail.com*

Introduction and study objectives

Along with the rapid progress in industry such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides etc., developed countries are daily fighting with an increase in the indirect or direct discharge of heavy metals in wastewater, which further leads to a significant increase in environmental pollution. The toxic heavy metals of particular concern in the treatment of industrial wastewaters are: zinc, copper, nickel, mercury, cadmium, lead and chromium.

Zinc is an essential element for human health especially for the physiological functions of living tissue and regulates many biochemical processes. However, an increase in the zinc concentration in the body can cause serious health problems including stomach cramps, skin irritations, vomiting, nausea and anemia.

Recently, various methods for heavy metal removal from wastewater have been extensively studied. Of these, ion-exchange, adsorption and membrane filtration are the most frequently applied.

The objective of this study is to develop novel nanocomposite beads based on gellan-gum and graphene oxide (GG/GO) for the successful removal of zinc ions from aqueous solution. Different pH solutions, zinc ions concentrations and contact times were investigated using equilibrium and kinetic studies. The equilibrium adsorption data were fitted to Langmuir isotherms and the maximum adsorption capacities of the GG/GO beads were found to be 40.7 $mg \cdot g^{-1}$ and 58.2 $mg \cdot g^{-1}$, respectively.

Methodology

Preparation of gellan-gum/graphene oxide (GG/GO) beads 1 g of phytagel was dissolved in 50 ml of distilled water at 80 °Cunder magnetic stirring in order to form 2 wt.% GG solution. After cooling at 50 °C, different concentrations of GO (0, 1 and 2 wt.% GO) were added to the solution and ultrasonicated for 1h at room temperature (RT) to obtain a homogenous solution. Briefly, the mixture was added dropwise into 1 wt.% $CaCl_2$ solution, previously prepared, under constant and gentle stirring using a syringe of 0.85 μm inner diameter to form the beads. The obtained gelled beads were stirred for another 30 min at RT into $CaCl_2$ solution. The beads were further filtered, washed several times with distilled water to remove the $CaCl_2$ excess anddried at RT for 48 h before being used.

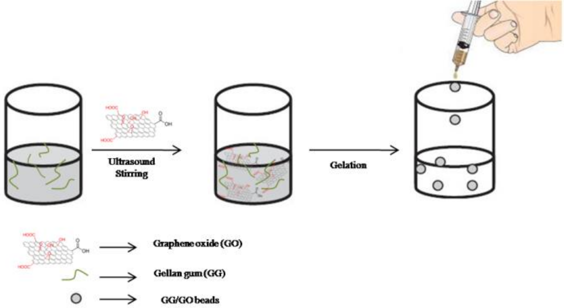

Figure 1: Preparation of gellan-gum/graphene oxide (GG/GO) beads

All experiments were accomplished with simulating wastewaters solutions, prepared from zinc cloride $ZnCl_2$ (Sigma-Aldrich), sulphuric acid (98%, Merck) (molar ratio 1:1) and deionized water to produce different solutions containing 1mg/L and 5mg/L, respectively.

The kinetic study was performed in aqueous solutions at various concentrations 1, 2, 3, 4 and 5 mg/L. For that, 100 mL of solution were contacted with $1 \pm 2 \cdot 10^{-4}$ g of nanocomposite beads, under batch conditions, for 30, 40, 60, 80, 100, 150, 200, and 300 minutes respectively. Also, the influence of pH, at different pH values including 2 ± 0.05, 3 ± 0.05, 4 ± 0.05 and 6 ± 0.2 was studied. The atomic absorption spectrometer Zeenit 700 Analytik Jena was employed to determinate the zinc concentration in aqueous solution.

Results and conclusions

The study was done in three steps:

- In the first step the GG/GO beads were prepared
- In the second step, the equilibrium adsorption data were fitted to Langmuir isotherms and the maximum adsorption capacities of the GG/GO beads were found to be 40.7 $mg \cdot g^{-1}$ and 58.2 $mg \cdot g^{-1}$, respectively.
- In the thirdstep, the GG/GO beads were immersed for 30 to 300 minutes into the aqueous solutions. The absorption rate for each individual integral kinetic curveswere calculated by using a pseudo-2 order model.
- The data obtained in the thirdstep were employed to establish the dependence of adsorption rate on zinc concentrations in aqueous phase and GG/GO by using the Langmuir – Hinshelwood model.

A NOVEL TWO-PHASE BIOREACTOR FOR TREATING INDUSTRIAL WASTEWATER AND RECOVERING VALUABLE COMPONENTS

M. Concetta Tomei[1,*], Domenica Mosca Angelucci[1], Valentina Stazi[1], Andrew J. Daugulis[2]

[1]Water Research Institute, C.N.R., Via Salaria km 29.3, CP 10, 00015 Monterotondo Stazione (Rome) Italy
[2]Department of Chemical Engineering, Queen's University, Kingston Ontario Canada K7L 3N6
[*]: tomei@irsa.cnr.it

Introduction and study objectives

Solid-liquid two-phase partitioning bioreactors (TPPBs) have been successfully applied for the treatment of aqueous contaminants and for soil bioremediation. Thermoplastic granular polymers as the partitioning phase added to a bioreactor have been employed to enhance the biodegradation of a large number of recalcitrant contaminants due to their capability to sequester, and thereby reduce substrate toxicity. A novel continuous TPPB (C-TPPB), in which the polymer beads are replaced by polymeric tubing, has been recently proposed. In the C-TPPB, the wastewater flows inside the tubing and the organic molecules can diffuse through the tubing walls towards the bioreactor side, containing the biomass, where the biodegradation can take place under controlled conditions. The mass transfer process occurs via diffusion and the polymer exhibits a barrier for ionic components such as metals, which are retained in the stream flowing inside the tubing. In this way, the biological reaction environment is not affected by the characteristics of the original wastewater (i.e. extremes of pH, ionic strength, salts, metals), which can negatively affect the biological process performance. This modified bioreactor configuration combines the advantages of conventional TPPB systems, in terms of toxicity reduction, with the separation of the biomass from the polluted wastewater. In addition, given the high affinity of the polymeric material for organic substrates, the separation of the organic and inorganic fraction can be achieved, and this is the first step for resource recovery. These features are of relevance for the treatment of industrial wastewater containing various pollutants including organic (potentially biodegradable) and inorganic components (e.g. metals), which, in many cases, after separation, can be usefully recovered and re-utilized. The objective of this study is to demonstrate the feasibility of the C-TPPB system for treating industrial wastewater in order to obtain effective biodegradation of the organic contaminants and the separation of the inorganic one (in the proposed case study represented by chromium (VI)).

Methodology

A schematic representation of the C-TPPB bioreactor (working volume: 3.3 L) is shown in Fig. 1. The polymeric tubing (length: 3.5-5.5 m; external and internal diameters: 6 and 5 mm), is made of Hytrel 8206 and it was kindly supplied by DuPont (Canada). In the first series of tests, the tubing was fed with synthetic wastewater containing 4-chlorophenol (4CP) (500-2000 mg/L), while in second series potassium dichromate as a source of Cr(VI) (Cr) (100 mg/L) was added to the 4CP. The bioreactor was inoculated with a microbial consortium previously adapted to 4CP. During each test, 4CP and Cr concentrations were monitored in the bioreactor and in the tubing, and the build-up of chlorides in the bioreactor due to 4CP biodegradation was measured to evaluate the biodegradation efficiency and the removal rate.

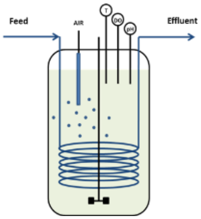

Figure1: C-TPPB schematic representation

Results and conclusions

Preliminary abiotic mass transfer tests were performed with the C-TPPB system to verify that 4CP transfer across the tubing walls occurred under the operating conditions chosen for the biological tests. In the second series of tests mass tranfer tests demonstrated the that Hytrel 8206 tubing does not absorb this metal in that there was no variation in Cr concentration in the tubing effluent during the experiments. As an example of the C-TPPB performace, Fig. 2a shows 4CP concentration profiles in the bioreactor and the tubing during the first series of tests performed with an influent concentration of 2085.1 mg/L, while Fig. 2b shows the 4CP and Cr concentration profiles in the tubing (t) and the bioreactor (b) detected in the second series of tests for tubing influent concentration of 1572.7 and 103.4 mg/L for 4CP and Cr respectively. The results in Fig. 2a show practically complete removal of 4CP from the wastewater: an efficiency of 99% is reached after 24 h from the beginning of the test. Similar results have been obtained in the second series with 4CP removal efficiencies ≥ 98% for influent concentrations up to 2500 mg 4CP/L, and, at the same time, complete separation of the Cr was achieved.

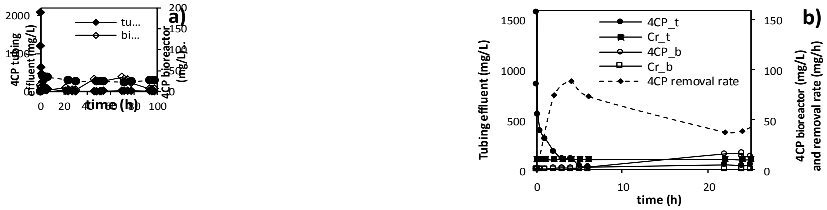

Figure 2: First series of tests (a): 4CP concentration profiles in the tubing effluent and in the bioreactor and removal rate. Second series of tests (b): 4CP and Cr concentration profiles in the tubing effluent (t) and in the bioreactor (b) and removal rate.

In conclusion, the results demonstrated the feasibility of the proposed C-TPPB for achieving effective removal of the organic load and separation of the inorganic components such as metals for possible resource recovery from the treated wastewater.

OPTIMIZING DESIGN OF AN AEROBIC GRANULAR SLUDGE BIOREACTOR USING NUMERICAL SIMULATION

Corina Boncescu[1,*], Adriana Mierloiu[2],
Lacramioara Diana Robescu[3]

1)Power Engineering Faculty, Department of Hydraulics, Hydraulic Machinery and Environmental Engineering, University POLITEHNICA of Bucharest, Romania ,
2)Power Engineering Faculty, Department of Hydraulics, Hydraulic Machinery and Environmental Engineering, University POLITEHNICA of Bucharest, Romania ,
3)Power Engineering Faculty, Department of Hydraulics, Hydraulic Machinery and Environmental Engineering, University POLITEHNICA of Bucharest, Romania,
**: corina.boncescu@gmail.com; mierloiu.adriana@gmail.com; diana.robescu@upb.ro*

Introduction and study objectives

Aerobic granular sludge (AGS) technology has become very attractive for wastewater treatment because a lower footprint of bioreactor and important energy savings comparing with conventional biological treatment of wastewater. This technology is applied at full-scale only in sequential batch reactor (SBR) configuration. Using continuous flow bioreactor for AGS technology seems to be more convenient for upgrading existing wastewater treatment plant (WWTP) with conventional biological treatment.

The experimental installation for study of the AGS technology in continuous flow configuration was made at National Institute for Research and Development in Industrial Ecology - ECOIND, Bucharest, Romania. The installation consists of a rectangular shape bioreactor, *7*, an area for settling and recycling of granules, *4*, followed by a settling tank, *5*, fig.1. Wastewater is supplied with a peristaltic pump through a hose, *1,* at 1.1 L/h. A perforated hose, *8,* is used for air supplying at 10 L/min. The inlet and outlet area for granules recycling is provided with blades, *2* and *6*. Treated wastewater is discharged into the area *3*.

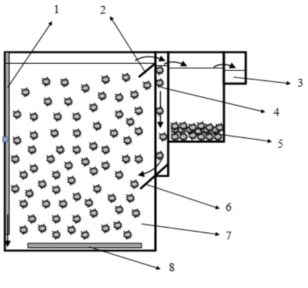

Figure 1: AGS experimental installation sketch

Following experimental research has been identified the main problem: in the recirculation zone the granules are maintain in suspension. The aim of this research is to identify the optimal geometry of the installation to achieve the recirculation of granular sludge.

Methodology

Operation of the installation shown a poor mixing that led to the formation of deposits of granular biomass in areas with low turbulence, inefficient granules separation in the recycling area and surface modification and grain structure.

Because the hydraulic and operational conditions are essential for aerobic granule formation the bioreactor has to be re-design both in terms of shape and of aeration systems. The theoretical simulation study was conducted using CFD technique for the simulation domain consisting of the bioreactor and area for recycling of granules. The model was meshed using an unstructured mesh and the solver used was a segregated solver as the flow is incompressible. Turbulent k-epsilon and 3D mixture model in FLUENT are considered. The flow in the domain of study was simulated in two situations: water and air-water mixture. Various simulations were conducted for different wastewater flow rates at the bioreactor entrance and different air velocities.

Results and conclusions

For the design of current bioreactors, simulations have shown that the velocities are very small in the recirculation area, v = 0.0026 m / s, and the aeration systems could not mix the entire mixture into the bioreactor. This has led to deposits in the lower corners of the bioreactor. To improve movement in the bioreactor a new aeration system and a new bioreactor form have been proposed. The air intake system was mounted in a circular form. It has been changed with several linear aeration systems mounted in parallel. To prevent the deposition of active sludge in the corners of the aeration tank, a wall was mounted at 30 degrees. These changes have led to a better functioning of the AGS installation. In the center of the basin, whirlpools have occurred which have led to an increase in the degree of turbulence resulting in the recirculation of sludge granules.

Acknowledgements

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OPTIMIZED EFFLUENT QUALITY CONTROL FOR IMPROVED ENERGY USE IN WASTEWATER TREATMENT PLANTS

Elfrida M. Carstea[*s], Cristina Liana Popa, Simona Dontu,
Dan Savastru

National Institute of Research and Development for Optoelectronics, INOE 2000,
Magurele, Atomistilor 409, 077125, Romania;
[*]: *elfrida.carstea@inoe.ro*

Introduction and study objectives

Climate change, population growth, urbanisation and pollution all mean that society faces an urgent need to adapt to reductions in natural resource availability and reductions in energy consumption. The water industry has a significant role to play in achieving this goal, as wastewater treatment is an energy-intensive operation. The largest energy usage in wastewater treatment is found in the vigorous aeration of settled sewage in the activated sludge process (ASP), which alone contributes to over 55% of the energy costs associated with wastewater treatment. Energy consumption has increased significantly in the last two decades, and further increases of 60% are forecast in the next 10-15 years. These increases have been brought about primarily in response to tightened legislation and regulation surrounding the discharge of final effluent from wastewater treatment plants (WwTPs) to watercourses. The quality of wastewater is generally assessed using physical, chemical and microbiological tests. Among these techniques, reliance is often placed on biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). However, these global parameters depend on expensive or time-consuming methods, offering only snapshots of moments in time. Consequently, water utilities often over-aerate in order to ensure compliance with final effluent standards. This means that there is a significant opportunity to save energy by optimizing aeration control in the ASP in order to minimize energy consumption whilst maintaining final effluent compliance. It is estimated that 40 % of the energy consumption in wastewater treatment works could be reduced if an effective method is used for effluent quality monitoring. Fluorescence has been shown to be a valuable technique in characterizing dissolved organic matter (DOM) and tracking sources of pollution in surface water. Fluorescence is the release of energy in the form of light when molecules or moieties, named fluorophores, are excited with a high-energy light source. The technique has been suggested for its multiple advantages: it is fast, inexpensive, reagentless, requires little sample preparation, is highly sensitive and non-invasive. According to several researchers, fluorescence monitoring could provide rapid feedback, allowing dynamic, high spatial and temporal resolution studies.

Fluorescence spectroscopy has been used successfully to characterize organic matter in seawater, freshwater or estuarine water. Also, it has been used to monitor riverine organic matter and diesel pollution, evaluate drinking water treatment processes or detect pesticides. Fluorescence spectroscopy has been used to assess the quality of raw sewage and effluents, industrial, or discharges into natural systems. Therefore, this study aimed to use fluorescence spectroscopy as an innovative and robust method to monitor and control the chemical and microbiological quality of wastewater in ASPs. The removal efficiency of DOM in five wastewater treatment plants, at different processing stages, was investigated. Moreover, the potential of using portable fluorimeters was explored in comparison to two different laboratory-based instruments.

Methodology

Samples were collected from 5 WwTWs serving different areas in the West Midlands, UK, and with different population equivalents (PE): Kidderminster (PE-95637), Worcester (PE-93789), Spernal (serving Redditch area, PE-72509), Finham (serving Coventry area, PE- 380888) and Minworth (Birmingham area, PE-1446426). Wastewater was sampled at three different times of the day (9 AM, 12 PM and 3 PM) to ensure variability of the organic matter present in the sample. Samples of crude, settled and secondary treated wastewater (activated sludge), and final effluent were collected. Analyses were made for fluorescence (using 2 steady state spectrofluorimeters and 2 portable fluorimeters), absorbance, biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and pH. Fluorescence was measured for unfiltered and filtered (0.45 and 0.20 µm) samples.

Results and conclusions

Good correlations were observed for filtered and unfiltered wastewater samples between fluorescence intensity, especially peak T (indicates microbial activity) and BOD ($r = 0.78$), COD ($r = 0.90$) and TOC ($r = 0.79$). BOD displayed a higher correlation at the 0.20 µm filtered samples compared to COD and TOC. Slightly better relation was seen between fluorescence and conventional parameters at the portable fluorimeters compared to laboratory-based instruments. Results showed that fluorescence intensity of organic matter was capable of detecting minor changes in influent OM quantity and issues with treatment process. Consequently, the results indicated that fluorescence spectroscopy could be used for continuous, real-time assessment of DOM removal efficiency in wastewater treatment works.

Acknowledgements

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WWTP MODEL CALIBRATION BASED ON DIFFERENT OPTIMIZATION APPROACHES

Vasile-Mircea Cristea[1,*], Melinda Várhelyi[1], Marius Brehar[1], Evelina Nemeş[1], Abhilash Nair[1], Paul Şerban Agachi[1,2]

1) Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, CAPE Research Center, 11 Arany Janos Street, 400028, Cluj-Napoca, Romania;
2) Botswana International University of Science and Technology, Palapye, Botswana
**: mcristea@chem.ubbcluj.ro*

Introduction and study objectives

Awareness of the need for the human society sustainable development has become an intrinsic objective for all of the contemporary activities. Water management is a major component of this responsible approach, as water is a requisite for any forms of life.

The wastewater treatment technology relying on biological cleaning processes has become the most widespread way of restoring the water quality, against contamination with carbon, nitrogen and phosphorous based pollutants. Improving efficiency of the biological Waste Water Treatment Plant (WWTP) is an ever-present objective, demanding continuous increase of the plant performance in order to conform to the severe water quality regulations.

Operating efficiently the WWTP is depending today on the computer based systems for monitoring and control. Both at the WWTP design and the operating level there is an obvious need for accurate representation of the plant, which usually takes the form of deterministic mathematical models. Optimization and advanced control are leaning on and taking benefit of the models. The state of the art in modelling WWTPs are the Activated Sludge Models ASM1, ASM2(d) and ASM3. Although the last developed activated sludge models are striving to overcome some of its limitations, the ASM1 remains the most widespread and used ASMs.

Most of the benefit emerging from the use of the ASM models is founded on their conceptual and theoretical improvements for the description of the complex physical, chemical and biological processes. Nevertheless, their straightforward application in practice is relying on the capability of calibrating the models by the use of data measurements from the plant. The present work is addressing this challenging calibration objective for the ASM1, considering the calibration of the municipal WWTP of Cluj-Napoca as case study.

Methodology

There is not yet a general well-structured and overall accepted calibration methodology. This study combines a set of representative calibration procedures, coupled with different optimization techniques, for the ASM1 calibration of the WWTP presented in Figure 1.

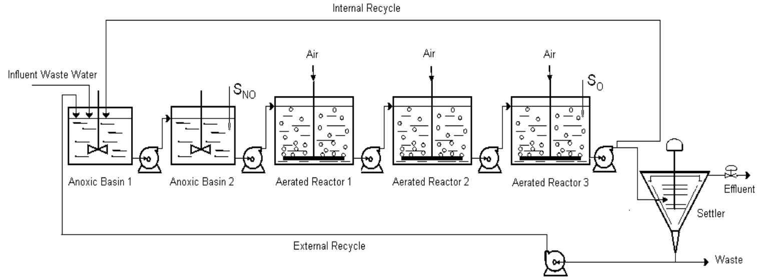

Figure 1: WWTP anoxix-aerated reactors and settler representation.

Calibration of the ASM1 uses the measurements from the municipal WWTP and aims two sub-objectives. The first one consists in the calibration of the WWTP influent wastewater variables while the second one addressed the calibration of model parameters. The calibration methodology used different optimization instruments for fitting the model simulation results with the municipal WWTP measured data. The following influent wastewater variables were calibrated: Soluble inert organic matter, Readily biodegradable substrate, Particulate inert organic matter, Slowly biodegradable substrate for the organic matter components, and Soluble biodegradable organic nitrogen, Particulate biodegradable organic nitrogen, Soluble biodegradable organic nitrogen, NH4+ &NH3 nitrogen for the nitrogen components. Kinetic, stoichiometric and settling parameters for the anoxic and aeration reactors, but also for the secondary settler have been also calibrated. Such parameters are: heterotrophic yield, heterotrophic decay rate, saturation constants, autotrophic maximum growth rate, hindered or flocculent zone settling parameters.

Two major objective functions have been used in the optimization algorithms. They accounted for the square or absolute value of the difference between the simulated model variables and the measured ones, in terms of the Chemical Oxygen Demand and nitrogen fractions.

For the minimization of the single or multiobjective optimization indices several optimization algorithms have been used, such as: nonlinear constrained optimization (Newton based methods), genetic algorithms, hybrid and and Pareto optimization (multiobjective approach).

For the considered case study the calibration work was performed using the ASM1 model implementation and optimization in Matlab&Simulink software environment.

Results and conclusions

The model calibration results show the match between the process values simulated by the model and the WWTP measurements, assessed by the considered optimization indices and comparatively presented for the different applied optimization approaches. Focusing on the efficiency evaluation of the optimization methods, the results of this work reveal their incentives and limitations for building a trustful calibrated model aimed to be further used for WWTP advanced control and operation optimization.

ENERGY BALANCE OF MICROALGAE-BASED WASTEWATER TREATMENT PLANTS

Joan García[1], Alessandro Solimeno[1], Raquel Gutiérrez[1], Fabiana Passos[2], Enrica Uggetti[1], Marianna Garfí[1], Maria Jesús García-Galán, Ivet Ferrer[1]

[1] GEMMA – Group of Environmental Engineering and Microbiology, Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya·BarcelonaTech, c/ Jordi Girona 1-3, Building D1, E-08034, Barcelona, Spain
[2] Environmental and Chemical Technology Group, Department of Chemistry, Universidade Federal de Ouro Preto, 35400-000 Ouro Preto, Minas Gerais, Brazil
** : joan.garcia@upc.edu*

Introduction and study objectives

The aim of this study is to assess the energy balance of a hypothetical microalgae-based municipal wastewater treatment plant (WWTP) designed for 10,000 inhabitants (flow of 1500 m^3/d) in the Mediterranean region (Barcelona, Spain). A year-round energy assessment was undertaken based on experimental data gathered over one year in pilot high rate algal ponds (HRAPs, fed with municipal wastewater) followed by anaerobic digesters, as well as from advanced mathematical simulations. These data and results were used to evaluate the energy balance.

Methodology

The hypothetical plant was dimensioned and designed according to our experimental results in previous works. It is assumed that the plant treats standard wastewater and consists of physical pretreament, two primary settlers, four high rate algal ponds (HRAPs), two secondary settlers, a thickener and an anaerobic digester. Prior to the anaerobic digestion, the thickened biomass and primary sludge are conveyed together to a thermal pretreatment (75 °C). Energy from the system is generated by means of a combined heat and power unit, that uses the biogas released during the co-digestion of both primary sludge and harvested biomass. Initially, and according to previous experience, only two of the four HRAPs would operate during warm months (this means 4-days HRT, from March to October), whereas all of them (4) would be operative during cold months (8-days HRT, from November to February). However, this operation strategy was optimized through mathematical simulations by means of a model named BIO_ALGAE, which can also predict the biomass production from the HRAPs depending on different environmental conditions. The model was implemented in the COMSOL MultiphysicsTM software, which solves the problem equations using the finite elements method. In order to do the simulations, and for the sake of simplicity, constant influent properties were used: pH= 7.68; alcalinity= 400 mg CaCO3/L; COD= 265 mg O2/L; NH4+= 49 mg N/L; and PO43-= 7.5 mg P/L.

Energy consumption calculations include the electricity for the HRAPs paddle-wheel and electricity and heat for both the anaerobic digester and the thermal pretreatment. The energy input for wastewater pretreatment, primary and secondary settlers is assumed to be a 50% of the total energy consumed by the plant, which has to be considered as a very conservative value. Energy is produced from methane (CH4) derived from the codigestion. Experimental studies on microalgae biomass codigestion have given CH4 yield values up to 0.46 m3 CH4/kg VS, but with great variation depending on the biomass/sludge ratio. For this reason a conservative value of to 0.25 m3 CH4/kg VS is assumed to calculate CH4 production. The electricity conversion efficiency of the CHP unit is supposed to be of 35%. Heat is assumed to be produced with a percentage of conversion of 55%.

The energy balance was conducted over a monthly basis in order to consider mean changes in environmental conditions (mostly solar radiation and temperature). Net energy ratio (NER) of electricity (NERelectricity) and heat (NERheat) are calculated as the energy output (energy produced by the system) over the energy input (energy consumed by the system).

Results and conclusions

Simulation results allowed to optimizing the performance of the HRAPS. Hydraulic retention time (HRT) had to be changed from 8 to 4 days in May, and from 4 to 8 days in September (note that according to our previous experience these changes had to be done in different months, as stated in methods Section). This was due to the fact that with previous HRT conditions effluent NH4+ concentrations were higher than 10 mg N/L in May as well in September. This new operation strategy gave as a result effluent NH4+ concentrations lower than 10 mg N/L all year round. NH4+ was selected as performance indicator because it is very sensitive to changes in water quality in HRAPs. According to simulations, biomass production had clearly seasonal trends, with lower values in winter (5-10 g/m2.day) and higher in summer (20-25 g/m2.day). Yearly average biomass production was approximately 15 g/m2.day. These trends observed in simulations were confirmed with available experimental data.

Seasonal changes observed in biomass production had a clear impact in NER, in particular for electricity. NERelectricity values during the winter were near to 1, while in summer were greater than 3. All in all, these results indicate that the treatment plant would be self-sustainable for electricity all year round. A different result is obtained for the NERheat, although seasonal trends were also observed. In this case, most of winter months values were slightly higher than 1 and therefore, the treatment plant is in the limit of neutrality in terms of energy for heating.

The results of this study indicate that a microalgae-based WWTP of 10,000 PE could be energetically self-sustainable in environmental conditions similar to those of Barcelona. However, a more in depth analysis of the data taking into account changes in key parameters is necessary since small deviations on the assumptions considered for calculations could give place to a no neutral system.

GREEN CHEMISTRY EXTRACTION METHOD FOR RECOVERY OF GOLD IONS FROM CYANIDE WASTEWATERS

Mădălina Ghercă[1], Dumitru Bulgariu[2,4],
Anca Mihaela Mocanu[3], Laura Bulgariu[1]

[1]Gheorghe Asachi Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, Iaşi, Romania
[2]"Al.I.Cuza" University of Iaşi, Faculty of Geography and Geology, Department of Geology, Iaşi, Romania
[3]Gheorghe Asachi Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, Department of Organic, Biochemical and Food Engineering, Iaşi, Romania
[4]Romanian Academy, Filial of Iaşi, Branch of Geography, Iaşi, Romania
**: madagherca@yahoo.com (M. Ghercă); lbulg@ch.tuiasi.ro (L. Bulgariu)*

Introduction and study objectives

Gold ions are usually removed from cyanide solutions by activated carbon adsorption, ion exchange and solvent extraction. Even if the adsorption on activated carbon and the ion exchange are considered environmental friendly methods, the solvent extraction is preferred for practical removal of gold ions at large scale, due to its higher efficiency and ease of operating.

It is well known that conventional solvent extraction is a widely used method for recovery of various metal ions, including gold, by adding organic solvents. Unfortunately, this method is considered as aggressive to the environment and harmful for human health because: (i) most of organic solvents are toxic, flammable and volatile, (ii) some times large volumes of organic solvents are required, and (iii) the cost becomes considerable, when a high selective extractant is used. Most of these disadvantages can be significantly reduced by using the aqueous two-phase systems in the extraction processes. The aqueous two-phase systems are spontaneously formed by mixing an aqueous solution of water-soluble organic polymer (such as polyethylene glycol, PEG) with inorganic salt aqueous solution, in specific concentration. Such aqueous two-phase extraction systems have several unique advantages over traditional extraction system because are efficient, have a low cost (the phase-forming components are commercially available and no so expensive) and do not required organic solvents. Because the formation of aqueous two-phase systems does not involve the use of any organic solvents, these extraction systems can be considered virtually non-toxic, and from these reasons they are strategically compatible with the principles of green chemistry.

In this study, an aqueous two-phase system, composed by PEG and $(NH_4)_2SO_4$ as phase forming components, was used for the removal of gold from cyanide wastewaters. The influence of various experimental parameters (such as: molecular mass of PEG, ratio of the two phases, pH of initial salt solution, initial gold ions concentration) on the extraction efficiency of gold ions was examined, in order to found the optimal experimental conditions. This method was evaluated for recovery of gold ions from cyanide wastewater, obtained from a local company.

Methodology

All extraction experiments were performed in batch system, by mixing various volumes (1 – 8 mL) of PEG (M = 2000; 4000 and 10 000 g/mol) stock solution (40 % w/w) and (NH4)2SO4 stock solution (40 % w/w) in a centrifuge tube. After adding gold ions solution (0.1 – 0.5 mL) and H2SO4 (pH = 1 – 8), the systems were centrifuged for 10 min at 2000 rpm, and before analysis the phases were separated. Around 1.0 mL from each phase was measured for the spectrophotometrically analysis of gold ions. For the validation of extraction method, 50 mL of cyanide wastewater was filtered, in order to remove solid impurities, and used both for the determination of initial gold ions concentration, and for extraction according with the procedure described above.

Results and conclusions

The experiments performed in batch systems have shown that the higher extraction efficiency is obtained in the following conditions: molecular mass of PEG – 2000 g/mol, volume ratio – 5:5, pH of initial solution – 1.05, at room temperature (20 ± 2 °C). Under these conditions, the extraction percents are higher than 98 %, on entire interval of initial gold ions concentration between 5 and 100 mg/L. Therefore these conditions were considered as optimum for gold ions removal.

In order to highlight the applicability of this extraction method, the removal of gold ions from cyanide wastewaters was carried out. The initial concentration of gold ions in the wastewater used in this study was adjusted at 150 mg/L. Different volumes of wastewater (0.5 – 4 mL) were used for gold extraction in an aqueous two-phase system obtained by mixing equal volumes of PEG(2000) and (NH4)2SO4 solutions (40 % w/w), at an initial solution pH of 1.05. The obtained values of extraction percents (E, %), illustrated in Fig. 1, indicate that in mentioned experimental conditions, the removal of gold from cyanide wastewater is quantitative, on entire studied gold ions concentration range.

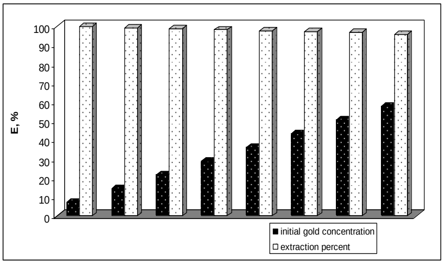

Figure 1:. Extraction efficiency of gold from cyanide wastewater, in optimum experimental conditions.

The obtained results indicate that the aqueous PEG-based two-phase system has potential for practical applicability in the removal of gold ions from cyanide wastewaters, both due to its extraction performances, and "green chemistry" characteristics.

Acknowledgments

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EVALUATION OF THE EFFECT OF PENDIMETHALIN HERBICIDE ON THE FUNGICIDE TEBUCONAZOLE BIODEGRADATION USING A PACKED BED REACTOR

**Joseph Trujillo García[1], Paola Chargoy Cruz[1],
Emanuel Mejía Jiménez[1], Deifilia Ahuatzi Chacón[2],
Oswaldo Ramos Monroy, Nora Ruiz Ordaz[2],
Juvencio Galíndez Mayer[2], Cleotilde Juárez Ramírez[2,*]**

[1]Becario BEIFI,
[2] BECARIO EDI, COFAA, SNI
Laboratorio de Bioingeniería Escuela Nacional de Ciencias Biológicas Instituto Politécnico Nacional, Avenida Wilfrido Massie S/N Ciudad de México
[*] : cleotildejr@prodigy.net.mx

Introduction and study objectives

Tebuconazole is a fungicide widely used to protect various crops social and economically interesting such as wheat, barley, grapes, tomatoes, chrysanthemums, etc. It is due to its intensive use that this fungicide has been detected in superficial waters, and has also been found before and after the treatment of municipal effluents causing severe problems of water contamination, tebuconazole is reported as a very toxic fungicide for aquatic organisms with long lasting harmful effects. Because of that is necessary to develop biological processes to remove it from the environment, however, due to the refractory to bodegradation of the molecule, has been reported a partial degradation of the fungicide which is used only as a source of nitrogen and it is necessary to add glucose as carbon source. The bibliography indicates that it is necessary the presence of a co-substrate for the efficient biodegradation of tebuconazole, the objective of the present work is to evaluate if the herbicide pendimethalin and/or some adjuvants present in the commercial mixture Prowl®400, would improve the degradation of the fungicide tebuconazole by a previously isolated microbial community.

Methodology

The evaluation of fungicide degradation was performed in a packed bed reactor with a microbial community previously isolated from agricultural soils and capable of degrading the herbicide pendimethalin. The commercial mixture Prowl®400 (active ingredient pendimethalin 37.4%) and Folicur®25 (active ingredient 25% tebecunazole) were used. The reactor was a glass column (70 cm height and 5 cm diameter) packed with the microbial community immobilized in fragments of volcanic rock (pomex stone), the packed bed reactor was operated at room temperature with an air flow of 0.03 VVM. The capability of the microbial community to degrade the tebuconazole fungicide was evaluated by feeding a minimal mineral medium with the fungicide at 25 mgL^{-1} to the reactor, the degradation of the herbicide pentimenthalin was evaluated at the same concentration, and finally the mixture of the two pesticides adding 25 mgL^{-1} of each pesticide. The volumetric loads of the contaminants (Bv, mgL^{-1}h^{-1}) were modified varying the flow of supply and once was reached the steady state the residual concentration of each pesticide was determined the efficiency by spectrophotometry and high performance liquid chromatography (HPLC) (wavelength of 194 nm for tebuconazole and 240 nm for pendimethalin). In addition, the chemical oxygen demand was determined as an alternative way of evaluate the degradation. Finally, was identified the most abundant cultivable bacteria in the microbial community by the 16S rDNA sequencing analysis.

Results and conclusions

The microbial community composed of six different bacteria of different morphology was able to degrade 15% of the fungicide tebuconazole only when the volumetric loads were low, probably due to the toxicity and refractory to biodegradation of the molecule. The herbicide pendimenthalin was found to be less toxic due to removal efficiencies were higher than 80% to volumetric loading rates of 10.5 mgL^{-1}h^{-1}, at higher volumetric loads the removal efficiency decreases due probably to the toxic effect of the herbicide. Finally, when the ability of the microbial community to degrade the mixture of pesticides was evaluated, it was possible to observe how the degradation of the two toxic compounds increased, obtaining removal efficiencies of about 90% to volumetric loading rates of 20 mgL^{-1}h^{-1} (Figure 1). The chromatographic profiles obtained by HPLC showed that the microbial community was able to degrade the two pesticides and almost all of the aromatic adjuvants present in the two commercial blends resulting in removal efficiencies of the chemical oxygen demand above 80%. It can be concluded that the presence of the fungicide tebuconazole did not affect the biodegradation of the herbicide pendimethalin, but the presence of this or of a co-subtrate in the commercial mixture significantly improved the biodegradation of the fungicide tebuconazole obtaining average removal efficiencies higher than 90%.

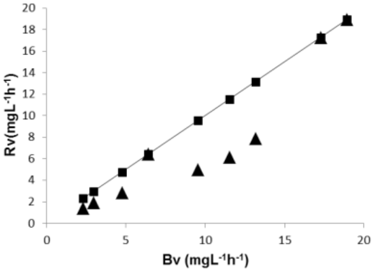

Figure 1. Volumetric removal rates of the two pesticides (▲fungicide; ■ herbicide) in packed bed reactor. The line continuous indicates theoretically removal efficiencies of 100%.

The bacterial genera that integrate the microbial community were: *Sphingobium* sp. (NZ JH992904.1), *Pseudomonas* sp. (NC020829.1), *Delftia* sp. (NC010002.1), *Kocuria* sp. (NC010617.1), *Variovorax* sp. (KX665557.1) and *Caulobacter* sp. (NC011916.1). All these genera have been reported in the literature as degraders of xenobiotic compounds.

PACKED-BED COLUMN STUDIES OF HEXAVALENT CHROMIUM REMOVAL AND TOTAL CHROMIUM BIOSORPTION BY QUERCUS CRASSIPES ACORN SHELL

Erick Aranda-García, Eliseo Cristiani-Urbina

Instituto Politécnico Nacional, Escuela Nacional de Ciencias Biológicas, Departamento de Ingeniería Bioquímica. Avenida Wilfrido Massieu s/n, Unidad Profesional Adolfo López Mateos. Ciudad de México, México.
**: ecristianiu@yahoo.com.mx*

Introduction and study objectives

Hexavalent chromium [Cr(VI)] is a heavy metal, whose high toxicity, mutagenicity, teratogenicity and carcinogenicity make it a serious health concern. In recent years, the search for efficient, environmentally friendly and cost-effective processes for detoxifying Cr(VI)-contaminated wastewaters has prompted the development of alternative and promising technologies that include biosorption.

Biosorption is a process that uses low-cost biomaterials (biosorbents) to bind and concentrate metal ions from aqueous solutions. Biosorption studies are usually performed in batch systems; nevertheless, the most economic and efficient practical application of biosorption is carried out in continuous packed-bed column systems. Furthermore, the analysis of the effect of operating parameters on biosorption performance based on lab-scale packed-bed column experiments provides reliable and helpful information that will enable scaling-up the biosorption process to pilot and industrial levels.

Current research aims to examine Cr(VI) and total chromium removal by acorn shell for varying process design parameters, such as solution pH, biosorbent dosage (bed height), flow rate, and inlet Cr(VI) concentration in a lab-scale continuous up-flow packed-bed column. Subsequently, breakthrough curves were analysed using Adam-Bohart, Thomas, Yoon-Nelson and Dose-Response models and the characteristic parameters were obtained.

Methodology

Cr(VI) and total chromium removal by oak (Quercus crassipes Humb. & Bonpl.) acorn shell was assessed in a continuous up-flow glass-column packed with 0.15-0.5 mm acorn shell particles. Cr(VI) and total chromium removal performance in a continuous system was evaluated as a function of pH (1.0-3.0), biosorbent dosage (1-4 g), flow rate (0.25-1.0 mL min-1) and influent Cr(VI) concentration (50-400 mg L-1). Effluent samples were collected at specific time-intervals in order to evaluate the shape of the breakthrough curves. Cr(VI) and total chromium concentrations were measured by the 1,5-diphenylcarbohydrazide and the alkaline hypobromite oxidation methods, respectively.

Ultimately, theoretical dynamic models for column biosorption studies were applied to describe breakthrough curves.

Results and conclusions

Evidently a decrease in the pH of feed Cr(VI) solution, caused breakthrough curves to shift from left to right, indicating that more Cr(VI) ions had been removed. Cr(VI) ions were not detected in the effluent during the first hours of the experiment ($t < 4$ h) when pH of inlet Cr(VI) solution was 1.0, 1.5, and 2.0. Contrastingly, at pH values of feed solution of 2.5 and 3.0, higher levels of Cr(VI) were found in the effluent. Lowest total chromium concentrations in the effluent solution were obtained at pH 2.0, whereas there was a higher total chromium concentration at lower and higher solution pH values. The highest bed capacity for total chromium biosorption was obtained at pH 2.0, with a value of 105 mg g-1.

Solution pH appears to be the most important parameter influencing biosorptive processes. Optimum pH for biosorptive removal of most adsorptive pollutants has usually been selected from batch biosorption results. In the present work, a solution pH of 2.0 was selected for the total chromium biosorption by Q. crassipes acorn shells, based on the findings in the continuous packed-bed column.

The removal of Cr(VI) and total chromium in the packed-bed column was largely dependent on the quantity of biosorbent present inside the column, so that as the bed mass increased from 1 to 4 g, there was a corresponding increase in the amount of Cr(VI) and total chromium removed, possibly due to the higher bed heights which permitted longer contact time between metal ions and biosorbent. Breakthrough curves became less steep as the influent flow rate decreased, which may relate to the fact that at lower rates Cr(VI) ions had enough time to contact with the biosorbent, resulting in greater removal of Cr(VI) and total chromium in the column. As the inlet Cr(VI) concentration increased, the saturation of the column was reached earlier, thereby reducing the operation time; this behavior may be the result of a higher concentration gradient, providing a higher driving force for the biosorption process.

At all operation times and design parameters assayed, total chromium concentration in the effluents was higher than Cr(VI) concentration, possibly resulting from the biotransformation of Cr(VI) to Cr(III) by reducing organic compounds present in the acorn shell.

The Dose-Response model showed good agreement of the experimental breakthrough curves with model predictions.

This study reveals that acorn shell from Quercus crassipes Humb. & Bonpl. exhibits remarkable potential for detoxifying Cr(VI)-contaminated aqueous solutions. Experimental data revealed that Cr(VI) and total chromium removal capacity of acorn shell was dependent on operating variables such as solution pH, biosorbent dosage, flow rate and influent Cr(VI) concentration. Total chromium biosorption data conformed best to the Dose-Response model.

NON-THERMAL PLASMA MINI-REACTORS FOR WATER TREATMENT

Radu Burlica*, Iuliana-Delicia Dirlau, Dragos Astanei

"Gheorghe Asachi" Technical University of Iasi,
Bd.Profesor Dimitrie Mangeron, nr.21-23, 700050 Iasi, Romania,
**: rburlica@tuiasi.ro*

Introduction and study objectives

Non–thermal plasma (NTP) is generated by an electrical discharge developed between two electrodes, in a gas flow, in order to maintain the low temperature of the gas. The low temperature plasma, considered to be an advanced oxidation technology, leads to the formation of positive and negative ions, electrons and other highly chemically active species such as ozone, hydrogen peroxide, and hydroxyl radicals. The non-thermal plasma has been proved to be an alternative technology for gas and liquid phase depollutant treatment. The goal of this paper is to emphasize the effect of the NTP mini-reactors with different electrodes in order to remove the soluble organic compounds; therefore, a soluble organic dye (Reactive Blue 19 dye) solution has been treated in a NTP mini-reactor. Also, the NTP effects on reactive species production in pure water, as hydrogen peroxide and nitrates have been studied. The efficiency of the NTP treatment was enhanced by spraying the solution into the plasma zone through a two-way nozzle. The organic dye removal from the solution and also the hydrogen peroxide and nitrates formed in water sprayed in the plasma has been measured using colorimetric methods. In order to optimize (from electrical and physical-chemical parameters point of view) the NTP treatment of the organic compounds dissolved in water, the energy efficiency (g/kWh) of the dye destruction have been calculated for different shapes of the electrodes.

Methodology

The water/solution spraying for treatment using NTP technology is applied through a two-port nozzle, one for air and another for solution, directly into the reactor. The NTP reactor is equipped with two planar (point to point) electrodes, placed in a narrow chamber, aimed to confine the plasma and force the water droplets to get into contact with the discharge. The electrochemical processes in plasma depend on the shape of the electrodes. For example, in Fig. 1 is presented an alternative high voltage (9kV), low power, electrical discharge, between the electrodes perpendicularly on the gas flow. The NTP plasma can be also generated in parallel with the gas flow direction in a longitudinal configuration of the reactor. The effect of the organic dye removal from water for four different shapes of the electrodes has been studied. The use of low power discharge does not thermally vaporize the water droplets in the reactor, and enhances the energy yield for NO_3 and H_2O_2 due to suppression of quenching reactions of radicals with other molecular species. Initially, pure water has been sprayed into the reactor and H_2O_2 and NO_3 (when air is used as carrier gas) have been measured. Experiments presented used Ar and air as carrier gas with a flow rate Q_g of 1.5 mL/min, constant, and water/solution flow rates between Q_s 5-15 mL/min. Four different shapes of electrodes connected to an AC high-voltage transformer (Tr, 9 kV) have been studied. The discharge current was approximately 4 mA. When a 50 mg/L Reactive Blue 19 solution has been treated in NTP reactor, the decreasing of color intensity has been measured using a UV-VIS spectrophotometer (Shimadzu).

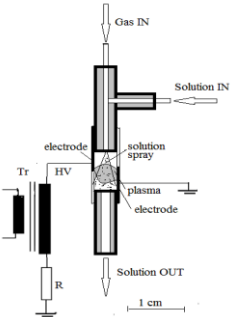

Figure 1: Experimental set-up

Results and conclusions

The results for H_2O_2 generated in water are presented in Fig.2. The decreasing of the dye concentration (calculated as the difference between the initial concentration of the solution C_0 and the concentration after one pass through the NTP reactor C_f), Δ[Blue19] = C_0 - C_f, is presented in Fig.3.

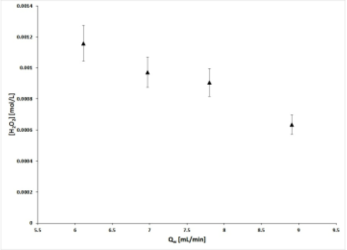

Figure 2: The evolution of H_2O

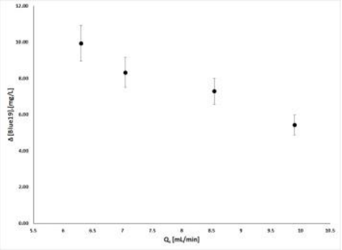

Figure 3: Dye removal in NTP reactor

In order to determine the optimal working point of the NTP reactor, as well as the best solution of the electrodes geometry, the energy efficiency (g/kWh) of the H_2O_2 generation also for the dye removal from the solution, for different electrical (u, i, P) and physical/chemical (Q_w, C_0, Q_g) parameters, have been calculated.

The main advantages of the NTP technology, comparing to the other classical physical/chemical procedures, are a higher active power and high specific energy efficiency of the discharge, which provide a higher reactive potential. Also, its technological simplicity and normal operating conditions (atmospheric pressure at industrial frequency), make it suitable for industrial application.

For the solution treated in NTP reactor, the efficiency of chemical compound destruction and hydrogen peroxide formation in liquid phase, for different solution/gas flow rates and electrodes geometry has been investigated by measurements regarding the processes specific energy. The results provide an optimal set of physical, geometrical and electrical parameters concerning the organic compound destruction efficiency. For practical applications, it is necessary to increase the volume of the solution treated, in our case, to develop and design a larger NTP reactor unit that uses a large number of mini-reactors working in parallel.

AIR BUBBLE DYNAMICS MODELLING AND SIMULATION IN THE WATER COLUMN

Corina Boncescu[1,*], Lacramioara Diana Robescu[2]

[1)] Power Engineering Faculty, Department of Hydraulics, Hydraulic Machinery and Environmental Engineering, University POLITEHNICA of Bucharest, Romania,
[2)] Power Engineering Faculty, Department of Hydraulics, Hydraulic Machinery and Environmental Engineering, University POLITEHNICA of Bucharest, Romania,
[*]: *corina.boncescu@gmail.com; diana.robescu@upb.ro*

Introduction and study objectives

Individual gas bubbles that enter and flow into an aeration system of wastewater determine an extra turbulence in the mixture. This process results in increasing dissolved oxygen concentration in the water. In the biological treatment systems, the most important phenomenon is oxygen mass transfer that influences decomposition of organic matter. Furthermore, oxygen supply has an important impact on the degree of homogeneity of water-air-activated sludge mixture. In this paper was used the volume of fluid (VOF) mathematical model to determine the velocity generated into an air-water mixture in a column of water and from the ascending air bubbles movement it was identified vertexes center. The obtained results were compared to experimental and theoretical available data from the literature.

The aim of this research is to study the impact of gas velocity on air-water mixture turbulent degree. It has also been determined the air volume fraction for the calculation oxygen mass transfer coefficient from air into water.

Methodology

The mathematical model used to determine generated and induced velocity in the air-water mixture by upward movement of air bubble was VOF model. Integrating math was done in 2D unsteady state with time step 0.0001 s. The equations used in this model were continuity equation and moment equation. The pressure was calculated with "body force weighted" model and for the relationship between pressure and velocity was used PISO method (Pressure Implicit with Split Operator).

In order to analyze the dynamics of air bubbles in the water body, the study field is a cross section of a column of water which has width 0.1 [m] and height of 0.2 [m]. It has considered three values of the air velocity: 0.17 m/s, 0.25 m/s, 0.4 m/s respectively, through an orifice diameter of 0.5 mm.

In this model the following hypothesis were considered: water velocity v_l=0 m/s, unsteady regime, flow was achieved at low Reynolds numbers;

constant surface tension coefficient, σ=0.072 N/m; gravitational acceleration was negative due to air upward movement, g(0,-9.81).

Results and conclusions

Mathematical and simulation modeling was conducted for 3 cases of air velocity. It was obtained generated and induced velocity values by air bubbles movement and swirl centers emerged. Figure 1 presents contour of air volume fraction and generated and induced velocity values into the water for air velocity v_g = 0.17 m/s. In this case was obtained mixture velocity value v_{am}=0.35 m/s. For air velocity v_g=0.25 and vg = 0.4 m/s was determinate mixture velocity v_{am}=0.43 m/s, v_{am}=0.63 m/s, respectively. The results of this research showed that if air velocity increase, the mixture velocity increase, too. Moreover, was observed that the number of vertexes center was increasing. In hydraulic terms, for the aeration tank from wastewater treatment plant, means that high turbulence degree ensures homogenization of air-water-activated sludge mixture.

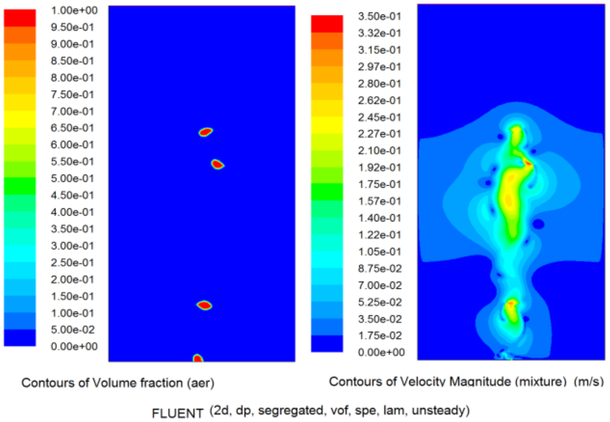

Figure 1: Contour of air volume fraction and generated and induced velocity in air-water mixture for air velocity vg = 0.17 m/s after t=1 s

The final objective of the research is to determine the theoretical oxygen mass transfer coefficient from air to water for different velocity values of air velocity and for different orifice diameters of air dispersion. Also, theoretical results will be compared with experimental research.

Acknowledgements

This work is supported by MEN-UEFISCDI within the framework of National Plan for Research, Development and Innovation 2007-2014, Partnerships in Priority Domains Program, PN-II-PT-PCCA-2013-4-1649, project no. 274/2014 and by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2016-1766, within PNCDI III.

METAL POLLUTANT CONCENTRATIONS MONITORING OF MINE WATERS FOR REDUCING WATER POLLUTION DEGREE USING MICROPOROUS SORBENTS

Andrei Szollosi-Moţa, Maria Prodan, Constantin Lupu, Angelica Călămar, Irina Nălboc

National Institute for Mine Safety and Protection to Explosion INCD INSEMEX Petrosani;
G-ral Vasile Milea Street no.32-34, Petroşani, Hunedoara County,
**: insemex@insemex.ro*

Introduction and study objectives

Industry and especially the mining industry uses significant amounts of water in technological processes of raw materials and ores. The technological water used in processing ores, contains large amounts of dissolved salts, heavy metals, acid pH. Often the purity of the process water cannot be controlled sufficiently. Waste dumps and tailings dams are significant factors of pollution of the environment, exerting constant pressure on the environment by pollution for decades, after ending the operations for minerals exploitation. Because of this, into the natural receptors reaches a significant number of contaminants such as salt and heavy metals (Zn, Mn, Cd, Ni, etc.). These pollutants disturb the natural balance of the aquatic fauna and flora, resulting in strong acidification of mine and surface waters. Historical mining has affected significantly the environment through pollution processes manifested on the air, water, soil environmental factors. Polluted mine water waters from mining units discharges get into the surface waters, affecting their properties and attributes. The aim of this work is to develop methods of mine water and surface water remediation from mining activities affected by historic mining. In order to determine the degree of pollution of the surface waters was necessary the sampling and the analysis by optical emission spectrometry with inductively coupled plasma.

After monitoring the water quality of Certej mining area, which is an area heavily affected by mining history, there were significant overruns in the case of heavy metals especially zinc and magnesium. Research has focused on reducing the concentration of heavy metals in surface waters fed and the runoff from waste dumps and tailing ponds in the mining area and the adjacent area studied.

Methodology

The determinations were performed with an experimental set-up in which in the columns arranged in steps have been introduced in various proportions microporous sorbents. Among microporous sorbents were chosen zeolite volcanic tuff and activated carbon. Also in the experiments were used other materials with ion exchange properties, namely clays. The activated charcoal sorbent is a microporous adsorption material with a high adsorption surface that can reach even 1500 m2/g, which is produced in organic materials which have a high carbon content. Water samples were taken from surface waters of the river Certej and using the method of analysis by optical emission spectrometry with inductively coupled plasma were determined the concentrations of heavy metals.

Water pollution is a particularly important factor for all the surface waters that are collected in the catchment area in question. Surface water pollution is an important factor, endangering the health of animals and people manifested through the food chain and consumption water. For determine the effectiveness of treatment an experimental stand was built up, described elsewhere, with tank and water purification columns, based on adsorption and ion exchange process.

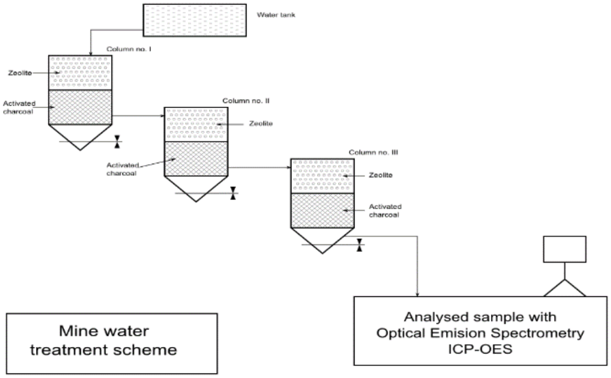

Figure 1: Mine water treatment scheme

Results and conclusions

After analyzing samples taken during the monitoring were obtained exceeding of ten times the maximum permissible concentration of heavy metals eg. for zinc (over 30 times) and for manganese (over10 times).

For the treatment of the water samples were conducted experiments in static regime, by keeping the sample in the columns for a specified time. After the static regime, it was experimented the dynamic mode. In another study, it was demonstrated the efficiency of the experimental module for the wastewater treatment using three columns of treatment arranged in steps, filled with zeolite originating from volcanic tufa. The zeolite experimented showed excellent selectivity for the cations investigated. Combining the zeolite with the activated charcoal proved to be an improvement for the treatment of the heavy metal pollution of the investigated samples.

AN ASSESSMENT OF BOTTOM SEDIMENT AS A SOURCE OF PLANT NUTRIENTS AND AN AGENT FOR IMPROVING SOIL PROPERTIES

Agnieszka Baran[1], Marek Tarnawski[2], Magdalena Urbaniak[3]

1) Department of Agricultural and Environmental Chemistry,
University of Agriculture in Krakow, Poland,
2) Department of Water Engineering and Geotechnics, University of Agriculture in Krakow,
3) European Regional Centre for Ecohydrology, Polish Academy of Sciences, Lodz, Poland;
**: Agnieszka.Baran@ur.krakow.pl; rmtarnaw@cyf-kr.edu.pl; m.urbaniak@unesco.lodz.pl*

Introduction and study objectives

Bottom sediment is a very important part of water system. Evaluation of sediments properties is important not only for assessment of water reservoir degradation but also for determining potential applications of dredged sediment. Dredging of the sediments accumulated in the reservoir has been proposed to remediate the problem silting. If the dredged sediement from the reservoirs does not pose a risk for the environment, reasonable method of such sediment management is their use one agriculture purpose. The reuse of sediment in soil restoration improving their physicochemical properties and therefore increases the productivity of soils. The aims of study were: 1) to determine of effect of bottom sediement to improve soil properties, 2) to assess the effect of bottom sediments on the concentration of macronutrients and trace elements in the plants test.

Methodology

The bottom sediment originated from the Rzeszów Reservoir situated on the Wisłok river in the Podkarpackie Voivodeship, Poland. The reservoir's initial capacity was 1.8M m^3; the impoundment area is 68.2 ha. Measurements conducted after 14 years of reservoir operation revealed that its capacity had diminished by approx. 66%, with a loss of 18.5 ha of impoundment area, constituting permanently or periodically overgrown islands and shallows. It has been estimated that currently the spontaneously forming islands and shallows cover over 30 ha of the reservoir area. The bottom sediment was sampled within the three zones of the reservoir: inlet, middle and outlet. The sediment was sampled using a Ekman sampler from the 0-15 cm layer.

The sediment was classified as a group of clay deposits with alkaline reaction, low content of heavy metals. The pot experiment was conducted on light soil, acid pH. The bottom sediments were added to the soil in the amount of

5, 10, 30 and 50% of air-dried sediment in relation to dry soil mass. The test plant was maize and field beans. The test plant was harvested after 86 (maize) and 60 (filed beans) days of vegetation. The soil samples after of the pot experiment were analyzed for parameters such as: pH, organic matter, cation exchange capacity, nitrogen and content of trace elements. The element concentrations in the solutions were assessed using ICP-OAS apparatus. The results were verified statistically using the one-way ANOVA at significance level α=0.05, by means of Statistica 11 programme.

Results and conclusions

In the studies was shown a positive effect of sediment to the soil on the maize and filed beans yield. Significantly highest shoots yield were demonstrated for the treatment with a 30% (maize) and 10% (filed beans) admixture of bottom sediment. Sediment supplements to soil caused a significant increase in N, decrease in K, P (all doses of sediement) and Ca, Mg (5, 10% of bottom sediment) in maize shoot in relation to the control. A bottom sediment addition significantly decreased all macronutritions concentration in shoot of filed beans. Sediment supplements to soil caused a significant decrease all trace elements concentrations in shoot biomass both plants in relation to the control. After a period of experiments the soil pH, depending on the experimental treatment, was between 5.70 (control treatment) to 7.10 (treatment with a 50% bottom sediment supplement). The sediment supplement to the soil caused a significant decrease value of hydrolytic acidity Hh and significant increase C – organic content. Doses of bottom sediment added to the soil significantly increased the content of copper, nickel and decreased of content of zinc, lead, cadmium in relation to the treatment without sediment.

In summary, if the dredged bottom sediments not constitute environmental risks, inorganic and organic pollution concentration in the sediments are below toxic thresholds, reasonable method of such sediment management is their agriculture purpose. However bottom sediments can not replace fertilizer, but they can by used as soil improving agents. We found that using bottom sediment form Rzeszów reservoir for plant cultivation should apply supplementary mineral fertilization.

Acknowledgements

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LIFE CYCLE ASSESSMENT OF A DRINKING WATER PRODUCTION SYSTEM

Andreea-Florina Gîlcă[1], George Bârjoveanu[1], Carmen Teodosiu[1*], Ioana Roman[2], Silvia Fiore[3*]

[1] „Gheorghe Asachi" Technical University of Iasi, Department of Environmental Engineering and Management, 73 Prof. Dr. Doc. Dimitrie Mangeron Street, 700050 Iasi, Romania
[2] SC Apavital SA Iasi, 10 M. Costachescu Street, 700495, Iasi, Romania
[3] Politecnico di Torino, Department of Environment, Land and Infrastructures Engineering (DIATI), Corso Duca degli Abruzzi 24, 10129 Torino, Italy
[*] : cteo@tuiasi.ro (C.Teodosiu); silvia.fiore@polito.it (S. Fiore).

Introduction and study objectives

Water resources are essential for humans and ecosystems, but due to problems such as climate change, industrialization, inadequate storage or insufficient wastewater treatment before discharge, qualitative improvements and integrated management of water resources are required. The main goal of water treatment is to avoid human health risks and to provide sufficient and good quality water for drinking, industrial purposes, and other economic activities by removing chemical and biological contaminants. However, these processes require increasing efforts in terms of technology, chemicals and energy inputs, which translates to increased secondary environmental impacts and added water production costs.

The objective of the study is to evaluate the drinking water treatment (DWT) system in Iasi City (Romania), by means of life cycle assessment and to identify and characterize its environmental impacts, to determine the weak points of drinking water production processes.

Iasi City is the most developed urban centre in Moldova Region (North Eastern region of Romania) and has a DWT facility providing water in accordance with European standards. The DWT system process comprises the following stages: coagulation/flocculation with ferric chloride (or polyacrylamide and powdered activated carbon) coupled with pre-oxidation (with chlorine dioxide), followed by sedimentation, pH correction with calcium hydroxide, rapid sand filtration, slow filtration on granular activated carbon (GAC) and final disinfection with chlorine gas.

Methodology

Life Cycle Assessment (LCA) approach implemented on drinking water production represents an adequate instrument to support environmental decision by identifying possible environmental impacts generated in the operational phase of the considered DWT system. Environmental evaluation is performed according to the ISO 14040 standardized LCA procedure with the SimaPro 8.1.1.16 software developed by Pré Consultants, 2016.

Results and conclusions

In this study LCA has been applied to assess the environmental performance of Iasi DWTP for 1 m^3 of potable water produced, considering the impact generated by energy consumption, technologies and reagents used. The electricity required by the different treatment stages has been accounted for the entire DWT plant, each equipment and water treatment parameters being monitored and controlled through a SCADA software.

In order to investigate the environmental impact of water production, the ReCiPe 2012 mid-point method was used, and the environmental profile for the characterization step is presented in *Figure 1.* The main contributors to impact in most of the categories are the electricity consumption and the iron chloride production used in coagulation/flocculation.

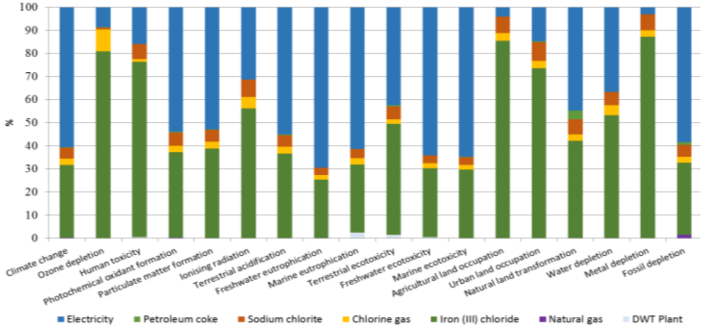

Figure 1: Environmental profile of Drinking water production system in Iași

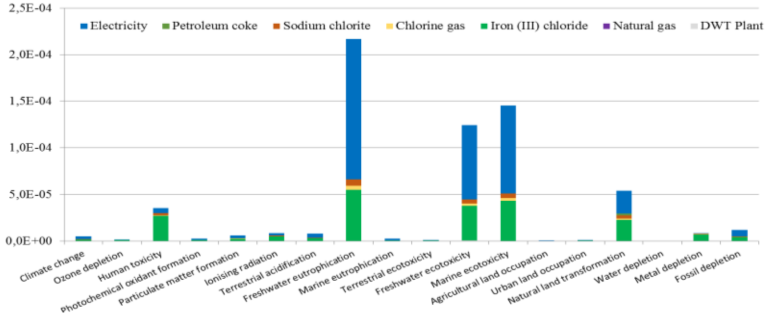

Figure 2: Environmental profile of the drinking water production system in Iași – normalized results

The normalized results presented in Figure 2 show that the most important impact categories are freshwater eutrophication and freshwater and marine ecotoxicity, and the most important contributors remain electricity and iron chloride.

The level of detail obtained for the inventory and the impact assessment steps may be considered as reference for future LCA studies, analysing other water treatment plants since the climate, technological, cultural and socio-economical differences clearly define the particularities of a DWT in a specific territorial context.

PLANT GROWTH PROMOTING BACTERIA: A SUSTAINABLE TOOL TO BOOST WATER FOOTPRINT IN AGRICULTURE

Francesca Mapelli[1], Valentina Riva[1], Ameur Cherif[2], Redouane Choukr-Allah[3], Ahmed Rashed [4], Sara Borin[1,*]

[1) University of Milan, DeFENS (Italy), Via Celoria 2, 20133 Milan, Italy;
[2) Institut Supérieur de Biotechnologie Sidi Thabet,, Manouba University (Tunisia);
[3) Hassan II Institut Agronomique et Veterinaire (Morocco);
[4) Drainage Research Institute (Egypt)
[: sara.borin@unimi.it*

Introduction and study objectives

Water scarcity and the ongoing increase of arid lands solicit the setup of innovative strategies in agriculture to increase safe food production, with particular efforts in minimizing the water footprint. Desert farming, combined with an improved wastewater recycling, might represent a smart solution to guarantee food access in arid countries to an increasing population. In this perspective, Mediterranean African Countries (MACs) provide interesting case studies to develop and test new sustainable practices. Plants live in association with complex microbial communities – the plant microbiome – tuned by the beneficial interactions occurring between them. Plant Growth Promoting (PGP) microorganisms exert direct and indirect mechanisms to improve the growth and health status of plants and once provided to crops can constitute sustainable tools to improve production yields.

Several mechanisms have been described in PGP bacteria able to specifically alleviate drought stress in plants and increase water use efficiency, having the potential to increase crop productivity in arid lands. The most suitable environment to isolate these PGP bacteria is the root system of drought-tolerant plant species, which microbiome is specifically adapted to the abiotic stresses typical of arid regions.

PGP bacteria have also the potential to be exploited for the improvement of growth and services provided by plants used in phytodepuration and phytoremediation. Here PGP bacteria can play a key role, both sustaining plant growth and cooperating with the plant in the remediation processes. The support to phytodepuration is of direct interest in arid lands in the water footprint context, potentially improving water recycling and thus decreasing the blue water demand of agricultural lands.

Aim of our research is the study of PGP bacteria associated to different plants growing in MACs, of interest in desert farming and phytodepuration, adapted to arid and/or saline soils. Considering the natural adaptation of extremophilic plants to adverse environmental conditions, we aimed in particular at their exploitation for the isolation of novel microbial resources for sustainable practices in arid land agriculture and the phytodepuration sector.

Methodology

We collected roots and rhizosphere - the soil layer surrounding roots - in MACs from several plant species, including *Sorghum* sp., *Argania spinosa* and *Salicornia* sp., naturally adapted to water scarcity and/or high salinity conditions of MACs' soils. Moreover, root and rhizosphere were sampled in constructed wetland (CWs) facilities in Morocco and Egypt. A large collection of rhizospheric and endophytic bacteria was established on different rich and selective cultivation media. All bacterial isolates have been genotyped at species-subspecies level by applying ITS-PCR fingerprinting and then identified according to the 16S rRNA sequence analysis. After discharge of all potential human and plant pathogens, a selection of isolates have been characterized *in vitro* for phenotypic traits related to PGP activity, antibiotic resistance and the ability to grow in presence of emerging organic pollutants. The PGP potential of the most promising isolates have been assessed *in vivo*, using tomato as a model plant, under limited irrigation simulating water stress conditions.

Results and conclusions

Endophytic and rhizospheric bacteria were isolated from common read specimens grown in CW and the drought tolerant plants *Sorghum* sp., *A. Spinosa* and *Salicornia* sp. The results of ITS-PCR fingerprinting showed that the bacteria collection was characterized by a high phylogenetic diversity. Overall, the adopted isolation procedure and downstream molecular analyses allowed to identify a rich and highly diverse cultivable fraction of bacteria associated to root and rhizosphere of MACs' extremophile plants.

The phenotypic characterization of the bacterial strains isolated from different extremophilic plants led to the selection of different strains for the *in vivo* assessment of PGP activity. These strains were i) classifiable as GRAS (Generally Regarded As Safe) organisms, basing on the literature screening about their species, ii) resistant to osmotic and saline stresses, typical of arid lands and iii) sensitive to different classes of antibiotics. In the frame of the global spread of antibiotic resistance, the absence of antibiotic resistance represents an important trait, generally neglected by the literature, for the choice of the best candidates for the setup of fertilizing bacteria inoculants.

The *in vivo* PGP tests were performed on tomato plants growing under controlled greenhouse conditions, artificially inducing water stress. Plant growth parameters, such as length and dry weight of root apparatus and aerial part, were measured at the end of the experiment. Accordingly, four bacterial strains belonging to the genera *Bacillus*, *Pseudomonas* and *Rhizobium*, demonstrated to significantly increase plant growth under drought conditions compared to the non-inoculated tomato plants.

Besides corroborating previous findings on the potential of extremophilic plant as source of PGP bacterial strains exploitable under adverse condition, in this study we identified promising candidates for the future development of biofertilizers tailored on the need of MACs, thus useful to increase the success of desert farming and phytodepuration technologies.

Acknowledgement

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THE PHOSPHORUS DYNAMICS IN INTEGRATED MULTI-TROPHIC AQUACULTURE SYSTEMS

Stefan-Mihai Petrea[1,*], **Alina Mogodan**[1], **Isabelle Metaxa**[1],
Sănduţa Plăcintă[1], **Mihaela Aida Vasile**[2]

1) Department of Aquaculture, Environmental Science and Cadastre, „Dunărea de Jos" University of Galati, Galati, Romania;
2) Department of Food Science, Food Engineering and Applied Biotechnology, „Dunărea de Jos" University of Galati, Galati, Romania;
[*]: stefan.petrea@ugal.ro

Introduction and study objectives

In order to offer a proper solution to the continuous growing demands of world population for food, aquaculture comes with the idea of integrating different production technologies. Thus, better growth performance, the safety and security of consumers and the little to none negative effects to the environment are the main desiderata of integrated multi-trophic systems. Since aquaculture sector registered a fast development in the last decade, implementing the integrated techniques in order to create different integrated multi-trophic aquaculture systems (IMTA) proves its efficiency. Searching for better solutions, from both technological and technical point of view, is the major objective in most of IMTA researches.

Phosphorus is one of the basic elements found in fish expanded feed, fact that makes notable its presence in aquaculture production systems. However, little it is known regarding the dynamics of phosphorus in IMTA systems based on ponds aquaculture.

This presents study is made by using IMTA ponds aquaculture systems and various cyprinids species, typical conditions that are encountered in Romanian aquaculture.

The objective of this research is to determine the relations between phosphorus levels and dynamics recorded in cyprinids meat, technological water and sediments in two IMTA systems, where different technical solutions and technologies were applied.

Methodology

For the present research, two ponds with an area of 0.45 ha each and an average water depth of 1.5 m, were used. The first pond (PCP) was used for rearing polyculture 2500 individuals of common carp (*Cyprinus carpio*), 100 individuals of grass carp (*Ctenopharyngodon idella*), 40 individuals of bighead carp (*Hypophthalmichthys nobilis*) and 40 individuals of silver carp (*Hypophthalmichthys molitrix*). The second pond was divided by using a net as follows: first part with an area of 0.15 ha CP (carp pond) and the second part with an area of 0.30 ha PP (polyculture pond). The CP pond was stocked with 2000 individuals of common carp specimens, while the PP with 500 individuals of common carp (*Cyprinus carpio*), 100 individuals of grass carp (*Ctenopharyngodon idella*), 40 individuals of bighead carp (*Hypophthalmichthys nobilis*) and 40 individuals of silver carp (*Hypophthalmichthys molitrix*). The experiments lasted two and a half months.

A 28% crude protein fish fodder was used, represented by a mix wheat lees, dry maize dregs, sunflower groats and flour protein, in equal amounts. Fish fodder was administered only in PCP and CP by using two daily feeding ratio (3% of biomass weight (BW) and 1.5% BW).

For determining the phosphorus concentration in fish meat, water and sediments, the atomic absorption spectroscopy was used. The determinations were made at an Analytik Jena ContrAA 700 spectrometer.

Results and conclusions

Significant statistically differences ($p<0.05$) were recorded between each of the tested species of cyprinids and also between both IMTA systems in terms of phosphorus concentration in fish meat. Also, the concentration of phosphorus in sediments registered significant statistically differences ($p<0.05$) between the tested production systems. A direct positive correlation between the amount of phosphorus administrated via fodder and the concentration of this element in fish meat and sediments was found. The phosphorus dynamics manifests an upward tendency throughout the experimental period, in both PCP and PC. The highest concentration of phosphorus in sediments and meat was recorded in case of PC, while the lowest was found at PP. However, the phosphorus concentrations in meat do not exceed the safety limits mentioned by EU regulations.

It can be concluded that by using the PCP IMTA production system, the concentration of phosphorus is distributed more uniform in the pond and among the fish individuals, compare with CP-PP IMTA production system. Also, both PCP and CP-PP are suitable for obtaining fish production with phosphorus concentration within the safety limits for human consumption.

The water exchange flow and the phytoplankton size and structure must also be taken into consideration for future similar studies, conducted in ponds aquaculture production systems.

A LIFE CYCLE ASSESSMENT APPLICATION TO EVALUATE ENVIRONMENTAL ISSUES IN SAVING AND REUSING WATER AT DOMESTIC LEVEL

Alessandra Bonoli[*], Martina Mastroddi

DICAM - Department of Civil, Chemical, Environmental and Materials Engineering;
Terracini Street 28, 40131 Bologna, Italy,
[*]: alessandra.bonoli@unibo.it

Introduction and study objectives

The paper would show the results of a project for the development and application of life cycle analysis (LCA) to domestic water consumption, with the aim of highlighting the importance of saving water resources and the convenience, in terms of reduction of environmental impacts, in the use of specific technologies for rainwater harvesting and gray water recycling, such as tanks. This will enable the recovery, treatment and reintegration of the resource for some specific uses only (like toilet and water intended for outside uses), in compliance with health and hygienic standards laid down in legislation, evaluating the impacts and the environmental, social and economic sustainability linked to the performance of this specific technology. The LCA analysis quantifies, therefore, the sustainability of the use of water resources, contributing to the improvement of the production chain, distribution and use of water and affecting the training phase of the consumption, so as to promote water saving and the reduction of withdrawals from the environment. In detail, the software used will enable to compare the sustainability of the current user's consumption conditions with respect to solutions allowing for the reuse of gray water and rainwater with resulting benefits in terms of wastewater's volume reduction to be purified and drained. Sustainability assessments will also take into account the global pressure factors, human activities, such as those resulting from climate change and population's increase. Results refer to the functional unit of 1 liter of water per person per day, consumed or saved, and are organized into four damage's categories, quantified by a score, allowing direct comparison between them. For a more reliable and comprehensive analysis, only inputs imposed to the system by the analyzed scenarios were considered, including water and energy consumption.

For the waste water's assessment, with the same assumptions above, reference was made to the Municipal treatment plant of a small town in Emilia

Romagna Region. Analysis boundaries extends from the water's collection, purification and distribution to the user, up to the leakage of the consumed water in the sewage and its treatment, including in the input any chemical substances needed for their treatment, during both deployment and disposal phases. All input are considered as a function of a mass balance, that has allowed to highlight the savings, both in terms of water resources and the environmental impacts.

Analysis' methodology and evaluation of impacts

The LCA sustainability analysis allows to collect, monitor and analyze the environmental performance of products and services, considering even complex lifecycles, according to ISO 14040 series recommendations. It contains several databases with different categories needed to the description of a "lifetime"; you can find in fact, classified and described in detail within each database, materials, processes, energy and transport systems, methods of waste disposal and treatment. The impacts' assessment method used for the water saving analysis is "IMPACT 2002+"; it is the result of the combination of the methodologies based on both the midpoint (with reference to the 14 impact categories) and the endpoint approach (based on four categories of damage). The structure of the methods is similar to that proposed by the ISO 14042 and includes classification, characterization, normalization and weighting. In the general structure of the IMPACT 2002+, all the results of the inventory analysis are connected through 14 midpoint impact categories to 4 categories of damage: Human health, Ecosystem quality, Climate change and Resources.

Results and conclusion

The results highlight the importance and convenience of rainfall water storage and use and gray water recycling , in order to protect natural resources and consciously regulate the usage habits for each individual user; in fact, the inclusion in the system boundaries of the treatment plant of the tested town allowed to evaluate the environmental impacts avoided thanks to the recovery and processing of the same in the tank, in addition to the impact avoided by withdrawing fewer liters of water, thanks to the recycling. This will encourage the increasing usage of these technologies in urban areas that today, more than ever, need a determined and strong sustainable initiative, designed to safeguard the environment and human health and the redevelopment of the entire urban context.

Acknowledgments

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EVALUATION OF A CONSTRUCTED WETLAND FOR WASTEWATER TREATMENT, WITH EMPHASIS ON THE REMOVAL OF EMERGING ORGANIC CONTAMINANTS AND ANTIBIOTIC RESISTANT BACTERIA

Stavros Christofilopoulos*, Andreas Kaliakatsos,
Konstantina Triantafyllou, Styliani Voutsadaki,
Nikolaos Nikolaidis, Venieri Danae, Nicolas Kalogerakis*

School of Environmental Engineering, Technical University of Crete, Chania, Greece
**: nicolas.kalogerakis@enveng.tuc.gr*

Introduction and study objectives

The presence of emerging organic contaminants (EOCs) in wastewater has attracted intense interest in the environmental engineering community, due to the high frequency of their detection, the adverse effects on human health and the environment, as well as their inefficient removal in wastewater treatment plants. Among EOCs, antibiotics are of great concern for public health as their presence in wastewater leads to the spread of antibiotic resistant bacteria (ARB) which gain high rates of resistance throughout the conventional treatments. Taking into consideration that nowadays wastewater discharges still constitute one of the major sources of EOCs and ARBs in the environment, addressing this threat has become a top-priority task. Among alternative treatment technologies, constructed wetlands (CWs) are proposed as a low cost, ecologically oriented technology that takes advantage of the synergistic effects of plants and their associated microorganisms. The objectives of this study were, firstly to investigate wetland's efficiency on the removal of bisphenol A (BPA), ciprofloxacin (CIP) and sulfamethoxazole (SMX), secondly to describe the abundance and elimination of antibiotic resistant fecal bacteria and lastly to examine changes in the antibiotic resistant profile through the CW treatment. For this reason, a horizontal flow pilot scale CW of 0.5 m^3, planted with *Juncus acutus* helophytes, was fed with spiked secondary treated wastewater from the municipal wastewater treatment plant of the city of Chania (Crete, Greece) and tested under different operating conditions.

Methodology

Five experimental runs each fourteen days long were monitored. Different treatments corresponded to different influent concentrations of the organic compounds and hydraulic residence time. A single run with primary treated wastewater in the influent and control runs without plantation or with no spiked contaminants in the influent stream, were also tested. Wastewater samples were taken from the influent and the effluent of the wetland. Separation and quantification of the organic compounds was conducted using a high performance liquid chromatography (HPLC) system, using direct elution or, in the case of BPA, the vortex-assisted liquid-liquid microextraction protocol. Antibiotic resistance was studied using broth microdilution method and estimating the Minimum Inhibitory Concentration (MIC) of the selected antibiotics, CIP and SMX. MIC is defined as the lowest concentration of an antimicrobial that will inhibit the visible growth of a microorganism after overnight incubation. Water quality parameters; total suspended solids, BOD5, total organic carbon and total nitrogen (TN) were conducted according to Apha standard methods. Total carbon, inorganic carbon and TN were measured in Analytik Jena's "multi N/C 2100S". TOC was determined as the numerical difference between TC and IC. Electrical conductivity and pH were measured by a Hach HQ40d multi parameter meter.

Results and conclusions

Results indicated the strong contribution of *J. acutus* in terms of BPA concentration removal. The planted CW was able to remove BPA concentration in the range 48-93%, depending on the treatment examined (influent concentrations: 2–131 μg L^{-1}), whereas in control treatment (without plantation) BPA concentration removal was less than 30%. Performance of the system was depressed in the case of inflow with primary treated wastewater. Regarding ciprofloxacin, even concentration removal was kept above 70% (influent concentrations in the order of mg L^{-1}) in the presence of plants, significant removal was also measured in the control treatment. Regarding SMX concentration removal, the unit did not perform similarly well. Results on water quality characteristics and nutrients removal were, generally, in conformity with other studies. Antibiotic resistance profiles were investigated in inlet and and outlet of the CW for the residual cells of *E.coli* and *Enterococci* for possible changes in the resistance profile. Our expirements showed variant bacterial responces in relation to bacterial indicator tested each time and antibiotis. Generally, ARB either proliferated or decreased depending on the operational condition in each case.

Acknowledgments

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PHOTO- AND BIOCATALYTIC TREATMENT OF SELECTED FUNGICIDES IN WASTEWATER SAMPLES

Monika Čvančarová[1,*], Nicolas Kalogerakis[2], Danae Venieri[3], Luc Girardin[1], Philippe F.-X. Corvini[1,3]

1) Institute for Ecopreneurship, School of Life Sciences, University of Applied Sciences and Arts Northwestern Switzerland, Gründenstrasse 40, Muttenz CH-4132, Switzerland
2) School of Environmental Engineering, Technical University of Crete, Polytechneioupolis, Chania, Crete, Greece
3) State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University Xianlin Campus, Xianlin Avenue 163, Nanjing 210023, China
**: monika.cvancarova@fhnw.ch*

Introduction and study objectives

Different fungicides are used in citrus fruit production for pre and post-harvest protection. Fungicides are commonly found in the industrial processing wastewater and they are recalcitrant to biological treatment. Integration of different techniques during wastewater treatment usually cause a more effective removal of persistent micropollutants.

The aim of this study was to investigate enzymatic degradation of fungicides in wastewater samples. Different laccases were selected for this purpose because these enzymes have a high technological importance. Laccases act on both phenolic and non-phenolic lignin-related compounds as well as highly recalcitrant environmental pollutants and can be efficiently used for xenobiotic degradation and bioremediation. Direct application of dissolved enzymes into wastewater is not sustainable for a long time. Half-life of the enzymes can be significantly increased by their immobilization onto nano- and resin particles. Immobilization has previously shown to stabilize the enzymatic activity and immobilized enzymes can be applied and recycled in different bioreactors.

In this study, the second investigated technique is photocatalysis. This method was used prior to the enzymatic treatment to increase efficiency of the fungicide removal. The main phototransformation products are usually hydroxy derivatives which are more amenable substrate for laccase degradation. It has been previously reported that photodegradation of fungicides by TiO_2 is relatively rapid in distilled water. However, in real wastewater samples the degradation efficiency significantly decreases. Release of TiO_2 particles into the environment might cause an additional concern, hence a glass reactor containing immobilized TiO_2 was prepared and tested. The aim of this study was to evaluate the combination of photo- and biocatalytic treatment of wastewater samples contaminated by fungicides.

Methodology

The wastewater samples were obtained from fruit and vegetable packaging plant located in Marroco. This company applies fungicides (imazalil, thiabendazol, orthophenylphenol and pyrimethanil) for fruit protection.

Residual concentration of the fungicides after photo- and biocatalytic treatment was determined by HPLC-UV. Fungicides were separated on a column Zorbax SB C18 (3.0 x 150 mm, particle size 3.5 μm) with a gradient of 0.05% phosphoric acid and acetonitrile. DAD detector collected data at 200, 245, 270 and 300nm.

Atlas Suntest XLS+ equipped with sunlight filter and operation up to 765W/m^2 was used to irradiate the samples. TiO_2 was immobilized onto surface of a glass plate.

Laccase activity was determined using a kinetic colorimetric assay with ABTS as a substrate. Protein content of enzyme solutions was determined by means of a Pierce® assay kit manufactured by Thermo Scientific.

Enzymes were immobilized onto different types of nanoparticles. The method consists in the sorption of the enzyme to amino-modified nanoparticles and the subsequent covalent cross-linking using glutaraldehyde. Enzymes were also immobilized onto polymethylmethacrylate spherical resin microparticles with amino-epoxide functional groups. Amino group is able to promote the physical adsorption of proteins and epoxy group is responsible for a covalent binding of the enzyme.

LC-MS analysis was performed to monitor the main transformation products. An Agilent 1200 Series LC system and an Agilent 6320 Ion Trap Mass spectrometer with electrospray ionization was used. The samples were separated on a column Zorbax SB C18 (3.0 x 150 mm, particle size 3.5 μm) with a gradient of 0.1% formic acid and acetonitrile.

Results and conclusions

Thiabendazole, imazalil, and pyrimethanil were found in the wastewater samples in concentration range of 1-20 mgL^{-1}. Orthophenylphenol was not detected.

To evaluate the potential of the immobilized laccases for the degradation of selected fungicides, the first experiments were carried out in controlled buffer conditions. No degradation was detected after 7 days of incubation either without or with selected redox mediators. However, significant degradation was observed in the real wastewater samples where 5-20% of the fungicides were removed. This can be caused by various compounds presented in the real samples which can be involved in the enzymatic reaction.

Biocatalytic treatment alone was not very successful and therefore an additional photo-oxidation step with TiO_2 was carried out. The first experiments were performed with suspended TiO_2 in distilled water. The results showed a rapid photodegradation of the selected fungicides which was completed in 60-90 min. LC-MS analysis revealed that the fungicides were mainly transformed to hydroxy derivatives which confirmed our presumption. Further experiments were carried out in the real wastewater samples. Degradation efficiency of the fungicides was strongly influenced by suspended solids and wastewater matrix. Mechanical stability and photocatalytic activity of the immobilized TiO_2 is currently tested and the whole photo- and biocatalytic process is optimized.

Acknowledgement

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DEVELOPMENT OF MICROEMULSIFIED MULTIWALL CARBON NANOTUBES (µE-CNT) AS ADSORBENT FOR OIL SPILLS CLEAN-UP

**Tatjana Juzsakova*, Noor Al-Jammal*, Zsofia Ifju,
Domokos Endre, Akos Redey**

*Institute of Environmental Engineering, University of Pannonia, Veszprem, 10 Egyetem St.,
Veszprem, 8200 Hungary*
*: *yuzhakova@almos.uni-pannon.hu; naljammal@almos.uni-pannon.hu*

Introduction and study objective

From the point of view of the environmental concerns, oil spill accidents have great importance and requires immediate attention. This is because the hydrocarbon compounds often result in both instant and long-term environmental damage, which not only results in global marine oil pollution but life threatening and residents are forced to breathe in dangerous emissions.

Hydrocarbon compounds in oil spills presents a great challenge. Carbon nanotubes (CNTs) are considered one of the high efficient adsorbents. CNTs and multiwall carbon nanotubes (MWCNTs) have generated a lot of attention as a new type of adsorbent due to their exceptionally high adsorption capacity for oil–water separation. The high hydrophobicity of CNTs makes them good candidates to enhance the de-oiling process from waters. This research aims at to find a novel approach to the potential oil removal technique to acceptable levels by using adsorption process at room temperature using modified micro-emulsified MWCNTs (µE-CNT).

Methodology

Commercial MWCNT was purchased from the Chengdu Organic Chemicals Co Ltd. (China). The MWCNTs have a particle length of 5-20 µm and 20–20 nm diameter ranges with purity of > 95%. Microemulsion technique was used on the commercial MWCNTs in accordance to the process described by De Castro Dantas et al., (2001). It was implemented by mixing of 10 %wt. surfactant (saponified coconut oil; mostly lauric acid, $CH_3(CH_2)_{10}COOH$, with some myristic acid, $CH_3(CH_2)_{12}COOH$ and 25 %wt. aqueous phase (deionized water). Coconut oil was saponified by standard procedure ASTM D-5558/1995 to form $CH_3(CH_2)_{10}COO^- \ Na^+$. The mixture was then mixed with 40 %wt. co-surfactant (isoamyl alcohol, 99% P.A.) and 25 %wt oil phase (heavy distillate). Due to the spontaneous formation of microemulsions, they can be prepared in one step by simply mixing the constituents. The order of the addition of the constituents is not considered a critical factor for the preparation of the microemulsion.

Unmodified and modified CWNTs have been used as adsorbent in this work and have been investigated by liquid N_2 adsorption (BET method), Fourier transform spectroscopy (FTIR), Energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) to obtain information about the structural, chemical and physical characteristics of the synthesized adsorbent. Oil removal efficiency was investigated by TOC (TOC Vario elementar, detection range of 4 mg/l to 40,000 mg/l) analyzer for the determination of organically carbon of treated water.

Results and conclusions

Surface area, pore size, pore size distribution and pore volume of studied MWCNT were determined by nitrogen adsorption / desorption isotherms measurements using BET method and the results are summarized in Table 1. S_{BET} and S_{BJH} surface areas of commercial MWCNT pretreated at 30 °C under vacuum are 155 and 159 m^2/g respectively indicating that material has pores close to cylindrical shape as expected. Average diameters (D_{av}) of pores is around 13 nm and it is in agreement with specification provided by company. The MWCNTs have mainly mesopore size (2-50 nm) and about 10 % of it surface area formed by micropores ($\leq$2nm). The pore volume ($V_{1.7\text{-}300nm}$) is 0.7781 cm^3/g. Treatment at higher temperature, at 160°C, leads to very slight modification in morphology of the raw CWNTs. This indicates the stability of material up 160°C (at least in non-oxidative atmosphere). Weight loss of sample during 160°C pretreatment under vacuum was less than 0.5 wt % indicating the surface purity free from adsorbed gases/components. Carbon based adsorbent are unable to adsorb polar molecules like water/water vapor due to its hydrophobic properties. Therefore this type of adsorbents is widely used in water/wastewater treatment.

The purpose of non-ionic microemulsion modification is to enhance adsorption of hydrocarbon on MWCNT surface. In this work, one of our aims is to devise and demonstrate the general procedure and preparation method of non-ionic microemulsions that can be applied as enhancement of CNT hydrophobicity for oil spills removal.

Primary TOC results show the adsorption capacity of untreated MWCNT is 25.9 and removal efficiency of 100 ml of 1% n-C_8H_{18} -water solution reached 97% using only 0.003g of unmodified MWCNT, at room temperature and 1 hr adsorption time. The adsorption capacity and removal efficiency of modified -MWCNT are expected to be higher with shorter time, less amount of adsorbent and high concentration of hydrocarbon mixture (kerosene, jet fuel and diesel) in water samples. The adsorptive capacity and selectivity of the studied adsorbents for hydrocarbon compounds is examined and compared on the basis of the isotherm, kinetic and breakthrough curves. The adsorption mechanism will also be studied and correlated with their adsorptive performance. For comparison another functionalization techniques are to be studied like polymerization of MWCNT surface.

Acknowledgement

This work was supported by ***GINOP-2.3.2-15-2016-00016*** project: Excellence of strategic R+D workshops: Development of modular, mobile water treatment systems and waste water treatment technologies based on University of Pannonia to enhance growing dynamic export of Hungary.

A PILOT SCALE CONSTRUCTED WETLAND AS TERTIARY TREATMENT OF WASTEWATER FOR THE REMOVAL OF PATHOGENS AND ANTIBIOTIC RESISTANT BACTERIA

Andreas Kaliakatsos, Stavros Christophilopoulos,
Kassandra Koumaki, Iosifina Gounaki, Nicolas Kalogerakis,
Danae Venieri*

School of Environmental Engineering, Technical University of Crete,
73100 Chania, Greece
**: danae.venieri@enveng.tuc.gr*

Introduction and study objectives

Pathogenic microorganisms contained in wastewater entail a potenital risk to public health, as they are considered virulent carriers of waterborne diseases. Their presence in high concentrations, resistant nature and rapid transmission illustrate the importance of their inactivation by means of effective sewage treatment. The list of pathogens includes various groups and species, such as bacteria and viruses, which may exhibit considerable resistance to environmental stressed conditions, like those imposed during wastewater treatment. Among them, enteric viruses, i.e. enteroviruses (EV) and adenoviruses (HAdV) are of great concern, as their destruction through wastewater treatment system is extremely variable and the numbers of surviving infectious virus particles depend highly on the number of viruses entering the treatment system as well as the type of treatment used in each case.

Apart from the essential pathogens elimination, researchers also focus on the antibiotic resistant bacteria (ARB) and their respective antibiotic resistance genes (ARGs), which may occur in high numbers in wastewater. During the last decades the excessive use of antibiotics has led to the proliferation of ARB, which comprises health risk to humans and animals. Whether resistance may develop during wastewater treatment is currently under discussion. Links are not yet well established between the presence of antibiotics in wastewater treatment plants (WWTPs) and the favoring of resistant bacteria as well as the transfer of resistance at concentrations as low as those found for antibiotics in the environment. However, reports state that wastewater, or even treated wastewater, contain higher proportions of various resistant bacterial populations in relation to the respective proportions contained in surface water. Therefore, the conditions in WWTPs seem to be favorable for the proliferation of ARB, which in turn may transfer resistance genes to non-resistant bacteria.

Constructed wetlands (CW) have been investigated as alternative low-cost systems for wastewater treatment, which could also meet the overall socio-economical and environmental requirements of small communities.

In this perspective and within the framework of the present study, a pilot scale CW was developed as a tertiary wastewater treatment system with the view a) to evaluate its potential to remove fecal bacterial indicators (*E.coli* and *Enterococci*), bacteriophages and enteric viruses (HAdV and EV) from municipal wastewater, b) to assess the elimination of ARB, c) to study possible changes in bacterial antibiotic resistance profile through treatment and d) to detect target ARGs prior to and post treatment.

Methodology

A Subsurface flow CW planted with *Juncus acutus* was used throughout the study. The CW treated secondary domestic wastewater received from the WWTP of Chania, Greece. Bacterial indicators of fecal pollution, namely *Escherichia coli* and Enterococci, F-RNA coliphages (MS2 bacteriophages) and enteric viruses (HAdV and EV) were monitored to measure the treatment efficiency of the CW system. Antibiotic resistance was studied using broth microdilution method and estimating the Minimum Inhibitory Concentration (MIC) of selected antibiotics (Amoxicillin and Tetracycline). MIC is defined as the lowest concentration of an antimicrobial that will inhibit the visible growth of a microorganism after overnight incubation. Real-Time PCR method was applied for detection of specific ARGs in the bacterial populations prior to and post treatment.

Results and conclusions

Results showed that CW can be an efficient tertiary system for the removal of bacterial indicators from wastewater. A 2 log reduction rate regarding *E. coli* and Enterococci from inlet to outlet of the system was achieved, while the same trend was observed for MS2 bacteriophages (Figure 1). On the contrary, both enteric viruses tested in this study (HAdV and EV) were detected at all sampling points across the system and they remained abundant in the effluent.

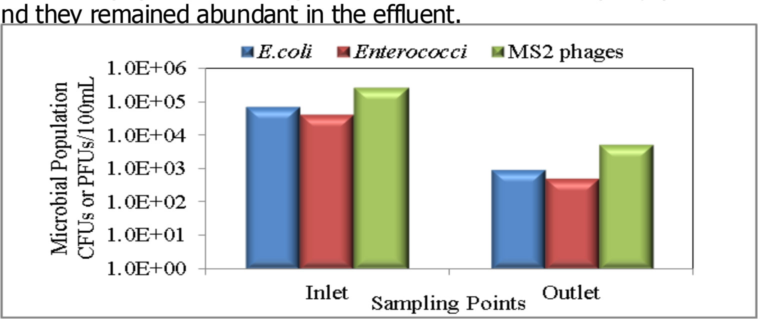


Figure 2: Bacterial indicators and Bacteriophages removal from the CW

Regarding ARB, although their elimination was satisfactory, the resistance levels and profiles of residual bacteria after treatment were diverse. The MIC measurement showed variant bacterial responses in relation to the type of bacterial indicator and the antimicrobial compound. The antibiotic resistance profile was affected to a certain extent, while the notable presence of target ARGs in surviving cells raises concerns about the potential of wastewater treatment to lower their abundance in effluents.

In conclusion, bacterial removal was achieved in satisfactory levels under the current operational conditions. However, concerns still remain about viruses' elimination and the dispersion of antibiotic resistance into the aquatic environment.

DUAL USE OF BORON-DOPED DIAMOND ELECTRODE IN ANTIBIOTICS-CONTAINING WATER TREATMENT AND PROCESS CONTROL

Nicoleta Lungar[1,2], **Florica Manea**[3,*], **AnaMaria Baciu**[3],
Aniela Pop[3], **Ramona Magurean**[3]

[1] SC Aquatim SA Timisoara, Str. Gheorghe Lazăr nr. 11/A, 300081Timişoara, Romania
[2] "Gheorghe Asachi" Technical University of Iasi, 73, Prof. Dr. D. Mangeron Street, Iasi, Romania
[3] Politehnica University of Timisoara, Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, Faculty of Industrial Chemistry and Environmental Engineering, V. Parvan 6, 300223 Timisoara, Romania,
[*]: florica.manea@upt.ro

Introduction and study objectives

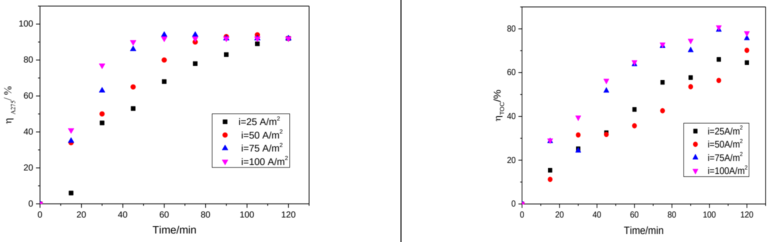
Continous increasing the amounts of pharmaceuticals in water requires their removal and monitoring in wastewater/water. Pharmaceuticals represent emerging pollutants in water, and antibiotics are one of the largest class of pharmaceuticals widely used in human and veterinary therapy. Electrochemical oxidation as advanced oxidation processes has been reported for the degradation of pharmaceuticals from water. Also, several types of carbon based electrodes allowed their detection in aqueous solution using different electrochemical technique. This study aims to investigate the dual role of boron-doped diamond electrode and electrochemical process to determine quantitatively and to degrade tetracycline (TC) as model for antibiotics from water.

Methodology

Two different geometries for boron-doped diamond (BDD) electrode were used. BDD disc electrode was used as working/detector electrode within a system of three-cell electrode besides the platinum counter electrode and saturated calomel electrode using an Autolab Pontentiostat/Galvanostat PGStat 302 (EcoChimie, The Netherlands) and cyclic voltammetry technique. BDD plates were used as anode in an undivided cell and stainless steel plates as cathodes in vertical arrangement for batch oxidation experiments. The electrochemical process performance was determined in according to the specific energy consuming and residual TC concentration. The concentration of TC was expressed in terms of absorbance recorded at 275 nm (A_{275}) and absorbance recorded at 358 nm (A_{358}). The biodegradability test of TC was determined based on chemical oxygen demand (COD) and biochemical oxygen demand (BOD) parameters. Also, total organic carbon (TOC) parameter was used to assess the mineralization degree of TC by electrooxidation using BDD electrode. Cyclic voltammetry technique and BDD electrode were used also for the quantitative determination of TC before and after electrooxidation.

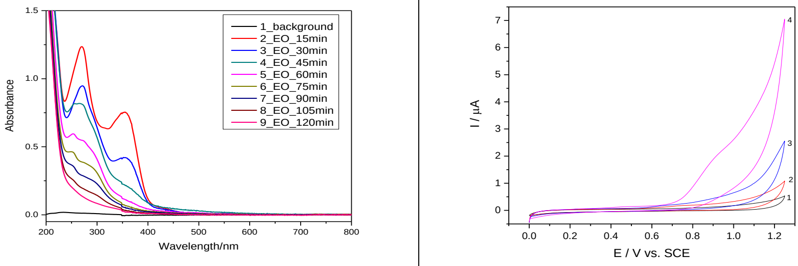
Results and conclusions

Cyclic voltammetry (CV) technique was used to characterize the electrochemical behavior of TC on BDD electrode in order to select the operational parameter for both degradation/mineralization of TC and its electrochemical detection. The operation conditions related to the current density, pH, TC concentration range were determined to assess the degradation degree of TC correlated with the specific energy consuming. For example, the effect of the current density on electrooxidation and mineralization degrees is shown in Figure 1a and b. Based on the technical-economic point of view, the current density of 50 A/m^2 is considered optimum for this TC concentration range. The evolution of UV-VIS spectra corresponding to TC concentrations during EO operated at 50 A/m^2 are presented in Figure 2a. Initial and final concentration of TC after EO applying was determined by electrochemical detection using CV and BDD electrode (Figure 2b), confirming this detection method for EO process control of TC and thus, the dual role of BDD electrode in TC detection and degradation. The aspects regarding the EO mechanism and kinetics are discussed. The biodegradability test determined for initial and residual TC containing water informed about the place of EO integration within advanced wastewater treatment technology.



a) b)

Figure 1: The effect of the current density on EO degree for TC expressed by A_{275} (a) and TOC (b)



c) d)

Figure 2: Evolution of TC concentration during EO process operated at 50 A/m^2, expressed by UV-VIS spectra (c) and cyclic voltammograms (d)

Acknowledgements

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NEW MULTIPLE CRITERIA DECISION MAKING TECHNIQUE IN THE DEVELOPMENT OF WASTE WATER TREATMENT FACILITIES

Jozsef Nemeth, Endre Domokos, Viktor Sebestyen,
Tatjana Juzsakova, Akos Redey*

Institute of Environmental Engineering, University of Pannonia, Veszprém, 10 Egyetem St.
Veszprém, 8200 Hungary
**:redey.akos@gmail.com , sebestyenv@almos.uni-pannon.hu*

Introduction and study objectives

There are several new challenges in the field of waste water treatment, which have been demanding ongoing innovation from the specialists. The UV filters, the disinfection of the waste waters or the microwave treatment of the waste waters are to be given among these as examples. The reuse of the water is an outstanding target and goal all over the world. The existing waste water treatment facilities should be prepared for the challenges of the 21st century. The decision making systems, the multi criteria decision making (MCDM) can be expediently used for the selection of the appropriate waste water treatment technology to be used. For the removal of the micro-pollutants several decision making criteria must be taken into consideration to provide appropriate technological alternative to comply with the requirements.

The objective of the research was to devise a new MCDM technique which is demonstrated on a case study.

Methodology

The MCDM techniques are expediently used to evaluate several alternatives characterized by large number of criteria. The alternative should be selected on the basis of several decision making options. These methods are dynamic and can be used by several ways to reach a decision in light of the engineering, environmental, strategic and management issues. These can be summarized in a matrix form.

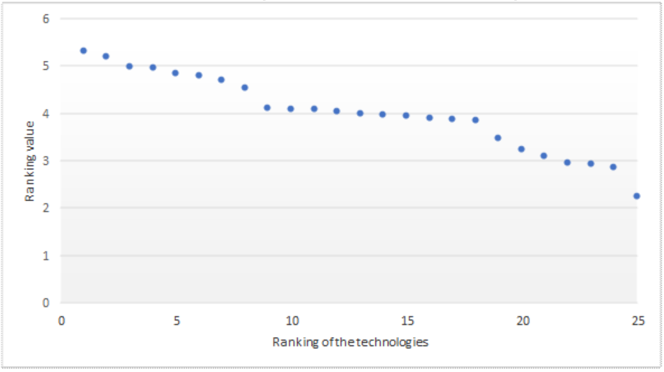
	C_1	C_2	…	C_n
A_1	x_{11}	x_{12}	…	x_{1n}
A_2	x_{21}	x_{22}	…	x_{2n}
…	…	…	…	…
A_m	x_{m1}	x_{m2}	…	x_{mn}

Where, A_m is the different Alternative, C_n is the different Criteria.

The decision making model consists of three major steps. The first one is the collection of the technological processes which theoretically can be taken into consideration and the setting up of the ranking system according to the criteria defined. The second step is the weighting based on pair-wised comparison. The third step is the evaluation process on the basis of the criteria and the identification of the selected technology.

Results and conclusions

The model elaborated is suitable for supporting the decison making process. The main advantage of the new model that several decison making ways are taken into consideration. The ranking of the technologies is a common decison making system element, however, it is not guaranted that the correct decision could be made in this way. The model devised evaluates the alternatives in multiple decision routes regarding the planning reqirements as well. Some of the alternative technologis: UV, hidrogen-peroxide treatment, fenton process, heterogeneous photocatalytic process, microfiltration, ultrafiltration, reverse osmotic process, microwaves process.



A target figure is to be generated on the basis of ranking figures of the technologies. A performance interval can be defined in which the selected technologies fully meet or overperform the requirement systems, or which technologies fail to comply with those, or the appropriate technologies which slighly meet the expectations. The figure shows the ranking of the listed technologies. On the basis of the decison making process the best technologies can be identified from the points of view of economic, engineering and environmental aspects as well.

Acknowledgement

This work was supported by ***GINOP-2.3.2-15-2016-00016*** project: Excellence of strategic R+D workshops: Development of modular, mobile water treatment systems and waste water treatment technologies based on University of Pannonia to enhance growing dynamic export of Hungary.

ANAEROBIC OXIDATION OF GROUNDWATER CONTAMINANTS WITH A NOVEL BIOELECTROCHEMICAL REACTOR CONFIGURATION

Enza Palma[1,2], Matteo Daghio[3], Andrea Franzetti[3], Marco Petrangeli Papini[1], Federico Aulenta[2,*]

[1)] Department of Chemistry – Sapienza University of Rome, P.le Aldo Moro 5, 00185 Rome, Italy
[2)] Water Research Institute (IRSA) – National Research Council (CNR), Via Salaria km 29,300, 00015 Monterotondo (RM), Italy
[3)] Department of Earth and Environmental Sciences – University of Milano-Bicocca, Piazza della Scienza 1, 20126 Milan, Italy
[*]: aulenta@irsa.cnr.it

Introduction and study objectives

Soil, sediment, and groundwater contamination by accidentally spilled petroleum hydrocarbons (PHs) is a widespread problem worldwide, which poses serious environmental and health concerns. Different physico-chemical and biological techniques can be applied to remediate sites contaminated by this class of compounds, with the latter typically receiving greater consideration being more environmentally and economically sustainable. Bioremediation exploits the vast metabolic diversity of microorganisms that use contaminants as carbon and energy sources in their metabolism. The majority of PHs are biodegradable under aerobic conditions, with PHs activation (i.e., a critical step to initiate microbial degradation) commonly triggered by oxygen-dependent mono- or di-oxygenases. Accordingly, common bioremediation strategies involve oxygen delivery into the contaminated matrix to enhance the metabolism of naturally occurring aerobic hydrocarbon-degrading microbial populations. Although widely applied, this strategy suffers of a number of limitations such as: (i.) the high energy requirements; (ii.) the low efficiency of oxygen utilization due to the poor solubility in water and the scavenging by reduced mineral substances such as Fe(II) and HS^-; (iii.) the unwanted stripping of volatile contaminants; and (iv.) the high growth yield of aerobic biomass which may cause clogging and obstruction problems near air/oxygen injection points.

In recent years, microbial electrochemical technologies (MET) have attracted considerable attention for remediation applications. MET are anaerobic systems in which microorganisms catalyse oxidation or reduction reactions using solid-state electrodes, suitably deployed in the contaminated matrix, as virtually inexhaustible electron acceptors or donors, respectively. Previous lab-scale studies have shown that MET can be employed to stimulate the anaerobic oxidation of a variety of reduced contaminants in soil and groundwater, including lower chlorinated compounds and PHs. In principle MET have several potential advantages compared to conventional aerobic bioremediation strategies, such as: (i.) the possibility to promote the oxidation of contaminants with no need for adding oxygen or other electron acceptors [such as nitrate or soluble Fe(III) species]; (ii.) the possibility to co-localize the microorganisms and the electron acceptor (i.e., the electrode), as well as (iii.) the possibility to drive, control, and monitor the biodegradation reaction (in the subsurface) with simple electrochemical means. In spite of their promise, however, field scale applications of MET for subsurface remediation are still limited by the poor understanding of the biochemistry, microbial ecology, and extracellular electron transfer mechanisms of involved microbial communities. Furthermore, scalable bioelectrochemical reactor configurations that are amenable for in situ applications are still lacking.

In this framework, the aim of the present study was to describe a novel bioelectrochemical reactor configuration which can be installed directly within a groundwater well and that can be applied for *in situ* treatment of organic contaminants, such as PHs.

Methodology

A laboratory-scale prototype of this bio-electrochemical reactor has been set up and operated in a continuous-flow regime, with phenol (25 mg/L) as a model groundwater contaminant. The reactor consisted of a glass column (total volume 500 mL) filled with graphite granules, serving as the bio-anode, and housing a concentric stainless-steel mesh, serving as the cathode. The graphite anode was kept physically separated by the stainless-steel cathode by means of a plastic mesh. An Ag/AgCl reference electrode was place on top of the column to control, by means of a potentiostat, the potential of the bioanode at the desired value. The liquid phase of the reactor was continuously recirculated at a flow rate of 75 mL/min. The performance of the bioelectrochemical reactor was analysed in terms of degradation rate and yield. Electrochemical techniques were used to characterize the catalytic behaviour of the reactor, while Next Generation Sequencing (NGS) was applied to shed light on the composition and dynamics of involved electro-active microbial communities.

Results and conclusions

The bio-electrochemical reactor was operated continuously for a period of 56 days, corresponding to 146 hydraulic retention times. The best performance was obtained when the reactor was inoculated with refinery sludge and the anode potentiostatically controlled at +0.2 V vs. SHE. Under this condition, the influent phenol (25 mg/L) was nearly completely (99.5±0.4 %) removed, with an average volumetric degradation rate of 77±4 mg/L d. Phenol removal was linearly correlated with electric current generation (5.3±0.2 mA), which accounted for 104±4 % of electrons deriving from the complete oxidation of the contaminant to carbon dioxide. NGS analysis revealed a remarkable enrichment of *Geobacter* species on the surface of the graphite granules, clearly pointing to direct involvement of this known electro-active bacterium in the current-generating and phenol-oxidizing process.

Acknowledgements

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EFFECT OF PRETREATMENTS ON BIOSORPTION OF DIVALENT COBALT BY *Lemna* sp.

Jessica Lizeth Reyes-Ledezma,
Allan Eduardo Ramírez-Rodríguez, Liliana Morales-Barrera,
Eliseo Cristiani-Urbina*

Instituto Politécnico Nacional, Escuela Nacional de Ciencias Biológicas, Departamento de Ingeniería Bioquímica. Avenida Wilfrido Massieu s/n, Unidad Profesional Adolfo López Mateos, Mexico City, 07738, Mexico.
**: ecristianiu@yahoo.com.mx*

Introduction and study objectives

Cobalt is a heavy metal that in trace amounts is required for metabolism. It is an essential constituent of vitamin B12, possessing a regulating role in blood pressure, and is necessary for appropriate function of thyroid. Nevertheless, exposure to high cobalt concentrations causes diverse adverse health problems such as asthma, dermatitis, allergy, nausea, neurotoxicological disorders, damage to the heart, thyroid and liver, as well as genotoxicity and cancer in human beings.

Industrial discharges from mining, metallurgical, electroplating, petrochemical, electronic and nuclear power plants usually contain high amounts of cobalt ions, which are toxic to living beings. It is therefore crucial to remove cobalt ions from contaminated water and wastewater. The conventional physical-chemical methods for removing heavy metals from industrial wastewaters pose several technical and economic constraints. Biosorption has great potential to replace conventional methods for the removal of heavy metals owing to its low operating cost, feasibility of recovering the heavy metals, ability of reusing biosorbents, and no generation of toxic chemical sludge. In order to improve the biosorption capacity of biosorbents, physical and chemical pretreatments methods can be applied.

The aims of the present investigation were to enhance the divalent cobalt [Co(II)] biosorption capacity of *Lemna* sp. by various physico-chemical treatments and to elucidate the functional groups involved in the removal of Co(II). The possible mechanisms involved in the biosorption of Co(II) ions were investigated on the basis of proximate chemical composition, FTIR, SEM and EDX analysis.

Methodology

Lemna sp. was collected from the Xochimilco channels in Mexico City, and thoroughly washed with distilled water. It was then oven dried at 60 ºC, milled and sieved. Particles ranging in size between 0.3 and 0.5 mm were used in the biosorption experiments conducted in this work.

To investigate the influence of *Lemna* sp. pretreatment on Co(II) biosorption, the native aquatic plants (5 g L^{-1}) were pretreated as follows: soaking in water (18 and 60ºC) for 30 min, soaking in acids at 0.1 M, 18°C for 4 h, soaking in alkalis and neutral salts at 0.1 M, 18°C for 30 min, as well as in organic solvent (1% v/v) solutions for 30 min at 18ºC. Once treated, the *Lemna* sp. biomass was washed and dried. Co(II) biosorption experiments using unpretreated and pretreated *Lemna* sp. were conducted with a 100 mg L^{-1} Co(II) solution, pH 7.0, and 18 ºC. After choosing the best chemical agent for enhancing *Lemna* sp. Co(II) biosorption, experiments were performed to determine its optimal concentration.

The unpretreated and pretreated *Lemna* sp. were characterized in terms of proximate chemical composition, zeta potential, FTIR and SEM-EDX. Co(II) concentration was determined spectrophotometrically by dimethylglioxime method at 400 nm.

Results and conclusions

The experimental data of equilibrium biosorption capacity revealed that, in general, acid pretreatments of *Lemna* sp. affected the biosorption of Co(II) ions adversely, in comparison with unpretreated biosorbent (Fig. 1). The highest equilibrium Co(II) biosorption capacity (30.67 mg g^{-1}) was obtained when *Lemna* sp. was pretreated with 0.1 M K_2HPO_4.

With increasing K_2HPO_4 pretreating concentration from 0.01 to 0.3 M, Co(II) biosorption capacity at equilibrium increased significantly (Fig. 2). No further increase in equilibrium Co(II) biosorption capacity was observed when the concentration of K_2HPO_4 was 0.4 M. Hence, 0.3 M is the optimal concentration of K_2HPO_4 for *Lemna* sp. pretreatment. The pseudo-second-order model fitted biosorption kinetics of Co(II) ions on K_2HPO_4-pretreated *Lemna* sp. better than other assayed kinetic models.

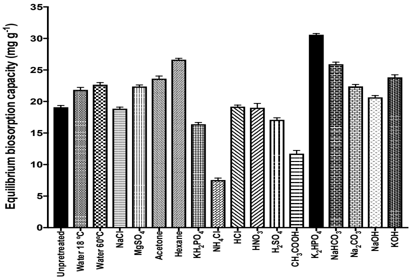

Figure 1: Effect of different physico-chemical pretreatments on Co(II) biosorption in comparison with the native *Lemna* sp

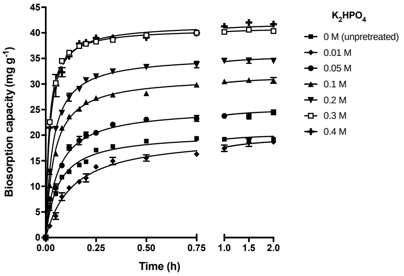

Figure 2: Effect of K_2HPO_4 pretreating concentrations on Co(II) biosorption by *Lemna* sp.

The proximate chemical composition analysis clearly revealed important differences in ash and raw fiber content of the unpretreated and K_2HPO_4-pretreated *Lemna* sp. Zeta potential analysis showed that the K_2HPO_4 pretreatment increased the negative surface charge (from -26 to -35 mV) of *Lemna* sp., thus improving the removal of Co(II). The main changes in the FTIR absorption spectra of unpretreated and K_2HPO_4-pretreated biosorbents occurred in the –OH, and –CH bands, which may suggest that carbohydrates are involved in the biosorption of Co(II) ions. From the SEM micrographs of the unpretreated and K_2HPO_4-pretreated *Lemna* sp., there is no evidence of alteration in the surface morphology of the biosorbent due to the pretreatment, but EDX analysis revealed a decrease of Na^+ and Cl^- ions after pretreatment, which agrees with the decrease in the ash content shown by the proximate chemical composition analysis. Results indicate that K_2HPO_4-pretreated *Lemna* sp. is a promising biosorbent with high biosorption capacity to remove Co(II) ions from aqueous solutions.

PCB-CONTAMINATED SEWAGE SLUDGE AND SEDIMENT AFFECT CHLOROPHYLL CONTENT AND CAUSE CHANGES IN THE ANTIOXIDATIVE SYSTEM OF CUCUMBER TISSUE

Anna Wyrwicka[1,*], **Magdalena Urbaniak**[2,3]

[1] Department of Plant Physiology and Biochemistry, Faculty of Biology and Environmental Protection, University of Lodz, Banacha 12/16, 90-237 Lodz, Poland
[2] European Regional Centre for Ecohydrology of the Polish Academy of Sciences, Lodz, Poland
[3] Department of Applied Ecology, Faculty of Biology and Environmental Protection, University of Lodz, Lodz, Poland
[*]: anna.wyrwicka@biol.uni.lodz.pl; m.urbaniak@unesco.lodz.pl

Introduction and study objectives

The increasing the amount of sewage sludge produced in recent times is accompanied by the problem of their responsible utilization and disposal. Likewise, sediments deposited at the bottom of urban reservoirs and sedimentation ponds undergo periodical dredging and need to be utilized. However, while these deposits often contain nutrients such as nitrogen and phosphorus that are useful for agriculture, they also contain a variety of toxic compounds including heavy metals, Persistent Organic Pollutants (POPs), Polycyclic Aromatic Hydrocarbons (PAHs), pathogens and other microbial pollutants, which pose a hazard to human health. One way to cope with increasing amounts of sewage sludge and urban lake sediments may be the use of phytoremediation techniques. Plants can be used to metabolize or concentrate these pollutants for easier disposal. Some species of Cucurbitaceae are known to accumulate higher levels of POPs, such as polychlorinated dibenzo-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and PCB, in their tissues than other plant species. The aim of the present study was to assess the impact of sewage sludge and urban reservoir sediment application on soil toxicity, measured as PCB concentration, lipid oxidative damages and changes in selected elements of the antioxidative system of *Cucumis sativus* L. (cucumber) grown on these soils.

Methodology

Sewage sludge from the resources of the Lodz Municipal Wastewater Treatment Plant and sediments from the Sokołówka Sequential Biofiltration System were collected. The sewage sludge and sediment samples were used as fertilizer for the cucumbers planted in the soil samples. Four treatments were used: a control C, in which no sludge or sediment was added, and three levels of sludge addition, 1.8 g, 5.4 g and 10.8 g per flower pot. The first corresponds to a dose of 3 tonnes ha^{-1}, the allowed dosage per year by the Regulation of the Minister of Environment of 6

February 2015 on municipal sewage sludge (Dz.U. Nr 2015 r., poz. 257); the second represents the permitted dose of 9 tonnes ha^{-1} applied on one occasion every three years; and the third, 18 tonnes ha^{-1}, is above the permitted level. PCB concentrations were determined in the control and amended soils before cucumber planting and after five weeks of cucumber growth.

The leaves of five-week old cucumber plants (*Cucumis sativus* L.) cv "Cezar" were ground and crude homogenate obtained after filtration was assayed for chlorophyll content. The filtrates of homogenized cucumber leaves were then centrifuged, and the supernatant collected. The activities of ascorbate peroxidase (APx) and catalase (CAT) were measured as indicators of plant antioxidative response, as were protein concentration and degree of lipid peroxidation in terms of thiobarbituric-acid-reactive substances (TBARS).

Results and conclusions

The addition of both sewage sludge and sediments led to an increase in the PCB concentration in the soil samples. The smallest PCB concentration was noted in the control soil and the highest in soil amended with the highest sewage sludge and the greatest sediment dose. The analysis conducted after five weeks of cucumber growth showed reductions of PCB concentration in control soil, as well as in soil amended with sewage sludge and sediments; in addition, this effect was more visible in the case of the use of sewage sludge.

Soil supplementation with sewage sludge as well as with sediments caused a gradual increase in chlorophyll content in cucumber leaves in a dose-dependent manner. However, this trend was more evident in the leaves of plants growing in sewage sludge amended soil. The low and medium doses of sewage sludge were associated with an increase in the degree of lipid oxidative damage, measured as a thiobarbituric-acid-reactive substances (TBARS). In contrast, sediment application did not cause significant changes in TBARS content. After sewage sludge and sediment application, APx activity in cucumber leaves showed a downward trend. The presence of sewage sludge in soil caused a significant decrease in leaf APx activity in a dose-dependent manner. Unlike APx, CAT activity tended to increase, but only in leaves of cucumber plants grown in sewage sludge amended soil.

The cultivation of cucumber plants on soil amended with sewage sludge or sediment reduces PCB concentration; however this effect is more evident in the case of sewage sludge. Sewage sludge application caused also more intensive changes in oxidative stress markers in plant tissues than sediment application. It cannot be excluded that the content of toxic compounds included in sewage sludge triggered more severe oxidative stress in cucumber plants.

Acknowledgements

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EMISSIONS OF GREENHOUSE GASES FROM FULL SCALE BIOLOGICAL TREATMENT OF LANDFILL LEACHATE

Anna Laura Eusebi[1,*], Matteo Spinelli[1], Mattia Pierpaoli[1], Nicola Frison[2], Diego Cingolani[1], Francesco Fatone[1]

[1)] Department SIMAU, Università Politecnica delle Marche, Via Brecce Bianche, 12, Ancona 60100, Italy
. *[2)] Department of Biotechnology, University of Verona, Strada Le Grazie 15, Verona, Italy*
[*]: *a.l.eusebi@univpm.it*

Introduction and study objectives

In the European countries the produced municipal wastes for capita was in 2010 equal to 500 kg/person/y, almost similar to the registered data in 2001 (520 kg/person/y). Moreover, for many types of wastes the main final destination remains the sanitary landfill method due to its economic advantages and simplified technological plant configuration. Therefore, the treatment of the leachate, produced from the degradation of the organic fraction and from the wet periods, has to be considered an important topic in the environmental scenario. The composition of the landfill leachates presents variations depending on the constituents of the landfill solid wastes, the type of the microbial flora, characteristics of the soil, and the pattern of the rainfall and the age of the landfill. Integration of physical, chemical and biological methods is realized for the efficient treatment of landfill leachate. Biological treatment methods are widely used for the removal of biodegradable compounds including ammonia nitrogen which is usually present in high concentrations in mid to old age landfills. However, the elevated nitrogen streams of leachate in the biological activated sludge processes enhance the production of gaseous nitrogen oxides. In this scenario, this paper deals with the results of monitoring and experimental tests for N_2O, NO and NO_2 quantification in full scale plant for leachate treatment.

Methodology

The full scale platform for the treatment of industrial liquid wastes has maximum capacity of 350 m3/d, composed by landfill leachate (87%) and liquid wastes from urban origin (10%). The wastes, after the discharge, are screened, de-gritted and submitted to chemical coagulation and flocculation. The effluent is equalized, fed to activated sludge process (500 m^3) and after the secondary clarifier coupled with ultrafiltration membranes. The reactor worked in two different configurations: A-total oxidation process and; B-intermittent aeration process. The final effluent is discharged in sewage system and sent to main urban wastewater treatment plant (80,000 PE). The chemical and physical characterization of the main flows is measured twice a week according to Standard Methods. Continuous measurement (MIR9000CLD Environnement Ltd) of main gaseous forms (N_2O CO_2, CH_4, NO and NO_2) were realized both in the biological reactor and in the membrane unit. The gaseous NH_3 was measured with online air probe (PCE Xgard-1-NH3). The respirometric rates of AUR and

NUR were carried out and the main operative parameters (DO, T, SRT, pH, MLSS, MLVSS) were considered to determine the link between the liquid and the gaseous forms. The dissolved N_2O in the liquid phase was measured to study the mechanism of dinitrogen oxides formation.

Results and conclusions

The influent flow rate to the biological reactor was of 220±2 m^3/d with 8.2±0.1 of pH favourable to stripping mechanisms in aerobic conditions. High total nitrogen concentrations were detected of 648±226 mgTN/L mainly constituted by ammonia (508±136 mgNH_4-N/L). Moreover, variable concentrations of COD were founded (2100±407 mg/L) by determining COD/TN of 3.2. High salinity (1320±180 mgCl/l) and elevated SRT characterized the biological reactor by reducing the nitritation activity. The biological transformations were via nitrite (kn rates of 0.143±0.03 kgNOx-N/kgMLVSS/d with percentages of nitrites of 65%-100%) without use of external reagents for the elevated concentration of Free Ammonia in the influent leachates (about 3 mgFA/l). The configuration A with total oxidation process caused elevated level of NO_2-N in the liquid phase (408±68 mg/l) although the consumption of alkalinity decremented the pH in the reactor up to 7.6 and reduced the percentages of produced nitrites.

Differently, during the configuration B with intermittent aeration process (2 hours of aeration and 4 hours of anoxic phase per cycle) the nitrites concentrations in the liquid phase were reduced up to 222±37 mg/l. The incomplete denitritation was related to the limiting COD/TN ratio for anoxic transformation of NOx-N in nitrogen gas. The effects for the main gaseous pollutants concentrations were reported in Figure 1.

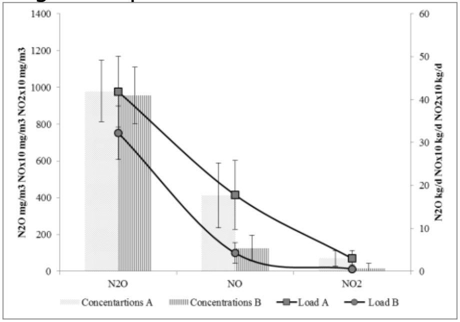

Figure 1: Gaseous pollutants concentrations and loads

The emission factors were for configuration A of 7.5 kgN_2O-N/kgTN and 5.1 gNOx-N/kgTN and for configuration B of 6.9 kgN_2O-N/kgTN and 1.4 gNOx-N/kgTN. Net decrement of the NOx-N was evaluated but only partial reduction of N_2O was founded. The global nitrogen mass balance and emission factors specific for MLVSS were calculated. The analysis of the N_2O in the liquid recognized the main role of the anoxic phase in the gases production. The impact of the emissions in the membrane unit was almost null. The CO_2 and CH_4 concentrations and mass loads were evaluated during the two periods with strict increment of the methane production related to the dissolved oxygen level.

SUSTAINABLE KAOLINITE ADSORPTION-FENTON AND ELECTRO-FENTON REGENERATION APPLIED TO COLOURED WATER TREATMENT

Emilio Rosales[1,*], **Delia Anasie**[1,2], **Marta Pazos**[1],
Iuliana Lazar[2], **M. Ángeles Sanromán**[1]

[1] Department of Chemical Engineering, University of Vigo, Campus As Lagoas-Marcosende
36310, Vigo, Spain
[2] Faculty of Engineering, "Vasile Alecsandri" University of Bacau, Calea Marasesti 157
600115, Bacau, Romania
[*]: emiliorv@uvigo.es

Introduction and study objectives

Dyes are used in several industrial processes including paper, textile or pharmaceutical processes. The release of uncomplete spent dyes becomes a problem to wastewater sources. It is well-known that some of these compounds have carcinogenic and mutagenic and their release to the environment has a potential effect in aquatic and human life. Removal of these compounds from effluents is often expensive but a legal requirement for these industries.

Several physical-chemical techniques have been proposed and used in the treatment of the wastewater. Among them, adsorption has been considered as an alternative due to the simplicity of design and the equipment easy going. This treatment reduces the concentration of pollutant in the water generating a solid waste that need a further treatment or disposal process. At the present time there are few researches focus on organic pollutant elimination and consequent adsorbents regeneration. Most of the spent adsorbents are regenerated at a high temperature with the expensive cost associated to this treatment. Therefore, new regeneration processes are required.

The aim of the work is the evaluation of different alternatives in the regeneration of spent adsorbent and the development of a novel and effective adsorption-regeneration system which facilitate the treatment of coloured wastewater. Initially, kaolinite, common clay, was selected as adsorbent and the adsorption process was studied for the selected organic pollutant, Rhodamine B. Then, two different alternatives for the pollutant degradation and recovery of the spent adsorbent were tested. The operational parameters associated to best process were optimised. Finally, the feasibility of the selected process in several adsorption-degradation cycles was evaluated.

Methodology

Adsorption assays were carried out in Erlenmeyer flasks (250 mL) with a working volume of 100 mL. A widely used dye Rhodamine B (RhB) was selected as pollutant. Dye solutions were mixed with different amounts of kaolinite (1-5 g) at natural pH 6.61. The flasks were shaken in an incubator (Thermo Scientific MaxQ800) at 120 rpm and 25ºC.

Regeneration experiments were performed using Fenton and electro-Fenton techniques. Fenton assays were done in glass tubes containing 1 g of polluted kaolinite and different ratios H_2O_2:Fe^{+2} (10:1 and 100:1). Electro-Fenton regeneration slurry assays were performed in a cylindrical reactor of 250 mL with an operation volume of 150 mL and 7.5 g of spent adsorbent. Carbon felt and boron doped diamond electrodes were selected as anode and cathode, respectively and current intensity of 300 mA was applied using a power supply. Na_2SO_4 0.01 M was used as electrolyte and pH was fixed to 3.

Adsorption-regeneration process was performed using cycles of adsorption (60 min) and regeneration by Fenton treatment (30 min) consecutively. For these assays, kaolinite (1 g) was put in contact with the dye solution (2 ml) for the adsorption, after total adsorption supernatant was eliminated by centrifugation and later on 2 mL of Fenton solution was added for the regeneration. This procedure was repeated during 6 cycles.

Results and conclusions

Firstly, the adsorption of the dye in the selected clay was investigated. The adsorption process was effective at the natural pH of the solution which means a significant advantage for the treatment and reduces the economic cost of the procedure. Then, different parameters such as contact time, adsorbent dosage or dye concentration were studied and optimised. Operating at these optimal conditions, the performance of kaolinite as adsorbent was studied by adsorption isotherms. A maximum uptake capacity of 51.5 mg RhB/g adsorbent was obtained. The adsorption data were analysed using the most usual isotherm models resulting on the best fitting when Langmuir model was considered.

Secondly, the dye degradation on the adsorbent surface and consequent adsorbent regeneration were carried out. Fenton and electro-Fenton were proposed for this task and the obtained results showed similar results for both treatments. However, the easy operational way of Fenton conducted to the selection of this technique for further investigation. The optimisation of different operational parameters such as reaction time and H_2O_2:Fe^{+2} ratio was carried out resulting in the use of 100:1 H_2O_2:Fe^{+2} ratio and the reaction time of 30 minutes.

Finally, the performance of the developed system was evaluated operating in six adsorption-regeneration cycles. High levels of adsorption and dye removal were reached in each cycle proving the feasibility of the combined process. Based on the obtained results the viability of the proposed techniques, as efficient alternatives in the simultaneous regeneration-pollutant degradation, was verified and a complete adsorption-regeneration system was proposed achieving high efficiency.

Acknowledgments

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BIOSORPTIVE REMOVAL OF ACID ORANGE 74 DYE BY HCL-PRETREATED *Lemna* sp.

Jessica Lizeth Reyes-Ledezma, Daniel Uribe-Ramírez,
Liliana Morales-Barrera, Eliseo Cristiani-Urbina*

Instituto Politécnico Nacional, Escuela Nacional de Ciencias Biológicas, Departamento de Ingeniería Bioquímica. Avenida Wilfrido Massieu s/n. Unidad Profesional Adolfo López Mateos. Mexico City, 07738, Mexico.
*: *ecristianiu@yahoo.com.mx*

Introduction and study objectives

Metal complex azo acid dyes are widely used in the textile industry because of their light and wet fastness properties. However, their mutagenic and carcinogenic effects are of serious health concern. Chromium complex dyes are the most important class of metal complex dyes.

Acid orange 74 (AO74) is a chromium complex monoazo acid dye. It is an industrial dye used for dyeing wool, silk, nylon, and leather. It contains a chromium ion bound to the azo group that confers stability to the dye structure. AO74 is considered as a non-biodegradable dye and must be removed from AO74-polluted water to protect public health and the environment.

Conventional treatment technologies for removing dyes from aqueous solutions have several technical and economical drawbacks. Biosorption has gained recognition as a way of treating dye-contaminated aqueous effluents, as it is effective, cheap and eco-friendly.

In the present work, we studied the biosorption and desorption of AO74 using HCl-pretreated *Lemna* sp. as a biosorbent. FTIR and SEM-EDX techniques were used to confirm the biosorption of AO74 dye on the biosorbent. Likewise, several biosorption and desorption cycles were implemented, indicating the possibility of recycling the biosorbent.

Methodology

Lemna sp. was collected from canals of Xochimilco in Mexico City and washed thoroughly with distilled water. It was then oven-dried, milled and sieved. The fraction with particle sizes of 0.3-0.5 mm was used. Subsequently, particles were soaked in 0.05 M HCl at room temperature for 4 h. Afterwards, we studied the effect of solution pH, initial AO74 concentration, temperature, and contact time on AO74 biosorption by HCl-pretreated *Lemna* sp. (HPL). Similarly, several eluent solutions were assayed for their ability to desorb AO74 from AO74-loaded HPL. We assessed the feasibility of regenerating HPL by applying three successive biosorption-desorption cycles.

AO74 dye concentration was quantified spectrophotometrically at 478 nm. FTIR analysis was used to detect possible changes in HPL functional groups after each biosorption and desorption step, throughout the cycles. SEM-EDX analysis was performed to detect possible changes on HPL surface and to confirm the presence and absence of the dye on AO74-loaded and AO74-desorbed HPL, respectively.

Results and conclusions

Apparently, the optimum solution pH for AO74 biosorption by HPL was 2.0. The high levels of AO74 biosorption observed at lower pH values can be attributed to the protonation of the active sites, resulting in electrostatic attraction between the positive charges of the ligands present on the HPL surface and the anionic AO74 dye. Likewise, the greater initial concentration of AO74, the greater biosorption of dye on the HPL surface. A maximum AO74 biosorption capacity of 64.24 ± 0.204 mg g^{-1} was obtained after 4 h. Increasing solution temperature caused an increase in AO74 biosorption capacity but decreased biosorption rate.

Modeling of AO74 biosorption kinetics showed that experimental data concurred well with the pseudo-second-order kinetics model at all the assayed solution pH levels, initial AO74 concentrations and temperatures.

Experimental equilibrium data for AO74 biosorption were evaluated for compliance with a variety of two-parameter, three-parameter and four-parameter isotherm models. The Toth isotherm model best described the AO74 biosorption equilibrium data. According to this isotherm model, the maximum AO74 biosorption capacity of HPL is 64.23 mg g^{-1}, which is very close to the experimental value (64.24 mg g^{-1}).

Of the ten different assayed desorption solutions (alkaline, acid and neutral), 0.01 M NaOH was the best eluent for AO74 desorption from AO74-loaded HPL, achieving a 100% AO74 desorption efficiency; hence, subsequent desorption experiments were conducted using 0.01 M NaOH solution.

The AO74 biosorption and desorption capacity in the first cycle was 64.24 mg g^{-1}. In two subsequent cycles, both the AO74 biosorption and desorption capacity decreased 25% (48.18 mg g^{-1}).

FTIR analysis showed that although carbohydrates have an important function in dye biosorption, proteins play a crucial role in the biosorption of AO74 by HPL.

SEM micrographs revealed little variation in the biosorbent surface for the three assayed cycles of AO74 biosorption and desorption. The EDX analysis confirmed the presence and absence of the chromium ion of the AO74 dye in the AO74-loaded and AO74-desorbed HPL, respectively, during the three cycles.

The above results clearly show that HPL exhibit a high capacity to biosorb AO74 dye from aqueous solutions and that can be used effectively for at least three succesive AO74 biosorption-desorption cycles. Therefore, HPL may have considerable application potential for the removal of AO74 dye from contaminated wastewaters.

SPATIAL DYNAMICS OF PCDDs/Fs AND DL-PCBs IN THE RIVER CONTINUUM AND POSSIBILITIES FOR THEIR REMOVAL USING ECOHYDROLOGY APPROACH

Magdalena Urbaniak[1,2,*]

[1] European Regional Centre for Ecohydrology, Polish Academy of Sciences, Lodz, Poland;
[2] University of Lodz, Department of Applied Ecology, Lodz, Poland;
[*]: m.urbaniak@unesco.lodz.pl;

Introduction and study objectives

The Water Framework Directive (WFD) establishing a framework for European Union community action in the field of water policy and to achieve and maintenance good ecological status for aquatic ecosystems. One of the conditions of achieving good water status is the elimination or reduction of emissions of the most dangerous substances. The WFD and the Environmental Quality Standards Directive (EQS) regarding priority substances in the field of water policy contain a list of 45 substances that constitute a serious threat to the aquatic environment. This list includes a group of priority hazardous substances, including polychlorinated dibenzo-p-dioxin (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (dl-PCBs), which should be completely eliminated from the environment because of their highly toxic nature, persistence and susceptibility to bioaccumulation.

The river ecosystem is particularly prone to these compounds. Its location at the lowest points in the landscape allows pollutants from various sources to accumulate through such processes as atmospheric deposition, runoff from urban and agricultural areas or inflow through point sources. The main factor determining accumulation of PCDDs/Fs and dl-PCBs high in aquatic systems is their extremely low water solubility that allows these substances to be associated with the particles present in water, and hence to be transported along the river, where they undergo gradual deposition and accumulation in sediments. These serve as long-term sources of PCDDs/Fs and dl-PCBs. Therefore, it is crucial to reduce the amount of these compounds in the environment as such reduction will contribute to securing the quality of the environment, and the health of the population, and will contribute toward achieving the goals of the European Union strategy.

In response to the above, the present study aims not only 1) to assess the concentration and toxicity of PCDDs/Fs and dl-PCBs in the river environment, but more importantly, 2) to define the roles played by the factors and processes determining their concentrations, 3) and to propose opportunities for their safe removal from the environment using ecohydrology approach.

Methodology

The 10 years long study has been performed in the area of the Pilica River catchment. Plica River is the longest left-hand tributary of the Vistula River, with a total length of 342 km and a total catchment area of 9 258 km^2, is one of the most significant rivers in Poland.

With regard to assess the concentration and toxicity of PCDDs/Fs and dl-PCBs in the Pilica River the water and bottom sediment were collected at different hydrological conditions, eg. flood, serene and low river flow. This enables us to define the roles played by the hydrological processes on the noted PCDDs/Fs and dl-PCBs values. To define the role of anthropogenic sources of pollution, including point sources, the treated wastewater from the outlets of 17 wastewater treatment plants (WTPs) divided into three size categories (small, medium and large) that discharge their wastewater into the Pilica River and its tributaries, have been collected.

The last aim of the study was achieved through analysis of the possibilities to use bio- and phytotechnologies for removal of PCDDs/Fs and PCBs from the environment. The research within this area is based on the concept of ecohydrology. One of the key elements of ecohydrology is the improvement of the environment by the use of ecosystem biotechnologies derived using specialized knowledge about naturally-occurring processes. Two of these approaches are microbial bioremediation and phytoremediation, or rather, the use of microbes or plants to remove pollutants or convert them into forms that are less toxic to the environment.

Results and conclusions

The obtained results indicate that hydrological conditions prevailing in the Pilica River play a determining role on the quoted PCDD/F and dl-PCB concentrations. The valus recorded during the flood season were around 23% higher than observed during the period of stable flow. Also the loads of PCDDsFs transported during the flood increased from 3- to 27-fold in the case of the total concentration and from 11- to 55-fold in the case of Toxic Equivalency (TEQ). The primary cause of such significant differences is the form of the hydrological conditions prevailing in the river itself and its catchemnt.

The results of wastewater analysis indicate that small WTPs had higher concentrations of the studied compounds than the larger ones. However, a completely different situation was observed when the obtained values were calculated into loads discharged to the Pilica River and its tributaries. In this case, the highest load was generated by large WTPs, while small WTPs despite high concentration discharged the smallest load of studied compounds into the recipients.

With regard to WTPs, in addition to discharging PCDDs/Fs and dl-PCBs into the aquatic environment, they also produce sewage sludge as the end product of the treatment process. There is also a need to utilize river and reservoir sediments contaminated with PCDDs/Fs and dl-PCBs as an effect of their discharge via WTPs outlets. The obtained results raveled that these pollutants may be removed by using the contaminated sewage sludge and sediments as plants fertilizer. Application of plants from the *Cucurbiatceae* family, for example, resulted in a decrease in PCB concentrations by an average of 39% for soil fertilized with sludge and 27% for soil fertilized with sediments. More positive results were observed when willow (*Salix* sp.) plants have been applied, with the average decrease of PCDDs/Fs and PCBs content of 74%.

IBUPROFEN BIODEGRADATION BY BIOAUGMENTED WASTEWATER SLUDGE

Jiménez-Silva Vanessa Abigail, Santoyo-Tepole Fortunata*, Ruíz-Ordaz Nora, Juvencio Galíndez Mayer

Instituto Politécnico Nacional, Escuela Nacional de Ciencias Biológicas, Laboratorio de Bioingeniería. Unidad Profesional Adolfo López Mateos, Avenida Wilfrido Massieu esquina cerrada Miguel Stampa S/N, CP 07338, Delegación Gustavo A Madero, Ciudad de México
*: *fsantoyo@ipn.mx*

Introduction and study objectives

In recent years, more attention has been paid to unregulated pollutants (emerging pollutants), which may be candidates for future regulation at the light of their potential effects on the environment and human health. Most of them are household organic substances, including pharmaceuticals, personal care products, detergents, and disinfectants. Ibuprofen (IBP) is one of the most widely consumed free drugs worldwide. It belongs to the pharmacotherapeutic group of non-steroidal anti-inflammatory compounds, and therefore it has anti-inflammatory, analgesic and antipyretic properties.

Currently, it has been reported in several countries as a frequent contaminant in wastewater treatment plants (WWTP), usually with concentrations alike or higher than other pollutants. As for its toxicity in aquatic species, chronic effects of enzymatic, hematic, biochemical, endocrine, oxidative and bio-accumulative stress have been reported.

Since the elimination of drugs in the WWTPs by conventional methods (activated sludge) is generally inefficient, the effect of wastewater sludge (WS) bio-enrichment with selected microorganisms able to degrade the IBP was evaluated. The objective was the WS improvement in the drug removal efficiency, reducing the negative impact of IBP on the operation of conventional WWTPs, which constitute just over 55% of the total of the functional plants in Mexico

Methodology

The selection of IBP degrading microorganisms was carried out using samples (CH, TX, CE) of wastewater sludge from the "Cerro de la Estrella" WWTP, Mexico City, and from agricultural soils (HX, TL, JC, XC). Using a minimal mineral medium (MMM) containing 10 mg/L of the drug in its commercial presentation "Advil liquid gels," the bio-enrichment of microorganisms able to degrade IBP were reached by successive transfers in batch culture. The COD and IPB removal efficiencies were used as criteria to select the most efficient microbial culture. The isolation and identification of microbial isolates were done by microbiological and molecular techniques. Also, the IBP removal of isolates was evaluated in axenic batch cultures.

The prototype reactor used had an operational volume of 4.5 L. The wastewater sludge WWTP was placed and stabilized, it was fed from the top with synthetic wastewater (SWW) at a flow rate of 0.085 L/h to keep a dilution rate value of 0.018 h^{-1}. After reactor's stabilization, it was fed with IBP concentration of 5 and 10 mg/L for each batch of sludge. The toxic effect of the IBP was determined by means of COD, TOC, sedimentary solids, turbidity and IBP concentration. To evaluate the bioaugmentation effect on IPB biodegradation, the inoculum was previously adjusted with 80% of SWW with a concentration of IBP of 10mg/L; then it was supplied to a new batch of stabilized sludge. In all experiments, the IBP was quantified by HPLC.

Results and conclusions

With the preselected CH, CE and TL cultures, the removal efficiency (% R) of commercial IBP were 99.63, 81.54 and 12.65% respectively. Then, a POOL of these microbial cultures was prepared, and its kinetic behavior in batch culture was assessed. With near 100% efficiencies, the CH and POOL cultures were selected to determine the removal rate (R_V) of IBP without excipients. Standard IBP was used to discard the possibility that the excipients were responsible for cometabolic degradation of the IBP. The removal efficiencies obtained with the standard were similar that those obtained with the commercial presentation.

As part of the pre bioenrichment evaluation, the ability to degrade to the commercial IBP was determined in axenic cultures, where no microbial removal was observed under the test conditions.

The toxic effect of the commercial IBP on biological sludge from the "Cerro de la Estrella" WWTP was evaluated, the results showed that IBP collapsed the activity and composition of the sludge, affecting the quality of the treated water directly. COD and TOC increases were observed according to drug accumulation into the reactor. Also, loss of suspended solids (SS) and turbidity increase were observed, resulting in a total collapse of the system at a final concentration of 10 mg/L.

When an IPB concentration of 5 mg/L was used, a recovery of the system was observed after 20 days of continuous operation. Finally, as a central part of the study, the effect of the proposed bio-enrichment on the quality of the treated was evaluated. When the selected community was inoculated into the reactor, simultaneously to the drug feed, the accumulation of IBP in the sludge was avoided; however, SS losses and fluctuation in turbidity values were observed. It is important to emphasize that the toxic response was slower and less exacerbated than when evaluating the feed of the drug without bio-enrichment. The results indicated that bioaugmentation improved the quality and activity of the sludge. So, this strategy was considered successful for the efficient removal of IBP, avoiding, in great extent the collapse of the system.

EMERGING PHARMACEUTICAL POLLUTANT DEGRADATION BY HETEROGENEOUS ELECTRO-FENTON PROCESS

Emilio Rosales[1,*], Silvia Diaz[1,2], Marta Pazos[1], M. Angeles Sanromán[1]

[1)] Department of Chemical Engineering, University of Vigo, Campus As Lagoas-Marcosende 36310, Vigo, Spain
[2)] Instituto Politécnico Nacional, Av., Instituto Politecnico Nacional S/N, Gustavo A. Madero, Lindavista, 07738 Ciudad de México, D.F., México
[*]: emiliorv@uvigo.es

Introduction and study objectives

Pharmaceutical and personal care products (drugs, perfume, sunscreens, etc.) are widely used by several segments of the population. Those compounds end in water sources when they get washed off or they are incompletely metabolised in the case of the prescription drugs. Several studies are reporting the adverse effects of these compounds in the aquatic life and becoming them in chemicals of emerging concern. For this reason, their environmental fate and arrival to water sources need to be tackled.

Classical sewage treatment plants are not able to completely remove these products from wastewater and their removal degree is too dependent on the technology implemented. Therefore, new technologies more efficient are required in order to treat these pollutants. Sonochemical, electrochemical and electro-Fenton technologies have arisen interest in the last years due to their ability to produce radical species in water with powerful oxidant properties and high efficiency.

The aim of this work is the development of new technologies for the removal of emerging pharmaceutical pollutants in wastewaters using diclofenac as model pollutant. Initially, a screening of different treatment technologies was performed (sonochemical, electrochemical and electro-Fenton) and their viability in the degradation of the pollutant at low concentrations was evaluated. The more efficient techniques were studied at high concentrations. After that, the degradation process was followed by the enhancement of the electro-Fenton process with the development of new heterogeneous catalysts. The working conditions including intensity, catalyst dosage, system reutilization… were optimised in order to establish the basis of a future continuous treatment system. Finally, a degradation pathway was proposed and several degradation intermediates were identified.

Methodology

The degradation assays were performed in a 250 mL cylindrical vessel with a working volume of 150 mL. The selected diclofenac concentration was from 10 to 150 mg/L. The ultrasound experiments were done fixing a power of 500 W and working at 120 KHz. In anodic oxidation and electro-Fenton experiments a current intensity of 300 mA was applied with a power supply using carbon felt and boron-doped diamond electrode as cathode and anode, respectively. Na_2SO_4 (0.01M) was added as electrolyte and the pH was adjusted to 6 with a phosphate-NaOH buffer. In the electro-Fenton experiments, different amounts of the prepared iron modified hydrogels beads were added as catalyst. Five different catalysts based in modified chitosan beads were obtained using iron impregnation (CBI), coprecipitation (CBP) and entrapment (CBE) processes. Another two catalysts based in modified alginate beads by coprecipitation (ABP) and entrapment (ABE) were manufactured. Iron sulphate was used for the impregnation and coprecipitation and iron (III) oxide was used to entrapment process.

Results and conclusions

Initially the selected treatments (sonochemical, electrochemical and electro-Fenton) were probed. A significant difference was detected in the degradation at low diclofenac concentrations (10 mg/L). Sonolysis studies reached almost total degradation after 90 min. However, electrochemical and electro-Fenton treatments achieved a complete degradation of the pollutant before 10 minutes showing a better performance in the treatment. Afterwards, these techniques were evaluated at high pollutant concentration (150 mg/L). The performance of the electrochemical treatment for the removal of diclofenac was evaluated reaching a degradation of 62.37% after 120 min. These values are substantially lower than those achieved when the electro-Fenton was carried out, approximately 100% in 60 minutes.

Then, the enhancement of the electro-Fenton was performed. For this purpose, five new catalysts were prepared by the iron immobilisation into chitosan and alginate. These catalysts were characterized by FTIR and homogeneous iron distribution in the surface of the catalyst was determined by scanning electron microscopy with X-ray microanalysis. Working with these catalysts a similar degradation profile was obtained in each case. All of them also demonstrated a high efficiency in the removal of diclofenac between 85-95% after 120 min, however the highest removal was obtained using CBE. The operational conditions with this catalyst (CBE dosage and intensity) were optimized resulting in a catalyst dosage of 3g and an intensity of 300 mA achieving 100 % of removal after 120 minutes and almost total TOC reduction after 180 min. This fact was also confirmed by the identification of degradation intermediates by HPLC. The catalyst presented good properties for its use in continuous process, and therefore, successive batches were performed to confirm the reusability without operational problems.

The heterogeneous electro-Fenton treatment has demonstrated to be effective for the removal of the selected pollutant and consequent mineralization. The use of the prepared modified hydrogels beads opens promising perspectives for fast and economical treatment of polluted wastewater.

Acknowledgments

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ENHANCED SELECTION OF PHA STORING BIOMASS VIA-NITRITE DURING THE TREATMENT OF ANAEROBIC SUPERNATANT

Arianna Cherubin[1], Nicola Frison[1], Anna Laura Eusebi[2], Francesco Fatone[2]

[1)] Department of Biotechnology, University of Verona, Strada le Grazie 15, 37134 Verona (Italy)
[2)] Department SIMAU, Università Politecnica delle Marche, via Brecce Bianche, 60131, Ancona (Italy)
[*]: f.fatone@univpm.it

Introduction and study objectives

Activated sludge from wastewater treatment plants (WWTPs) is a well-known source of PHA-storing organisms that store these polymers as carbon and energy reserve. Despite the process is well known, the integration of nutrient removal in wastewater treatment systems with the PHA production cycle is currently a challenge because of the aerobic and energy intensive selection process. In this work, the PHA storing biomass selection was integrated with the biological nitrogen removal via nitrite process for the treatment of anaerobic supernatant by the use of sieved cellulosic sludge from the wastewater. It is based on the selection of PHA storing biomass in a Sequencing Batch Reactor (SBR) by the alternation of aerobic feast conditions (ammonia conversion to nitrite) followed by anoxic famine conditions (denitritation driven by internally stored PHA). The selection degree of PHA storing biomass was evaluated in terms of VFAs uptake rate and yield of PHA production at 5 and 10 days of sludge retention time (SRT). Moreover, FISH analyses were carried out in order to link the operating conditions of the selection SBR with the presence of Thaurea, which are involved in the nitrogen removal via-nitrite cycle.

Methodology

The Short-Cut Enhanced PHA Recovery (SCEPHAR)process can be summarized into five main steps: i) sieving of wastewater to recover cellulosic primary sludge; ii) VFAs production from cellulosic primary sludge (acidogenic fermentation); iii) oxidation of ammonia to nitrite in a nitritation reactor via the short-cut pathway; iv) selection of PHA-storing; v) PHAs accumulation up to the maximum production capacity.

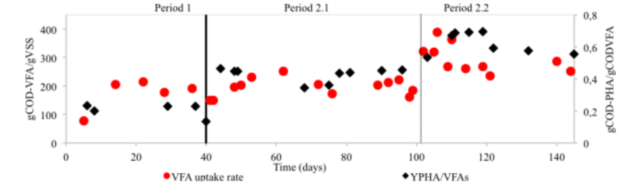
The Selection SBR had a working volume of 28 L and was inoculated with activated sludge taken from the WWTP of Carbonera (Treviso, North of Italy). The SBR operated according with the operating conditions reported in the following table.

Parameter	**Period 1 (0-39 days)**	**Period 2.1 (40-106 days)**	**Period 2.2 (107-145 days)**	**Previous study Frison et al., 2015**
Type of Carbon source	VFAs from synthetic acetic and propionic acid	VFAs from synthetic acetic and propionic acid	VFAs from cellulosic primary sludge	VFAs from real cellulosic primary sludge
Electron acceptor for famine phase	Nitrite	Nitrite	Nitrite	Nitrite

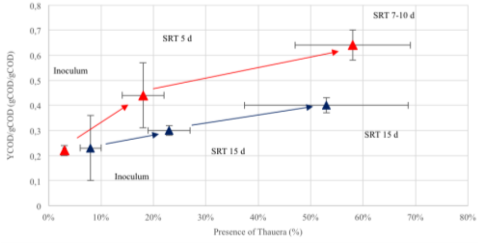
vNLR (kgN/m3)	0,61	0,48 ± 0,19	0,56 ± 0,02	0.50 ± 0.11
tOLR(gCOD/m3d)	1.32±0.12	1.32±0.12	1.18 ± 0,32	1.39 ± 0.11
F/M (gCOD-VFA/gXa)	1,16 ± 0,25	0,67 ± 0,19	0,63 ± 0,09	0,37 ±0,07
SRT (d)	5	7-10	7-10	12 ± 3

Results and conclusions

In period 1 (0-40), losses of floating biomass were frequently observed during the discharge phases: indeed, the biomass raised due to the uncontrolled denitrification and abundant N2 gas production during the settling phase. These conditions favoured the denitrifying organisms, which affected the degree of PHA biomass selection. In period 2 (46-107), the higher SRT (7-10 days) led to an increase of biomass concentration in the reactor up to around 2.5 gMLVSS/L (data not shown), which boosted the nitrite removal (up to around 92%) and the PHA degradation efficiencies during the famine conditions. From days 40, the YPHA/VFA increased gradually during Period 2, specifically from 0.22 to 0.65 gCODPHA/gCODVFA.



The presence of Thauera was analysed through FISH analyses and then linked with the operating performances of the selection SBR. Its presence increased when the system showed the higher stability at SRT of 7-10 days (Period 2.1 and 2.2). Moreover, it seems that the presence of Thauera is stable for SRT in the range between 7-15 days. On the other hand, the increase of the YPHA/VFA from 0.42 to 0.64 gCOD/gCOD could be attributed by the presence of other types of organisms such Paracoccus and Azoarcus.



The SRT between 7-10 days seems the optimal to achieve high yield of PHA storage (up to 0.65 $gCOD_{PHA}/gCOD_{VFA}$) as well as to perform high efficiencies of nitrogen removal via-nitrite (up to around 92%) in the selection SBR. The microbial community profile showed that the high presence of *Thauera* at SRT between 7-10 days was comparable with previous findings conducted at SRT of 15 days.

UPGRADING OF THE SHORT-CUT ENHANCED NUTRIENT ABATMENT (SCENA) BY INTEGRATED FERMENTATION OF CELLULOSIC SLUDGE

Arianna Cherubin[1], Nicola Frison[1], Anna Laura Eusebi[2], Francesco Fatone[2]

[1)] Department of Biotechnology, University of Verona, Strada le Grazie 15, 37134 Verona (Italy)
[2)] Department SIMAU, Università Politecnica delle Marche, via Brecce Bianche, 60131, Ancona (Italy)
[*]: f.fatone@univpm.it

Introduction and study objectives

Anaerobic sewage sludge digestion results in the release of soluble organic nitrogen-containing compounds, ammonium and orthophosphate from the sludge mass into the bulk liquid, so that the reject water generated by the dewatering of the digested sludge has elevated nutrients concentrations. Recycling it to the headwork of the WWTPs, it increases nutrient loadings, causing an increase in air supply, energy demand and chemicals requirements for biological nutrients removal (BRN). To minimize these negative impacts and the high operating costs, the reject water from anaerobic digester should be treated separately before it is recycled to the headwork of the WWTPs. Thus, short-cut nitrogen removal (SCNR) through the ammonium oxidation to nitrite and its subsequent reduction to gaseous nitrogen has gained increasing attention. Thanks to its autotrophic characteristics and its economic advantages, this process can be coupled with suitable bioprocesses for phosphorus removal and for the production of high added value products, overcoming the problems of operational and environmental sensitivity, and low yields, it is subjected to. The process deals with the accumulation of phosphorus in Phosphorus Accumulating Organisms (PAO) under aerobic and anoxic conditions and to achieve an effective nitrogen and phosphorus removal via-nitrite. Readily biodegradable COD should be provided; thus cellulosic primary sludge from sieved municipal wastewater should represent a valuable substrate to produce Volatile Fatty Acids (VFAs) by acidogenic fermentation.

Methodology

Production of VFAs from cellulosic primary sludge

The fermentation of cellulosic primary sludge (CPS) was carried out at mesophilic conditions in a Sequencing Batch Fermentation Reactor (SBFR) with a stable hydraulic retention time (3 days). The resulted fermentation liquid was used as carbon source for the SBR. VFAs composition of cellulosic sludge fermentation liquid was examined and data are reported as follows: HAc 58%, HPr 27%, HBut 14%, others <1%.

The short-cut Sequencing Batch Reactor

The lab-scale SBR (scSBR) had a working volume of 28 liters and it was inoculated with thickened WAS of Carbonera WWTP. The oxygen concentration during the aerobic phase was kept at a concentration range of 1.5-2.5 mgO_2 L^{-1}. The whole experimental periods (around 100 days) involved two main periods: 1) PAOs enrichments, where the SBR alternated anaerobic and aerobic phases; 2) Short-Cut EBPR, where the SBR accomplished anaerobic, aerobic and anoxic phases.

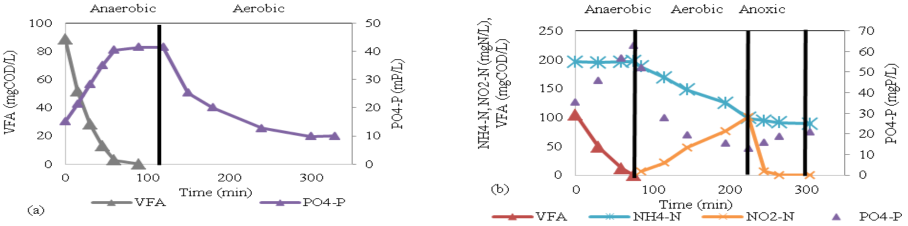
The operating conditions were set as follows:

	Period 1	Period 2
Total vNLR applied (kgN $m^{-3}d^{-1}$)	-	0.55 (0.42-0.64)
vPLR applied (gP $m^{-3}d^{-1}$)	32.9 (28.35-38.7)	41 (31.9-51.7)
vOLR applied (kgCOD $m^{-3}d^{-1}$)	0.52	1.77 (1.64-1.89)
SRT	8	12

Results and conclusions

PAOs enrichment using fermented cellulosic primary sludge

Figure 1.1(a) shows the typical profiles obtained during the period 1 dedicated to the enrichment of PAOs. During the anaerobic phase, the VFAs from the cellulosic sludge were uptaken by the biomass according with 30-40 mgCOD $gVSS^{-1}h^{-1}$.



As a consequence of the VFA uptake, around 35 mgP/L were released during the first 60 minutes of anaerobic phase and then stabilized at around 40 mgP L^{-1}. During the aerobic phase, the uptake of PO_4-P was observed with a maximal rate of 10.9 mgCOD $gVSS^{-1}h^{-1}$, which is considered a good P bioremoval activity by Janssen et al., 2002. The VFAs produced by the cellulosic primary sludge were suitable to establish a stable and effective enhanced bio-P removal process. In period 2, although the bio-P removal capacity was maintained, the sPRR and the sPUR decreased to 3.7 and 4.7 mgCOD $gVSS^{-1}h^{-1}$ respectively.

The Short-Cut EBPR was validated at lab scale SBR using VFAs derived from the fermentation of cellulosic primary sludge for the treatment of anaerobic supernatant. The results of the experiments pointed out that phosphorus could be uptaken at high rate in the biomass cell under aerobic and anoxic conditions. The phosphorus concentration in the biomass cell achieved 57 mgP gTS^{-1}, where around 14% was phosphorus precipitated and thus chemically-bounded. The presence of high level of nitrite might partially inhibit the activity of PAOs bacteria if not acclimatized. On the other hands, the ratio sPRR/VFAs was an effective indicator of the competition between PAOs/GAOs, which was then confirmed by the FISH analyses. The latter showed that the presence of PAOs decreased from around 50% to 20% when the short-cut EBPR was established, probably due to the increase of presence of GAOs.

OLIVE MILL WASTEWATER VALORISATION THROUGH POLYPHENOLS ADSORPTION AND SUBSEQUENT ANAEROBIC DIGESTION

Giorgia Rubertelli, Davide Pinelli, Dario Frascari

With their high content in phenolic compounds (PCs, 0.5-18 g/L) and COD (20-200 g/L), Olive Mill Wastewaters (OMWs) can be valorized as a source of chemicals and energy. The goal of this work is to develop an OMW valorization process through polyphenol separation by adsorption and anaerobic digestion of the dephenolized OMW, with the co-objective to produce a treated wastewater suitable for irrigation according to the ISO 16075 standard.

A pilot scale plant was utilized, composed of: i) microfiltration unit (cut- off diameter 60 nm), ii) 2-m modular adsorption column loaded with vacuum distillation unit for the recovery of the desorption solvent (ethanol + HCl $5{\cdot}10^{-4}$ M) and iv) 30-L continuous-flow anaerobic digester. The plant was fed with an actual OMW (polyphenols 1.7 g/L, COD 78 g/L, suspended solids 3.3 g/L). As shown in Figure 1 the AMBERLITE XAD16 resin has been characterized by means of a polyphenol adsorption isotherm at 21 °C. The best model to fit the experimental data resulted to be the Langmuir model (R^2 = 91%) and the XAD16 adsorption capacity resulted equal to 154 $mg_{polyphenols}/g_{dry\ resin}$.

Step disturbance tests were conducted on the pilot scale plant to assess the packed bed effective porosity (0.74) and longitudinal dispersivity (0.015 m). Microfiltration determined a 99% suspended solid removal. Adsorption breakthrough tests aimed at optimizing the superficial velocity (1-4 m/h) and bed length (0.5-2.0 m) are in progress. On the basis of preliminary results, an adsorption test conducted at 3.05 m/h and 24°C with a 2 m bed length was performed. Figure 2 shows the total PCs and COD dimensionless concentrations monitored at the column exit. The average PCs and COD levels at the inlet were used to normalize the corresponding outlet values. The experimental tests were continued up to 20 hydraulic residence times (HRT), calculated as (column length)/(OMW interstitial velocity). The adsorption performance will be quantified by means of the following indexes, referred to a 0.2 dimensionless concentration as breakpoint value: i) adsorption yield ($Y_{ads,i,}$), evaluated as $m_{i,adsorbed} / m_{i,fed}$; ii) PCs/COD adsorption selectivity, expressed as the corresponding adsorption yield ratios; iii) resin utilization efficiency (η_{resin}), defined as (PCs mass sorbed at the breakthrough point) / (total PCs mass that could be adsorbed if all the resin was saturated); iv) PCs/COD enrichment factor, defined as the ratio between the PCs content in the total COD of the adsorbed matter (g_{PCs}/g_{COD}) over that in fresh OMW. As PCs adsorption on polymeric resin is typically a non-equilibrium process where mass transfer and dispersion are key controlling phenomena, the experimental normalized PCs and COD breakthrough curves will be interpreted by means of a 1-D convection-dispersion model with solid-liquid mass-transfer, in order to evaluate the process performance and to set up the basis for a model-based process scale-up:

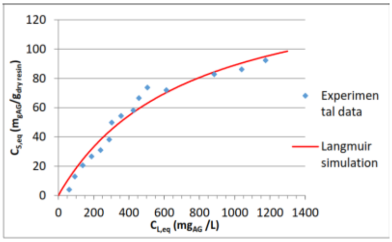


Figure 1 – PCs adsorption isotherm at 21°C for Amberlite XAD 16

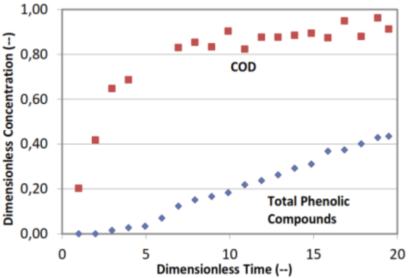


Figure 2 – PCs and COD breakthrough test for Amberlite XAD 16 (24°C, v_{sup} 3.05 m/h, column length 2 m)

$$\frac{\partial C_{L,i}}{\partial t} = -v_{int} \cdot \frac{\partial C_{L,i}}{\partial z} + D_{eq} \cdot \frac{\partial^2 C_{L,i}}{\partial z^2} - k_L a \cdot \left(C_{L,i} - \frac{C_{S,i}}{K_{eq,i}} \right) \qquad (1)$$

$$\frac{\rho_b}{\epsilon} \cdot \frac{\partial C_{S,i}}{\partial t} = k_L a \cdot \left(C_{L,i} - \frac{C_{S,i}}{K_{eq,i}} \right) \qquad (2)$$

where: $C_{L,i}$ is the PCs or COD liquid phase concentration, $C_{S,i}$ the solid-phase concentration, k_La the mass- transfer coefficient referred to liquid volume, ρ_b the resin bulk density, ε the resin porosity, $K_{eq,i}$ the PCs or COD equilibrium adsorption constant and D_{eq} the equivalent diffusion coefficient (calculated as $\alpha_L \cdot v_{int}$, with the longitudinal dispersivity αL estimated by means of fluid-dynamic tests). $K_{eq,PC}$, $K_{eq,COD}$ and k_La are estimated by best-fit on the experimental PCs and COD concentrations following the Gauss-Newton method. Figure 2 shows that the COD breakthrough is significantly faster than that of PCs, indicating a good resin selectivity for PCs. Nevertheless, even though a complete data elaboration has not been performed yet, a deeper investigation is necessary to improve the purity of the desorbed mixture, which is characterized by a relevant presence of non-phenolic compounds. The low PC purity of the final product is a result of the very low (PCs / total COD) ratio of OMWs. Different strategies will be tested to increase the PCs purity of the final desorbed product, such as i) re-suspension in water of the desorbed material (after ethanol evaporation) and execution of a second adsorption step, or ii) multi-solvent desorption.

Anaerobic digestion tests conducted with the dephenolized OMW resulted in a high methane production yield (310 Nm^3_{CH4}/tVS), in an acceptable methane production rate (0.13 $Nm^3_{CH4}/m^3/d$) and in a 99% COD removal.

This study represents the first attempt to develop an integrated OMW treatment process that includes high-added value product recovery and anaerobic digestion, with the final aim to produce an effluent reusable in agriculture.

Acknowledgments

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SECTION III

SUSTAINABLE WASTE MANAGEMENT AND EXPLOITATION FOR CHEMICALS, MATERIALS AND ENERGY RECOVERY

PERVAPORATION FOR EFFECTIVE IN-SITU BUTANOL RECOVERY IN ABE FERMENTATION

Martin Miltner[*], **Florian Kirchbacher, Antonia Rom, Walter Wukovits, Michael Harasek, Anton Friedl**

Institute of Chemical Engineering, Vienna University of Technology, Austria
Martin Miltner, Getreidemarkt 9/166, A-1060 Vienna, Austria.
[*]*: martin.miltner@tuwien.ac.at*

Introduction and study objectives

Promoted by the increase of industrialization and population the global demand for energy and material products is steadily rising. Since the primary sources for energy and chemicals are mainly based on fossil resources, this growth provokes significant issues in terms of environment, economy and society. Thus, the supply of renewable energy and sustainable chemicals became one of the major societal targets of the current century. Energy and chemicals from biogeneous resources are accepted amongst the most promising pathways for covering the growing demands both in a sustainable and economic way. Biobutanol can be treated as a possible key substance in these regards as it acts as an energy carrier or fuel (supplement for gasoline, diesel and kerosene superior to ethanol) and as a commodity chemical (base chemical for organic synthesis, solvent in chemical industry).

While Acetone-Butanol-Ethanol(ABE)-fermentation as the main production route of biobutanol is a well-established technology, experts agree that still remarkable optimization potential is given. Significant efforts in contemporary research are undertaken towards the selection of fermentation feedstock, development and optimisation of biomass-pretreatment and hydrolysis as well as metabolic engineering of the involved microorganism strains (clostridia) to enhance butanol yield and substrate utilisation. Persistent challenge is the limitation of ABE fermentation by high product toxicity of butanol resulting in reasonably dilute product concentrations (up to 20 g/l). Consequently, constant in-situ separation of butanol from the fermentation broth is mandatory to sustain stable production. Furthermore, butanol has to be concentrated from fermentation levels up to 99.9 wt% for further utilisation (downstream processing). Distillation is no option as the energy demand for separations at these low product concentratios would exceed the thermal energy content of the product by more than 200%. Thus, alternative technologies for purification or pre-enrichment like gas stripping, adsorption, extraction or membrane separation have to be developed and applied [1].

The scope of current work is the analysis and development of membrane-based pervaporation process [2] for in-situ butanol recovery from ABE fermentation. Results from extensive lab-scale experiments shall be used for development of mathematical models for improved process description targeting for optimisation and upscaling of the pervaporation process.

Methodology

Experimental analysis is performed using a laboratory pervaporation setup with a feed flowrate in the range of 100 to 200 l/h in a closed loop. Feed temperature is maintained by a thermostat and heat exchanger. Feed depletion from the feed tank is monitored with a balance. The setup can be equipped with flat-sheet membranes with an active area of 144 cm^2 or with commercial hollow-fiber membrane modules of appropriate size. Vacuum in the range of 10 to 20 mbar(a) is applied on the permeate side with a rotary vane vacuum pump providing the driving force for the process. Transmembrane or permeate flux is totally condensed in cold traps cooled with liquid nitrogen and weighted out at given timestamps. Compositions of feed and permeate are analyzed by GC.

This setup is used to analyze the pervaporation performance of different membrane materials and membrane modules under fermentation conditions in terms of specific transmembrane fluxes, butanol enrichment in the permeate as well as permeance and selectivities for ABE solvents and water. The influence of feed solvent concentration, residual glucose concentration, presence of salts and organic acids, feed temperature and pH value is studied. Regarding membrane materials, both commercially available as well as experimental materials like PDMS and POMS are considered.

Results and conclusions

Results indicate that the butanol enrichment factor in the permeate reaches values of around 20 in a single separation step (1 wt% BuOH in the feed, 20 wt% BuOH in the permeate) depending on the membrane material. This remarkable enrichment is mainly contributed to the activity coefficients, vapor pressures and membrane selectivity which prefers solvent over water transport due to its hydrophobic nature. Furthermore, the influence of additional components in synthetic fermentation broth is of minor importance in the investigated ranges. No interference on pervaporation performance has been detected for glucose contents of up to 50 g/l, ammonium chloride contents of up to 3 g/l, and organic acids contents of up to 4 g/l (acetic acid and propionic acid). Above all, no flux decline after experiments with synthetic fermentation broth has been detected from which follows that fouling phenomena did not occur. Experiments with real fermentation broth applying effective cell retention underlined this conclusion also for the real process. In conclusion, current work shows that membrane-based pervaporation represents a highly effective technique for in-situ recovery and pre-concentration of butanol produced in ABE fermentation.

Acknowledgements

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NEW VALORIZATION ROUTES OF DIHYDROXYACETONE, A GLYCEROL DERIVATIVE, TO OBTAIN BIO-BASED POLYMERS

Maria Barbara Banella[1], Marc von Czapiewski[2],
Annamaria Celli[1], Michael Meier[2]

[1)] *DICAM – Department of Civil, Chemical, Environmental and Materials Engineering, Alma Mater Studiorum - University of Bologna, Via U. Terracini 28, 40131 Bologna (Italy).*
[2)] *Institute of Organic Chemistry (IOC), Materialwissenschaftliches Zentrum (MZE), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
*: *mariabarbara.banell2@unibo.it*

Introduction and study objectives

The field of polymers derived from non-petrochemical feedstocks is gaining a great deal of momentum from both a commercial and academic sense, as several issues are in fact associated to petrol. A big environmental damage takes place when extraction, transportation and processing of oil take place: water bodies located next to the extraction sites or to the processing plants are very frequently polluted. Furthermore, in the end of the lifecycle of petrochemical products a significant release of carbon dioxide (stored during the fossilization process) occurs. It leads to an evident greenhouse effect that causes, in turn, global warming. Moreover it is provided that the cost of oil is likely to increase in the future, since in current years the maximum exploitation of the world's crude oil reserves has been reached. Global stocks will consequentially run out, given its very long period of renewal. In view of all these considerations, current industrial and academic studies are increasingly oriented towards the preparation of chemicals and materials starting from renewable resources.

At present, fats and oils are the most widely used renewable raw materials in the chemical industry, since they offer widespread possibilities for different applications. The glycerol backbone is found in all lipids belonging to the category of triglycerides. Glycerol is also a by-product of the biodiesel production. Dihydroxyacetone (DHA), the simplest of all ketoses, can be prepared from glycerol by following different routes. The first one consists of a mild oxidation of glycerine, for example with hydrogen peroxide and a ferrous salt as catalyst. DHA can also be prepared in high yield and selectivity at room temperature from glycerol using cationic palladium-based catalysts with oxygen, air or benzoquinone acting as co-oxidants. A third strategy provides for the fermentation of glycerine.

The availability of DHA from renewable resources in addition to its functional groups, make this triose an attractive potential building block for a range of new polymeric biomaterials such as polycarbonates and polyesters. Furthermore, the chemistry of DHA is surprisingly versatile since it is available in the dimer form (Figure

1a), but it is converted into the monomer (Figure 1b) in acetone; both of these forms possess OH groups which are available for polycondensation reactions leading to polymers bearing different structures.


(a) (b)

Figure 1: dihydroxyacetone (DHA) in the dimer (a) and monomer form (b).

The objectives of this work consist in exploiting DHA both in the monomer and in the dimer forms to get new totally biobased polycarbonates and polyesters by reacting it respectively with carbonates and diesters from natural resources. The diesters could be extracted from natural oils, more precisely from fatty acids, whose worldwide availability and relatively low price make them attractive and feasible.

Methodology

DHA (monomer and dimer) was subjected to polymerization studies together with dimethyl carbonate (a molecule obtainable from natural resources, for instance through the oxidative carbonylation of bio-methanol) in order to find the optimal reaction conditions. The thus obtained polycarbonates were characterized. The same was done by exploiting diesters coming from natural resources such as plant oils to get polyesters exhibiting polar units alternating with long aliphatic chains. These polyesters were also characterized.

Results and conclusions

To prepare the above mentioned polymers the effect of different parameters was studied. One of these was the influence of the catalyst type and amount. Both metal based catalysts and organic coupling agents were employed in different amounts. It was possible to find out that coupling agents were the most suitable catalysts to get polycarbonates while the metal based ones were more indicated to prepare polyesters. The first ones were used in higher mole percentages. Furthermore the polymerizations were subjected to several temperature and pressure scans. Also the influence of solvents was taken into account. Homogenizing high-boiling solvents can promote polycondensations reactions to get polycarbonates; they can in fact help to overcome the issue connected to the low miscibility of the highly polar dihydroxyacetone and the long aliphatic chains diesters.

The polymers obtained with the optimized procedures were subjected to different analysis in order to determine their properties. A correlation between the polymers properties and their chemical structure has been found.

As a conclusion, the platform of glycerol derivatives has been enlarged by developing new routes of valorization of the dihydroxyacetone to produce new families of bio-based polymers.

PHENOLS RECOVERY AND BIOMETHANIZATION FROM OLIVE MILL SOLID WASTE AFTER STEAM-EXPLOSION PRE-TREATMENT

Antonio Serrano[1], Fernando G. Fermoso[1], Bernabé Alonso-Fariñas[2], Guillermo Rodríguez-Gutiérrez[1], Juan Fernández-Bolaños[1], Rafael Borja.[1,*]

[1)] Instituto de Grasa, Spanish National Research Council (CSIC), Campus Universitario Pablo de Olavide – Ed. 46, Ctra. de Utrera, km. 1, 41013-Seville, Spain
[2)] University of Seville, Higher Technical School of Engineering, Department of Chemical and Environmental Engineering, Camino de los Descubrimientos, s/n, Seville, Spain
[*]: rborja@cica.es

Introduction and study objectives

Two-phase Olive Mill Solid Waste (OMSW) is an olive oil by-product composed by the olive husk, olive pulp, and olive vegetation water. OMSW must be correctly managed to avoid severe environmental impacts such as negative effects on agricultural soil quality, pollution of aquatic ecosystems and release of phenols and sulfur dioxide to the air. OMSW is a lignocellulosic biomass with a significant concentration of phenolic compounds, which could be recovered due to its high economic interest. Among the different phenolic compounds present in OMSW, hydroxytyrosol is one of the most important because it has excellent properties as a pharmacological and antioxidant agent. Steam-explosion is one of the most effective methods for the pretreatment of lignocellulosic biomass. Steam-explosion has been proposed to allow the extraction of phenolic compounds from OMSW by their displacement to a liquid phase generated during the pre-treatment. In the steam-explosion pre-treatment, the OMSW is heated with high-pressure steam for a certain period of time, and then the pressure is reduced to atmospheric pressure as quickly as possible. The solubilization of fibers during the steam-explosion entails an increase of the phenolic compounds to be extracted, as well as an enhancement in the biodegradability of the substrate.

Due to the energy requirements of the steam-explosion process and the need of managing the resulted pre-treated substrate after the phenol recovery, the anaerobic digestion has been proposed as a subsequent step. Anaerobic digestion allows to stabilize the susbtrate and obtain biogas at the same time, that can be used as energy source. However, phenolic compounds have been widely described as inhibitory of the biomethanization process, being necessary to evaluate the feasibility of the process.

The aim of this research was firstly to evaluate the effect of a steam-explosion pre-treatment on OMSW characteristics. A phenols recovery process and its effects on the subsequent anaerobic digestion process were also evaluated.

Methodology

Steam-explosion pre-treatment was carried out in a 2-L pilot-scale reactor, with a maximal operating pressure of 42 kg/cm2, equipped with a ball valve opening. The samples were steamed for 5 minutes at 200 ºC, prior to a rapid decompression (explosion). Then, the pre-treated material was centrifuged and separated into a solid phase (SP) and a liquid phase (LP), in a ratio of 69:31, in VS, respectively. Phenols were recovered from LP using an industrial chromatographic system under patent (WO 2013/007850A1), resulting in a dephenolized liquid phase (DLP).

The anaerobic digestibility of untreated OMSW and the different pre-treated phases was evaluated by biochemical methane potential (BMP) tests. Additionally, the mixtures SP:LP and SP:DLP, in a ratio of 69:31, in VS, were also assayed. BMP tests were carried out in 250 mL Erlenmeyer flasks at mesophilic temperature (35ºC), using a working volume of 220 mL.

Results and conclusions

Steam-explosion increased the sCOD (soluble Chemical Oxygen Demand) up to 10.7% in the sum of LP and SP, in comparison with the untreated OMSW, although 0.7% of sCOD was released to the air during the steam-explosion process. Soluble compounds were mainly displaced to the LP, which retained around 86% of sCOD. Hydroxytyrosol was the main individual phenol in the LP, allowing the obtaining of 2098 mg per kg of OMSW. However, steam-explosion led to the formation of recalcitrant compounds and/or inhibitors such as hydroxymethylfurfural or vanillin. These compounds were indeed generated in LP, up to concentrations of 77 ± 9 mg/L and 42 ± 3 mg/L of hydroxymethylfurfural and vanillin, respectively. Nevertheless, the subsequent extraction by an industrial chromatographic system presented an efficiency of 47.9% for total phenols. Hydroxymethylfurfural and vanillin were partially removed in DLP with efficiencies of 87.0% and 57.1%, respectively.

BMP tests were performed to evaluate the anaerobic digestibility of the different phases and mixtures. Table 1 shows the kinetic parameters obtained from the modified-Gompertz equation applied to the experimental accumulated methane productions. LP and DLP reached an improvement in G_{max} of 23.5% and 26.8%, respectively respect to the untreated OMSW. However, R_{max} values showed that inhibitory compounds generated during steam-explosion affected to LP, i.e. a R_{max} 26.4% lower than untreated OMSW. Extraction of phenols resulted in a marked improvement of R_{max} in DLP, i.e. 26.4% and 71.8% higher than untreated OMSW and LP, respectively. SP and co-digestion of SP:LP and SP:DLP presented slightly lower values of G_{max} and R_{max} than untreated OMSW, probably due to the formation of recalcitrant compounds during the steam-explosion in SP, which rule the degradation kinetics even with the decreased inhibitory compounds present in DLP (Table 1).

Table 1. Kinetic parameters obtained from the modified-Gompertz equation applied to the different BMP tests.

	OMSW	**SP**	**LP**	**DLP**	**SP:LP**	**SP:DLP**
G_{max} (mL/g VS)	280 ± 3	261 ± 1	346 ± 7	355 ± 4	294 ± 2	261 ± 3
R_{max} (mL/(g VS·d))	106 ± 8	90 ± 3	78 ± 9	134 ± 1	91 ± 5	108 ± 9
λ (d)	0	0.17 ± 0.05	0	0	0	0
r^2	0.9871	0.9957	0.9814	0.9897	0.9882	0.9828

COMPARATIVE EVALUATION OF GREENHOUSE GAS EMISSIONS RESULTED FROM E-WASTE MANAGEMENT SYSTEMS IN ITALY AND ROMANIA

Daniela Cailean (Gavrilescu)[1], Dumitrita Ibanescu[1], Carmen Teodosiu[1,*], Silvia Fiore[2,*]

[1] Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection, Gheorghe Asachi" Technical University of Iasi,73 Prof. Dr. D. Mangeron Street, 700050 Iasi, Romania
[2] Department of Engineering for Environment, Land and Infrastructures (DIATI), Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy
**: cteo@ch.tuiasi.ro (C. Teodosiu);, silvia.fiore@polito.it (S. Fiore)*

Introduction and study objectives

The accelerated development of technology, the attractiveness of electric and electronic equipment (EEE) due to smart functions, as well as the pleasant design and human necessities to improve the living standards are the main causes of increasing rates of waste electrical and electronic equipment (e-waste or WEEE). In the European Union, generated WEEE represents a fast growing category that is expected to increase up to 12 million tons by 2020, and subsequently stringent necessities for a sustainable approach in the collection and treatment of WEEE is required.

The main focus of this paper is to compare the sustainability of the waste electrical and electronic equipment management systems in two countries, Italy and Romania, in terms of environmental impacts, expressed as greenhouse gas emissions (GHG), calculated for each treatment option (recycling, incineration and landfilling). The selected countries have different economic situations: Italy is classified as major developed economy while Romania as a developing country by the International Monetary Fund, but they have the same situation in the solid waste management efficiency, namely performing under average, based on a European Report released in 2012.

According to the European legislation, Directive 2012/19/EU, the WEEE stream is very diverse and is classified into 10 categories, such as: large household appliances; small household appliances; IT and telecommunications equipment; consumer equipment and photovoltaic panels; lighting equipment; electrical and electronic tools (with the exception of large-scale stationary industrial tools); toys, leisure and sports equipment; medical devices (with the exception of all implanted and infected products); monitoring and control instruments; automatic dispensers. An average composition of WEEE and associated treatment options considered in the calculations of the carbon footprint (GHG emissions) are summarized as follows: ferrous metals, aluminum, glass, plastics and wood, accounting for 74.85% of the total material are undergoing recycling with the scope of material valorization; oil, refrigerants, printed circuit boards and capacitors are undergoing thermal treatment, considered for the calculation as incineration (2.42%) and non-recyclable and other components accounting for 22.71%, which are being landfilled.

Methodology

To be able to make the comparison, a life cycle approach based on the material flows, in the WEEE management systems, was considered for both Italy and Romania, over a selected period of 7 years, 2007-2013. The evaluation is based on the greenhouse gas emissions calculated as the carbon footprint (CF) of WEEE systems (expressed as CO_2e t/year), according to equation 1:

$$CF=\Sigma\ Qm_{i,j}\ \times EF_{i,j} \qquad \text{(eq. 1), where:}$$

$Qm_{i,j}$ – material flow i, which undergoes the treatment method j (tone of waste material/year);

$EF_{i,j}$ – emission factor of each material i, in each treatment j ($kgCO_2e$/tone waste material).

The calculations give results according to 5 aggregated models proposed by Smith at el. (2001), EPA (2006), Chen and Lin (2009), Christensen et al. (2009) (with minimum and maximum values). Furthermore, carbon footprints of each treatment stage, specifically CF recycling, CF incineration and CF landfilling were obtained. The Greenhouse Gas Emissions Efficiency indicator, expressed as total carbon footprint (TCF) of treated WEEE/tone of treated WEEE was also analyzed.

Results and conclusions

Irrespective of the model used in calculations and the year, the total carbon footprints of the WEEE management system were found to be negative, showing that this waste stream is treated in a sustainable manner, both in Romania and Italy. Overall, the total carbon footprints register decreasing values over the analyzed period in both countries, due to factors such as increasing recycling rates of WEEE components and imposed collection and management targets. However, over the 2007-2013 period, the TCF values of Romanian WEEE management system are one or two orders of magnitude higher than the corresponding values of the Italian WEEE management system, this meaning that the Italian system is more efficient in dealing with this type of waste. It is worth mentioning that Romania implemented its legislative framework on waste (and specifically on WEEE) starting with 2007, while Italy implemented it since 2002.

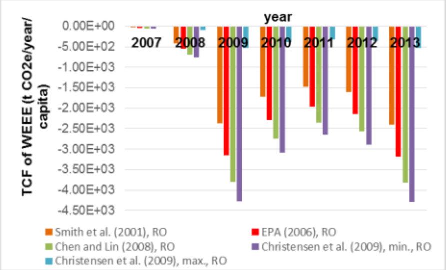

Figure 1:(a) TCF of WEEE in Romania

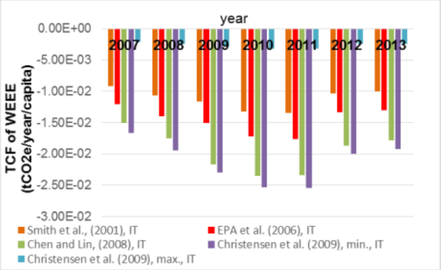

Figure 1:(b) TCF of WEEE in Italy

Figure 1 shows that if the TCF of treated WEEE is divided per capita, then each Romanian inhabitant has a lower contribution to the GHG emissions compared to an Italian inhabitant. Irrespective of the model, in 2007, the calculated GHG Efficiency Indicator of Italy was lower than the corresponding Romanian value. In 2013, the values are reversed, reflecting the improvements in the Romanian WEEE management system, but results have to be discussed in the context in which Italy treats 20-30 times larger quantities of WEEE as compared to Romania.

THE EFFECT OF BIOCHAR COMBINED WITH PGPR AND COMPOST ON AN ACIDIC SANDY SOIL – A POT EXPERIMENT

Mónika Molnár, Virág Kordisz, Emese Vaszita,
Nikolett Uzinger, Márk Rékási, József Kutasi, Viktória Feigl,
Mária Tolner, Katalin Gruiz, Éva Farkas

Budapest University of Technology and Economics, Department of Applied Biotechnology and Food Science, 1111 Budapest, Műegyetem rakpart 3,
**: mmolnar@mail.bme.hu*

Introduction and study objectives

Biochar is the solid product of biomass pyrolisis. Its application to agricultural soils might promote crop yield and biological activity, resulting in improved water and nutrient dynamics. Biochar could be used with organic amendments to increase their stability and reduce organic matter solubility having positive effects on soil fertility, crop yield, nutrient retention, meanwhile mitigating erosion of degraded acidic sandy soils. The incorporation of biochar into agricultural soils enables simultaneous application of plant growth-promoting rhizobacteria (PGPR) by using the biochar as an inoculum carrier, facilitating handling and mixing of the inoculant into the soil.

The objective of this study was to monitor in two 60 days pot experiment series the effect of grain husk and paper sludge biochar, PGPR inoculated biochar, PGPR and compost on the physical, chemical biological and ecotoxicological properties of an acidic sandy soil. The biochar, PGPR and compost were applied to the soil in various combinations and at various rates.The experimental set up allowed statistical evaluation of the results both in a linear, single variable system and in a Box–Wilson statistical design aiding selection of the ecologically most optimum treatment prior to field application.

Methodology

Biochar-inoculant (PGPR)-compost treatment combinations were applied to an acidic sandy soil in two pot experiment series (a linear experimental set up and a Box Wilson experimental design) to determine changes induced in the physical, chemical, biological, and ecotoxicological properties of an acidic sandy soil. The two pot experiment series rely on each other.

We used grain husk and paper sludge biochar (pyrolysis temperature 500 Co, residence time 20 minutes), acidic sandy soil from Eastern Hungary (Nyírlugos) and plant growth promotion rhizobacteria (PGPR) adapted to sandy soil.

The aim of the "linear", single variable 60 days pot experiment series was to monitor the effect of each treatment individually. The treatments (in triplicate) at various rates were the following: control (untreated acidic sandy soil), soil+biochar (15, 30 and 45 kg/ha) soil+PGPR (5, 10 and 15 kg/ha); soil+PGPR inoculated biochar; soil+biochar+PGPR; soil+compost (5, 10 and 15 t/ha).

The multivariable 60 days pot experiment series had the aim to study the pair wise interaction of various treatment combinations to determine the optimum. The Box-Wilson experimental matrix included 54 treatments comprising biochar, PGPR, compost, at various rates and combinations and the untreated acidic sandy soil as control.

The treatments were monitored by an integrated methodology including physical, chemical, biological methods and ecotoxicity tests (Sinapis alba root and shoot elongation test, Tricitum aestivum root and shoot elongation test, Folsomia candida mortality test).

The following physical, chemical and biological parameters were determined: pH, EC, WHC, dry matter content, NPK and ignition loss, Biolog® microbial substrate utilization (AWCD), Biolog® substrate number (S), concentration of aerobic heterotrophic bacteria and fungi (CFU-Colony Forming Unit).

One-way analysis of variance (ANOVA) was applied to determine the significant changes compared to the control. Fisher's LSD (least significant difference) was used to compare the treatment combinations (p <0,05).

Results and conclusions

The single variable pot experiment shows that biochar and PGPR inoculated biochar had advantageous effects on the monitored physical-chemical properties of the treated soil compared to the control. According to the AWCD the microbial activity intensified in case of biochar+PGPR and compost treatments. The treatments improved the microbial activity of soil compared to the control the most favorable treatments were the PGPR inoculated biochars (1%, 1.5%). Biochar treatment had no ecotoxic effect on the soil ecosystem, compared to the control, but the PGPR inoculated biochar and the biochar+PGPR treatment had no favorable effects on the test organisms. According to the multivariable pot experiment series (Table 1), biochar, biochar+PGPR, biochar+compost treatment improved the physical, chemical and biological properties of the treated soils in many cases, but the improvement was not always proportional with the treatment rate.

Table 1: Statistical evaluation summary of the experiment series results

		Linear direct effects			**Pair-wise effects**			**Secondary direct effects**		
	control	biochar	PGPR	compost	biochar + PGPR	biochar + compost	compost + PGPR	biochar	PGPR	compost
pH	***	***	N	N	N	N	N	N	N	N
EC	***	***	N	N	*	N	N	N	N	N
WHC	***	N	N	N	***	N	***	N	N	N
Biolog AWCD	***	***	N	N	N	N	N	**	N	*
Biolog S	***	**	N	*	N	**	N	*	N	*
CFU Bacteria	***	N	N	**	**	**	N	**	N	N
CFU Fungi	***	***	*	**	N	N	*	N	N	N
Sinapis alba shoot length	***	*	N	N	**	N	N	*	**	N
Sinapis alba root length	***	N	***	N	N	***	N	N	N	N
T. aestivum shoot length	***	N	*	N	***	N	N	N	N	N
T. aestivum root length	***	N	N	N	**	N	N	N	N	N

***: significant effect at 99 P % confidence level, **: significant effect at 95 P % confidence level, *: significant effect at 90 P % confidence level, N: no effect

Acknowledgement

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EFFECT OF OPERATIONAL PARAMETERS IN THE CONTINUOUS ANAEROBIC FERMENTATION OF CHEESE WHEY ON TITERS, YIELDS, PRODUCTIVITIES, AND MICROBIAL COMMUNITY STRUCTURES

Joana M. B. Domingos[1,*], Gonzalo A. Martinez[1],
Alberto Scoma[2], Serena Fraraccio[1],
Frederiek-Maarten Kerckhof[2], Nico Boon[2], Maria A. M. Reis[3],
Fabio Fava[1], Lorenzo Bertin[1]

1) Department of Civil, Chemical, Environmental and Materials Engineering (DICAM),
University of Bologna, via Terracini, 28, I-40131 Bologna, Italy
2) Center for Microbial Ecology and Technology – Faculty of Bioscience Engineering,
Gent University, Coupure Links 653, B-9000 Gent, Belgium
3) Department of Chemistry, UCBIO-Requimte, Faculty of Science & Technology,
New University of Lisbon, 2829-516 Caparica, Portugal
**: joana.bendada@unibo.it*

Introduction and study objectives

Volatile fatty acids (VFAs) are short chain aliphatic carboxylic acids, which represent the final product of anaerobic acidogenic fermentation of organic matter. Cheese whey (CW) is a by-product produced in large amounts from dairy industry. It has an important lactose content (44-52 g.L^{-1}), which is responsible for a high chemical oxygen demand (COD), and it can cause severe pollution problems if discharged in the environment. Since lactose can be bioconverted into VFAs under anaerobic acidogenic conditions, VFAs production from CW can represent a valuable alternative to the waste disposal in agreement with the biorefinery concept. One of the most promising perspectives for VFAs employment is their use as the substrate for polyhydroxyalkanoates (PHA) production.

VFAs mixture obtained during the acidogenic process affects the type of obtained PHA. Because of that, it is important to control the process conditions during the acidogenic fermentation such as pH and hydraulic retention time (HRT). Alternatively to the conventional continuous process, cell immobilization strategies can be explored. The packed-bed bioreactors (PBBRs) present some advantages such as the achievement of a higher cell density as well microbial robustness. This allows working at lower HRT by avoiding washout problems and conserving the microbial consortium.

In the present study, the valorisation of CW by producing VFAs by employing an anaerobic acidogenic packed bed bioreactor was proposed.

Methodology

All tests were carried out using a liquid stream composed of water and cheese whey powder (CWP), courtesy of Lactogal (Porto, Portugal), with a final lactose concentration of 15 and 25 g.L^{-1}. No other supplements were added. The inoculum was an anaerobic acidogenic consortium obtained from a membrane bioreactor fed with the same CWP solution.

Small-scale batch experiments were carried out in quadruplicate in 100 mL Pyrex bottles with immobilized material. Three preliminary sequential batches were carried out in order to allow biofilm formation. Afterward, liquid suspensions were centrifuged and pellets re-suspended in fresh CWP solution. The packing material was not washed nor new inoculum added between runs. The final experimental batch run was started by replacing the liquid with fresh CWP solution. Incubation conditions were 37 °C, pH 6 and 150 rpm.

VK samples were withdrawn from microcosms at 0, 5 and 12 days of the last incubation for microbial community characterization, and PCR-DGGE analysis.

A PBBR was set up for continuous process tests with immobilized cells. The PBBR consisted of a 1 L glass column filled with VK (PBBR-VK). The temperature was maintained at 37°C and a recycle line guaranteed the mixing of the liquid phase. The bioreactor outlet and gas were collected in a bottle hydraulically connected to a "Mariotte system". It was operated initially under batch conditions for biofilm development. Thereafter, the PBBR operated under continuous mode at a HRT of 6 days. After 49 days, a third pump was added to continuously supply a NaOH solution (10 M), which sensibly reduced pH variations (HRT6_15). HRT was then decreased to 4 days (HRT4_15). Finally, CWP concentration and HRT were increased to 25 $g_{lactose} \cdot L^{-1}$ and 6 days (HRT6_25).

Liquid samples from PBBRs were withdrawn to analyze the metabolites concentrations. Lactic and lactose concentrations were determined with a HPLC-IR and VFAs with GC-FID. Biogas volume production in small scale batch experiments was measured using a graduated glass syringe, while a "Mariotte" system was connected to the PBBRs. Biogas composition was measured with a µGC, model 3000 A.

Results and conclusions

Small scale batch tests showed that the whole VFAs production process occurred in 9 days via two sequential phases: (a) conversion of lactose into lactic acid and (b) conversion of lactic acid into a mixture of VFAs. The VFAs mixture was mainly composed by acetic, butyric and propionic acids.

The effect of the hydraulic retention time (HRT) and organic loading rate (OLR) were then studied in a benchtop bioreactor (PBBR), which operated continuously. All HRT conditions (4 and 6 days) and lactose feed concentrations (15 and 25 $g \cdot L^{-1}$) allowed yields higher than 75% ($Cmol_{VFAs} \cdot Cmol_{lactose}^{-1}$). As for the VFAs mixture composition, the accumulation of propionic acid was mainly affected by the pH, being it more produced when pH was continuously controlled.

Higher VFAs productions were observed when the PBBR was operated with a HRT of 6 days, ORL of 4.2 $g \cdot L^{-1} \cdot d^{-1}$, and pH 5.8–6, this resulting in 16 $g \cdot L^{-1}$ of total VFAs produced, with a yield higher than 75% ($Cmol_{VFAs} \cdot Cmol_{lactose}^{-1}$). Characterization with Illumina-based sequencing suggested that high VFAs productivities were obtained when microbial community structures developed in the biofilm reactor were highly enriched in few genera.

DIMENSIONAL AND QUANTITATIVE ANALYSIS OF PRODUCTION WASTES FROM PACKAGING INDUSTRY FOR THEIR REVALUATION. THE CASE STUDY OF A ROMANIAN MANUFACTURER

Igor Crețescu[1, *], Teofil Câmpean[1,2],
Teodor Constantin Nechita[1], Adrian Cătălin Puițel[3],
Teodor Măluțan[3], Dan-Alexandru Gavrilescu[3],
Camelia Smaranda[1], Petronela Cozma[1], Maria Gavrilescu[1,4,*]

[1)] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
[2)] Rondocarton SRL, Cluj-Napoca, 2 Aviatorilor Street, 407042 Apahida, Cluj-Napoca, Romania
[3)] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Natural and Synthetic Polymers, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
[4)] Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
[*]: icre@tuiasi.ro, mgav@tuiasi.ro

The ambitious *Circular Economy Package* adopted by European Commission in 2015 proposes actions for product lifecycle safeguarding by "closing the loop" in the production process and bringing benefits for both the environment and the economy through a myriad of recycling/reuse practices. However, there are industrial areas where the circular economy model is based on much more than just recycling. One example is the sector of corrugated board and cardboard packaging manufacturing, where the principles of circular economy can handle all stages of a product's and process' lifecycle: design, production, distribution and use, but also life cycle extending. The present study is developed on this basis, addressing the revaluation of production waste resulted during corrugated board production (A) and carboard box manufacturing (B) (Fig. 1). In the first step (A - production of corrugated board), after conditioning, the paper is corrugated and then non-corrugated, layers are glued over the corrugated paper to form a continuous sheet of cardboard. This is dried and cut into the required dimensions of the packaging plate to be manufactured. In the second step (B - manufacturing of corrugated cardboard boxes), the packaging boxes are made by cutting sheets, folding flaps and gluing the edges. These wastes are in the form of cardboard strips, edges or other similar formats.

A Romanian manufacturer (RM) was selected for dimensional analysis of cardboard waste, because RM established a program to produce other pieces and subassemblies manufactured from corrugated board sheets, perfectly designed, ensuring their optimum operation and thus reducing required storage space and transport costs, compared to similar subassemblies made from wood. We identified the potential of RM to close the production cycle through the efficient reuse of recyclable materials represented by production waste resulted as described above, in the two stages of the technological process, to produce these pieces and subassemblies in the context of existing modern technologies.

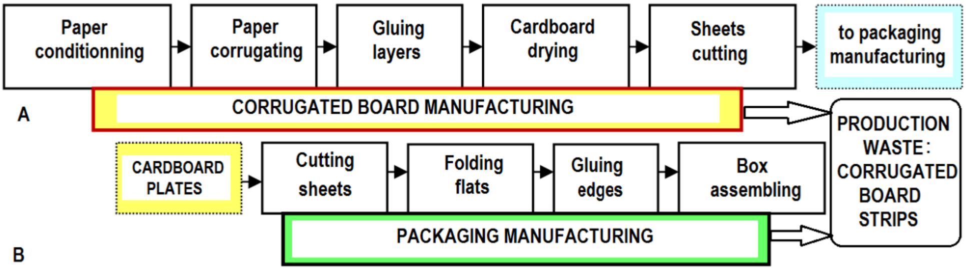

Figure 1: Sources of production waste in corrugated board and packaging boxes manufacturing

In this way, the manufacturers will be able to ensure a longer life cycle of production and products and advanced integrated environmental strategies in activities and decisions regarding production process optimization and development leading towards the zero emissions target in line with the principles of circular economy. This involves the application of strategies and technological solutions based on eco-innovation and eco-design to close the production cycle in an eco-efficient way so as to achieve an ecologic product, potentially marketable and having a great constructive and functional flexibility, in accordance with the requirements of the beneficiaries. Therefore, the eco-innovation principles will be applied for subassemblies so as to be manufactured from production wastes, and then eco-designed according to their final function and eco-efficiency goals.

In order to accomplish this objective, the production wastes will be characterized and estimated in terms of their quantity and production rate, as well as in terms of their dimensions based on a statistical analysis of suitable samples. The applied methodologies will enable waste analyses to achieve results at or above a minimum statistical accuracy in a cost effective way. At least four stages will be covered in the view of waste characterization: (i) pre-investigation; (ii) analysis design and planning; (iii) implementation of waste analysis; (iv) evaluation of waste analysis and interpretation of results.

The versatility of corrugated board production waste will allow their exploitation as valuable materials with enormous potential design capabilities and instant product recognition, reflecting technical and economic realities. In the following phases of the study, the sustainability and ecological footprint of this approach and new product will be assessed based on life cycle methodology.

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AGRO-RESIDUES SUSTAINABLE MANAGEMENT IN SILICATE MATERIALS

Fernanda Andreola[1], Luisa Barbieri[1], Teresa Cotes Palomino[2], Romina D. Farias[2], Isabella Lancellotti[1], Carmen Martínez García[2]

[1)] Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Via P. Vivarelli 10, 41125 Modena, Italy
[2)] Department of Chemical, Environmental and Material Engineering, High Polytechnic School of Linares, University of Jaen, Linares Scientific and Technological Campus, Cinturon Sur, s/n, 23700 Linares, Spain
[*]: luisa.barbieri@unimore.it (L. Barbieri)

Introduction and study objectives

Up to now, the agro-industrial sector is an important resource for the global economy, with very different production realities (milk and derivatives industry, slaughtering of animals and production of cold cuts, manufacturing and processing of fruits and cereal, etc.). In view of this great variety and quantity of waste and by-products becomes strategic their management, within the circular economy point of view. Each type of agro-residue often contains a lot of high value-added substances that constitute a new raw material for possible applications of commercial interest. A sustainable management of such materials may allow, on one side, to reduce the environmental impact of agro-chains, to the other to lower the production costs of new goods.

In this work we report some case studies related to the possibility to exploit the technical characteristics (in particular chemical and mineralogical composition) of some agro-wastes and by-products (rice husk ash, sawdust, grape seeds, cherries seeds, sugar cane ash, sludge from beer wastewater treatment plant, animal bone flour or flour ash and corn cob) in silicate materials (sintered and vitrified) useful for both building and agronomic sector.

Methodology

Agro-residues were firstly characterized mainly by chemical, thermal, mineralogical and microstructural analyses, particle size distribution, carbonate content, etc.. Agro-residues were ground and sieved in order to obtain grain size suitable for the use as raw materials in ceramic batches.

Ceramic bricks were obtained by introducing rice husk ash, RHA, (up to 20 wt%) as silica source or sawdust, grape and cherries seeds (up to 10 wt%) as pouring agents in clays mixtures. The dried and fired brick specimens were characterized following the technical rules. In particular, linear shrinkage, water absorption (24-h immersion), weight loss, rupture modulus, apparent density, CIELab colorimetry, efflorescence were determined on the laboratory fired samples in order to make a comparison with the standard ones.

Spherical pellets of lightweight aggregates were prepared by mixing different percentages (up to 15 wt%) of sludge from beer wastewater treatment plant, animal bone flour and corn cob in two different clay-based mixtures and thermal treated at 900 and 1000°C for 1 hour. Technological parameters such as bulk and absolute density, total porosity, water absorption, pH and electrical specific conductivity were determined in order to test their potential use in agriculture. The characterization was completed by XRD and SEM analyses.

Animal bone flour ash was also used to formulate glass and glass-ceramic fertilizers, with a low and controlled solubility in water of macro nutrient elements useful for plants as P and K.

Results and conclusions

Rietveld-RIR analysis showed that RHA used is mainly constituted by amorphous silica and together with low amount of tridymite and cristobalite phases. The introduction of RHA into brick bodies influences the sintering behavior, in fact higher amounts of RHA avoids the densification due to the presence of residual carbon (8 wt%). This phenomenon did not affect the linear shrinkage% values achieved that remained almost constant and similar to the standard brick (≈0%). On the contrary water absorption% values showed an increase as RHA content increases, addition up to 10 wt% of the residue revealed satisfactory data according to industrial tolerance (WA%=22%). From the mechanical point of view, samples with up to 5 wt% resulted satisfactory (12 MPa) comparing to the industrial limit (10 MPa).

Sawdust, grapes and cherries seeds, due to their organic substances content, during their combustion, bring an energetic support in the bricks firing phase and act as pore forming agent. In particular, grapes and cherries seeds, added in a percentage of 5 wt% to a brick formulation, have better influence with respect to the sawdust, maintaining the mechanical properties of the fired brick (950°C), showing modulus of rupture around 21–23 MPa with a weight reduction of 3–10% with respect to the standard one.

From the preliminary results of sludge from beer wastewater treatment plant and corn cob, it is possible to hypothesize their poring effect in the realization of lightweight aggregates for different application fields. As lightweight substrate/soil for agricultural use: mixtures of 10 and 15 wt% of sludge which presents pH between 7-8. As pH corrector for acid soils, because the mixture of 15 wt% of corn cob showed pH between 8-9. On the other hand further tests were conducted by adding to these mixes (clay-poring agent) 10 wt% of animal bone flour ash or a fertilizer glass-ceramic (P2O5+K2O > 12wt%) obtained from glass cullet, potassium carbonate and animal bone flour. In order to verify the nutrients release of the functionalized lightweight aggregates, tests following European and Italian rules using citric acid solution (2%vol) and distilled water were performed. The results highlighted that mix containing the bone ash releases more amount of nutrient in a short time (30 min) on the contrary the compositions containing the fertilizer glass showed a high release at longer time (21 days). This aspect is important from the environmental point of view because the slow release can avoid the leaching by rain of nutrient elements and their concentration in groundwaters.

EXTRACTION OF PHENOLIC ACIDS FROM WHEAT BRAN WITHIN THE BBI AGRIMAX PROJECT

Maura Ferri[1,2,*], Giulio Zanaroli[2], Annamaria Celli[2], Laura Sisti[2], Annalisa Tassoni[1]

[1)] University of Bologna, Dept. of Biological Geological and Environmental Sciences
[2)] University of Bologna, Dept. of Civil, Chemical, Environmental and Material Engineering
[*]: maura.ferri@unibo.it

Introduction and study objectives

Cereals are the most widely cultivated crops worldwide. Cereal grains are consumed universally and are considered to be one of the most important sources of dietary proteins, carbohydrates, vitamins, minerals and fibres for people all over the world. Wheat, together with maize and rice, accounts for about 90% of the world's cereal production, and for about half of the total cereal production within the EU. Based on previous data wheat has a great importance on EU economy and wheat-derived by-products can be considered as a feedstock for biorefinery development. Current worldwide wheat global production is more than 700 Mt/year and about one-fifth of the cultivated wheat total weight is converted into bran (90 to 150 Mt/year). Currently, it is mainly used as a feed supplement, while the application in the food sector plays only a minor role. However, there is great interest toward innovative strategies for valorising wheat bran through its transformation into added-value biomolecules.

Wheat bran is multi-layered (pericarp, testa, hyaline, aleurone layers and residual starchy endosperm) and consists of different cell types with different chemical compositions. Generally, it comprises approximately 12% water, 13-18% proteins, 57% carbohydrates, 4% fats and 1% phenolic acids. Wheat cell wall contains high amounts of oligosaccharides (such as arabinoxylan dietary fibres) and phenolic acids, mainly ferulic acid that acts as a cross-linker binding to sugar residues. The general composition of wheat bran offers the potential to be used as a substrate in a biorefinery process in order to obtain valuable compounds. To this purpose, different routes of wheat bran valorisation have been recently carried out aiming at the extraction of carbohydrate and/or non-carbohydrate-based products. Target substances in the non-carbohydrate fraction are phenolic acids, vanillin, proteins, amino acids and wheat bran oil. The most abundant phenolic acid in wheat bran is ferulic acid which is mostly linked to cell wall polysaccharides or to lignin via ester and ether bonds. This compound shows several beneficial activities for human health (such as antioxidant, anti-cancer, improving vascular function), and thus has a high potential of application in the food, health and cosmetic industry, but also could be used as key intermediate in the manufacture of polymers such as polyesters.

Methodology

Within the project AGRIMAX (Agri & food waste valorisation co-ops based on flexible multi-feedstocks biorefinery processing technologies for new high added value applications) financed and under the Bio-Based Industries Public-Private Partnership scheme (grant agreement n. 720719), total wheat bran and different bran fractions were collected from Barilla's (Parma, Italy) production site.

The wheat total bran was subject to alkali hydrolysis and enzymatic hydrolysis. Total polyphenol, total hydroxycinnamic acid, protein and reducing sugar releases were quantified by spectrophotometric assays. Ferulic acid yield was evaluated by means of HPLD-DAD analysis.

Results and conclusions

Preliminary results indicated that total polyphenol and total hydroxycinnamic acid yields from alkali hydrolysis may be largely increased (up to 80% for polyphenols) by pre-treatments with protease and/or α-amylase enzymes. Maximum achieved polyphenol level was 32 gGA/kg (g of gallic acid equivalent per kg of bran) and, in the same extract, 237 g protein/kg and 415 g glucose equivalent/kg were also present.

When wheat bran was enzymatically hydrolysed, total polyphenol and total hydroxycinnamic acid yields were slightly lower with respect to sodium hydroxide treatments. Each process leads to two extracts with different composition: the first, obtained after protease/α-amylase pre-treatment, is rich in sugars, amino acids and peptides, the second, obtained at the end of the cell wall enzymatic hydrolysis by xylanase and feruloyl-esterase, is enriched in ferulic acid and shows small amounts of proteins and reducing sugars. Maximum polyphenol level was in total 18 gGA/kg (sum of the two extracts).

HPLC-DAD preliminary quantification of ferulic acid content in the extracts, demonstrated that highest yield was obtained after sodium hydroxide process (up to 2.5-3 g/kg). Xylanase and feruloyl-esterase enzymatic digestion yielded a lower amount of ferulic acid (up to 0.9 g/kg). In both cases, at the end of the process, ferulic acid was recovered with an average purity of 85% (based on HPLC-DAD data).

The results seem to confirm the valorisation of wheat bran by enzymatic processes in order to obtain valuable compounds with several potential industrial exploitations. In the frame of the BBI AGRIMAX project, possible exploitations of the recovered phytochemicals are going to be tested. In particular, ferulic acid will be polymerised for bioplastics, the aqueous residue will be tested as fungi growth medium or for biogas production, and the solid fibrous residue will be tested for nanofiber and biocomposite materials production.

APPLICATION OF STATISTICAL METHODS FOR THE OPTIMIZATION OF THE COMPOSITION OF FEEDSTOCK MIXTURES FOR ANAEROBIC DIGESTION PROCESSES

Giorgia Liberati, Mohammadali Mozafarian,
Gonzalo A. Martinez, Joana M. Bendada Domingos,
Fabio Fava, Lorenzo Bertin*

Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna
*: *lorenzo.bertin@unibo.it*

Introduction and study objectives

Anaerobic digestion is a biological process used industrially to produce biogas from organic matrices. The simultaneous co-digestion of more substrates can improve the stability of the process through the balancing of nutrients, this leading to a higher biogas yield, and the dilution of toxic and inhibitory effects related to a pure substrate. Moreover, this strategy allows the integrated waste management in a predetermined geographic area. However, the substrate features and their relative proportion affect the process. Hence, preliminary tests are necessary to determine the best feedstock mixture. Conventionally, numerous biomethane potential (BMP) tests are carried out on different substrate compositions, this representing a significant commitment in terms of time and resources.

The objective of this study was to evaluate the applicability of experimental designs and statistical methods in order to minimize the number of tests, to identify the optimal substrate composition and to be able to predict the biogas production. In particular, the mixture experimental design has been used to evaluate the synergistic and antagonistic interactions due to the combination of corn stover (CS), grape pomace (GP) and solid residue of olive mill wastewater (OMW). Indeed, the response surface methodology has been used to select the optimal mixture to maximize the co-digestion process in terms of methane yield (ml_{CH4}/g_{VS}) and productivity ($ml_{CH4}/d/ml$). A further objective was therefore to verify the possibility to step forward to anaerobic co-digestion continuous processes, using the proposed statistical approach for optimized-productivity.

Methodology

The selected experimental design was the augmented three factors simplex lattice mixture design. The mixture space is a triangle, whose vertices correspond to pure mixtures (Fig. 1). The second and third edge points correspond to binary mixtures of components, while the internal points correspond to mixtures with different ratios of components. Substrate ratios were fixed as independent variables, while methane yield and productivity were the response variables. Micro-batch reactors were fed with different substrate ratios according to the 22 points of the experimental design. BMP tests were performed in triplicate under thermophilic conditions (50 ± 5°C), using a methanogenic inoculum obtained from an anaerobic co-digestion plant. The micro-reactors consisted of Pyrex bottles with a total volume of 110 ml, fed with a total mass of substrate of about 13 g, an inoculum volume of 36.4 ml and the amount of distilled water needed to reach the operative volume of 50 ml. Therefore, a blank assay with water and inoculum was carried out in triplicate. The total solid content ranged from 10 to 20% while the inoculum substrate ratio ranged from 0.30 to 0.45.

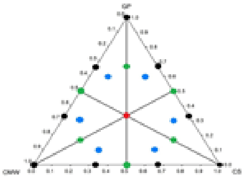


Figure 3: Experimental design mixture space

The experiment lasted 76 days and was monitored three times per week. Each monitoring consisted of the evaluation of the produced biogas, in terms of volume, composition, and pH adjustment (at 7.5).

Results and conclusions

The highest yield of biomethane was obtained from a mixture of the three substrates, and in particular by the assay with the higher proportion of CS and the lower proportion of OMW. The collected experimental data were then fitted to the best polynomial order, and evaluated through the analysis of variance. The quartic and cubic models were chosen for methane yield and productivity, respectively. After having eliminated the insignificant terms, the fitted model for the methane yield was expressed by the equation below, where $\hat{Y}CH_4$ represents the predicted response:

$$\mathbf{\hat{Y}CH_4} = 1000.01\,X^3_{GP}X_{CS} + 1000.01\,X^3_{CS}X_{GP} - 2000.02\,X^2_{GP}X^2_{CS} + 328.01\,X^2_{GP}X_{OMW} - 420.03\,X^2_{GP}X_{CS} + 408.73\,X^2_{CS}X_{OMW} + 420.03\,X^2_{CS}X_{GP} - 328\,X^2_{OMW}X_{GP} - 408.73\,X^2_{OMW}X_{CS} + 172.58\,X_{GP}X_{OMW} + 254.93\,X_{OMW}X_{CS} + a90.11\,X_{GP} + 0.87\,X_{OMW} + 90.71\,X_{CS}$$

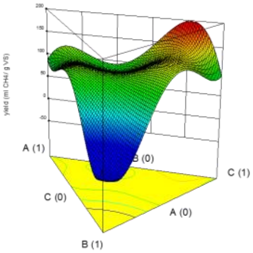


Figure 4: Methane yield fitted model surface

Quadratic and quartic terms allowed the model to predict synergistic and antagonistic interactions. The equation represents the modeled blending surface, graphically visualized by contour and 3D plots. Equivalent equation and plots were obtained for productivity. Employing a response surface method to maximize both responses variables simultaneously, the optimal combination of substrate mixture resulted to be 73% CS, 23% GP and 0% OMW. The predicted response variables values were 183.90 ml_{CH4}/g_{VS} and $0.68ml_{CH4}/d/ml$. The desirability of the mixture was found to be 97.3%. The BMP conducted with the optimum compositions obtained validated the model and the values were found to be comparable with the predictions.

In this study, it was possible to correlate biological behavior and statistical results. Specific evaluations to test the applicability of the predicted values in continuous process are underway. Hence, statistical analysis resulted to be a valuable tool to evaluate the best mixture to use in anaerobic co-digestion processes.

INFLUENCE OF DIFFERENT HYDROTHERMAL PRETREATMENTS ON THE OLIVE MILL SOLID WASTE CHARACTERIZATION AND ITS ANAEROBIC DIGESTION

Fernández Rodríguez María José [1,2],
De La Lama Calvente David[1]; Jiménez Rodríguez Antonia[2]; Borja Padilla Rafael[1]; Rincón Llorente Bárbara[1,*]

[1)] Instituto de la Grasa (CSIC), Campus Universidad Pablo de Olavide. Edificio 46. Ctra. de Utrera Km. 1, 41013 Sevilla, Spain.
[2)] Departamento de Sistemas Físicos y Naturales, Universidad Pablo de Olavide. Ctra. de Utrera, km 1, 41013 Sevilla, Spain
[*]: brlloren@cica.es

Introduction and study objectives

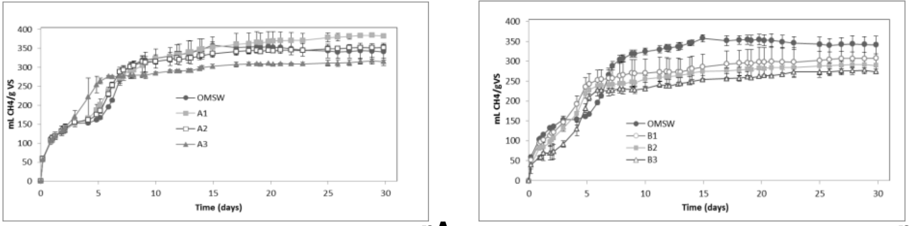
A total of 1,275.700 tons of olive oil is being produced worldwide every year, generating tons of olive mill solid wastes. Olive mill solid waste (OMSW) is the main waste of the olive oil two-phase elaboration system. Due to the high content in organic matter of the OMSW and the high amounts of OMSW produced (800 kg/200 kg of olive oil produced), it is necessary to seek a sustainable treatment for OMSW. Anaerobic digestion has been shown as an effective treatment for organic material reduction and energy production. Because of the composition of the OMSW, with a high content in lignin and celluloses, substrate pretreatments could be a feasible option to increase the methane production during the anaerobic digestion. Pretreatments, in most of the cases, allow the breakage of the complex structures and the solubilization of the organic matter favoring the microorganisms attack and the digestion. This study was focused on how a hydrothermal pretreatment under different conditions affected the OMSW and the subsequent production of methane during anaerobic digestion.

Methodology

Two-phase olive mill solid waste was collected from an Experimental Olive Oil Mill Factory located in the 'Instituto de la Grasa (CSIC)', Seville (Spain). The OMSW was sifted through a 2 mm mesh to remove olive stone pieces before the hydrothermal pretreatments. Two different hydrothermal pretreatments were tested on OMSW in an autoclave (Raypa RFG). Pretreatment A (pA) carried out at 121ºC and a pressure of 1.1bar for 15, 20 and 30 minutes (A1, A2 and A3, respectively) and pretreatment B (pB) carried out at 133ºC and 2.1bar for 15, 20 and 30 minutes (B1, B2 and B3, respectively). The OMSW was analyzed before and after each pretreatment. All substrates were characterized by the measurement of total and soluble chemical oxygen demand (COD and SCOD), total (TS) and volatile solids (VS), total alkalinity (TA), total nitrogen (TN) and pH. Total phenols were also measured. The anaerobic sludge was obtained from an industrial UASB reactor treating brewery wastewater located in Sevilla (Spain). Its main characteristics were: pH: 6.77, TS: 28.7±2.7 g/kg and VS: 22.8±2.3 g/kg. The biochemical methane potential (BMP) test was carried out in a multi-batch reactor system continuously agitated (450 rpm) and thermostated at 35±2 ºC. The ratio inoculum: substrate was 2 (VS basis). Three reactors with inoculum without substrate addition were used as controls.

Results and conclusions

Fig. 1 shows the total methane production obtained for the untreated OMSW (341±20 mL CH_4/g VS) and after pA and pB over a period of 29 days. For both pretreatments, A and B, the methane production increased when the time of the pretreatment increased from 15 to 30 min. For pA the methane obtained was higher than the methane obtained for untreated OMSW for an exposure time of 20 and 30 minutes (A1 and A2) but lower for 15 min exposure (A3) (383±2, 352±8 and 315±10 mL CH_4/g VS for A1, A2 and A3, respectively). For pB the methane production was lower than the obtained for the untreated OMSW in all the cases (308±39, 290±16 and 274±6 mL CH_4/g VS for B1, B2 and B3, respectively).



pA **pB**

Figure 1: pA) Biochemical methane potential (mL CH_4/g VS added) of untreated OMSW (●), treatment A1 (■), treatment A2 (□) and treatment A3 (▲). pB) Biochemical methane potential (mL CH_4/g VS added) of treatment B1 (○), treatment B2 (■) and treatment B3 (△).

SCOD increased from 52,149±555 mg O_2/L to values from 57,121 to 70,925 mg O_2/L in all the cases. Total phenols concentration increased from 2.49±0.1 mg galic acid/g in the untreated OMSW to values from 3.00 to 3.44 mg galic acid/ g for pA and to 3.21-3.51 mg galic acid/g for pB. As a consequence of both pretreatments certain phenols such a as 3,4 dihydroxytyrosol and vanillin (31.8 mg/L and 170,4 mg/L, respectively in the untreated OMSW) were released increasing their concentration over the untreated OMSW. The increase of these phenol concentrations was not inhibitory, it was beneficial. For pA1, the pretreatment which gave the highest methane production, the 3,4 dihydroxytyrosol and vanillin concentrations achieved (563 mg/L and 24.9 mg/L, respectively) were one of the highest obtained. Tyrosol also increased with the pretreatments, nevertheless concentrations of this phenol higher than 290 mg/L, obtained for pB (B1, B2 and B3), gave methane productions lower than the obtained for the untreated OMSW. In this way, this concentration could be considered inhibitory for the process.

The kinetics for methane production was composed for an initial exponential stage, followed for a lag phase and a final sigmoidal stage in all the cases. For pB, the most drastic, the kinetic of the anaerobic process changed slightly. The lag phase was shortened and the sigmoidal part of the curve was smoothed. Despite the shortening of the lag phase during B pretreatment, the final methane production was lower than the methane production obtained for the untreated OMSW. This situation could be produced because during pretreatment B, the most drastic, inhibitory substances for the anaerobic digestion process were solubilized.

Acknowledgements:

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PRODUCTION OF 2,3-BUTANEDIOL FROM GLUCOSE BY *BACILLUS LICHENIFORMIS* ATCC9789: EFFECT OF OXYGEN MASS TRANSFER

Stefano Rebecchi*, Davide Pinelli, Dario Frascari, Fabio Fava, Giulio Zanaroli

Department of Civil, Chemical, Environmental and Materials Engineering (DICAM),
University of Bologna, Bologna, Italy
DICAM, Via Terracini 28, 40131 Bologna, Italy,
**: stefano.rebecchi3@unibo.it*

Introduction and study objectives

2,3-butanediol (2,3-BD) is a platform chemical that is used in pharmaceutical, cosmetics and food industries applications. 2,3-BD can be produced biotechnologically by fermentation of sugars, agricultural residues, glycerol and biomass hydrolizates. Among 2,3-BD producing microorganisms, those of the genus *Bacillus* are non-pathogenic and thus more suitable for industrial application. In particular, *Bacillus licheniformis* is a facultative anaerobe in which 2,3-BD production occurs under microaerobic conditions, being several by-products produced depending on oxygen availability. As the process selectivity is strongly influenced by the dissolved oxygen concentration, a fine tuning of the oxygen mass transfer is necessary in order to maintain proper microaerobic conditions required to obtain a high yield in 2,3-BD. Furthermore, the optimization of the aeration conditions is mandatory in order to scale-up the process. The Design of Experiments (DoE) can be a useful tool to address the optimization of the process, since it allows predicting the impact of variables on one or more responses. Its application to the agitation, namely the rotational speed in a mechanically agitated vessel, and aeration, namely the gas phase volumetric flow rate, as the input variables, can be useful in order to optimize the process and provide a sophisticated tool to control dissolved oxygen concentration in the fermentation medium.

The main aim of the present work was to maximize the fermentation performance (2,3-BD yield and process productivity) and minimize the production of by-products (acetoin and glycerol), by acting a fine tuning of oxygen mass transfer. Specific objects were: i) to apply the DoE to identify the best microaerobic conditions, ii) to estimate an optimal range of oxygen mass transfer rate.

Methodology

Bacillus licheniformis ATCC 9789 was obtained from American Type Culture Collection. The growth medium contained 10 g/L beef extract, 10 g/L peptone from soybean and 5 g/L sodium chloride, whereas a glucose concentration between 20 and 40 g/L was added in the 2,3-BD production phase. The bioproduction tests were carried out in microaerobic conditions in a 1L BIOSTAT B-Twin bioreactor (Sartorius AG, Germany) equipped with pH, temperature, foam and dissolved oxygen probes. The fermentation was carried out at 30 °C and pH 6. Impeller rotational speed (agitation) and gas (air) flow rate (aeration) were set according to the *Central Composite Circumscripted Design* in the range 250-500 rpm and 0.1-0.5 vvm, respectively, and maintained constant during each test. 2,3-BD yield, productivity and selectivity (ratio between masses of 2,3-BD and all products) were chosen as responses. Experimental design and ANOVA were performed with the software MODDE 10.1 (Umetrics, Umeå, Sweden). Moreover, the volumetric mass transfer coefficient (k_La) values were estimated for all the conditions studied in the bioproduction experiments applying a conventional dynamic method. Finally, the actual oxygen transfer rate was estimated measuring the composition of the gas in the bioreactor headspace during the fermentation.

Results and conclusions

According to the ANOVA, the best fitting models for the chosen responses are quadratic equations: yield = $0.458 - 0.017*A + 0.001*B - 0.011*A^2 - 0.034*B^2 - 0.010*AB$, productivity = $0.896 + 0.019*A + 0.131*B - 0.010*A^2 - 0.077*B^2 - 0.048*AB$, selectivity = $0.752 + 0.009*A + 0.109*B + 0.007*A^2 + 0.015*B^2 - 0.017*AB$ (where A=agitation, B=aeration; coded factors). High R^2 (>0.9) and adjusted determination coefficient (R^2 Adj.) for each of the responses indicated the goodness of the models, i.e., that models are capable of fitting the experimental data. Furthermore, the *p*-value and F-value of the models were all <0.05 and the *p*-value of the lack of fit >0.05, indicating the models could be considered significant. Within the range of aeration and agitation considered, the most significant parameters towards BDO yield are aeration and its quadratic term, whereas agitation and its quadratic term are the most significant towards productivity and the process selectivity, being in particular acetoin production favoured at high rpm and glycerol at low rpm. Models validation was assessed performing fermentations at agitation and aeration values chosen randomly within the range considered (data not shown), as well as at values predicted to maximize the 2,3-BD yield, productivity and selectivity (460 rpm and 0.1 vvm). Observed 2,3-BD yield (0.44±0.05 gBD/gGL), productivity (0.86±0.12 g/L/h) and selectivity (88±6 %), were consistent with the models prediction (0.45±0.01 gBD/gGL, 0.95±0.04 g/L/h and 84±3 %, respectively).

The process performance was correlated to the k_La values. A very narrow range of oxygen mass transfer values was determined in which the performance is maximised. These conditions correspond to 9÷15 mmol of oxygen transferred per hour per litre of fermentation medium. Using the same microorganism and glucose as substrate, other researches obtained comparable BD yields (0.42÷0.47 gBD/gGL) with lower or similar productivities (0.12÷0.86 g/L/h). This comparison shows the effectiveness of the DoE approach that allowed a significant improvement in performance. A further significant enhancement in productivity is expected optimising the growth phase.

Acknowledgements:

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DEHALOCOCCOIDIA PHYLOTYPES DEHALOGENATE AROMATIC AND ALIPHATIC ORGANOHALIDES IN TWO SEDIMENTS FROM ADRIATIC SEA

Andrea Nuzzo*, Marco Rocca, Maria Elena Antinori,
Fabio Fava, Giulio Zanaroli

Dept. Civil Chemical Environmental and Material Engineering (DICAM) University of Bologna, via Terracini 28, 40131, Bologna (Italy)
**: andrea.nuzzo@unibo.it*

Introduction and study objectives

Several areas of the Adriatic coast (Italy) are impacted by human activities. Pollutants affecting the area include highly hydrophobic toxic compounds, such as organohalides, which tend to persist into the environment and accumulate in the anoxic layers of sediments. Organohalide-respiring bacteria which grow anaerobically in these layers are able to remove chlorine atoms from such compounds, converting them into less toxic and more biodegradable products. Such activity is known to be carried out by *Dehalococcoidia* microorganisms in freshwater sediments, whereas less is known about its occurrence in marine conditions and the responsible microorganisms.

The aim of this study is to test the dehalogenation capabilities against different organohalides of native microbial communities from sediments of the Venice Lagoon (VL) and the Ravenna harbor (RH) under *in-situ*-like biogeochemical conditions and to identify the main organohalide respiring phylotypes. The organohalides tested were hexachlorobenzene (HCBe), 1,2,3,5-tetrachlorobenzene (TeCBe), pentachlorophenol (PCP), 2,3,5-trichlorophenol (TCP) and trichloroethene (TCE).

Methodology

Slurry microcosms were set up with marine sediment collected from either Venice Lagoon or Ravenna Harbor at 20% dry w/v sediment suspension in their own site water, in 120 ml serum bottles with N_2: CO_2 70:30 headspace, under strict anaerobic conditions. HCBe, TeCBe, PCP, TCP and TCE were spiked at final concentration of 20 mg/l of slurry. Chlorobenzenes were analyzed via batch extraction with 3 volumes of hexane:acetone mixture (9:1) and analyzed via GC-ECD; chlorophenols were analyzed via preliminary separation of water and sediment phase, extraction from sediment with 2 volumes of ethanol and injection of both aqueous phases in HPLC-UV/DAD; chloroethenes were monitored by headspace analysis in GC-ECD and GC-FID using Henry's constant to infer concentrations in the liquid phase. Microbial population was monitored via PCR-DGGE of the 16S rRNA gene of total bacteria and Chloroflexi bacteria.

Results and conclusions

No dehalogenation occurred in any of the sterile controls. Spiked chlorobenzenes were completely depleted in both VL sediment cultures. In particular, HCBe was converted in 9 weeks into 1,3,5-DCBe, and then into 1,3-DCBe; TeCBe followed the same dechlorination pattern (Tab.1). On the other hand, complete depletion of both HCBe and TeCBe occurred in RH sediment cultures accompanied by the accumulation of 1,3,5-TCBe only (Tab.1). No significant dechlorination of PCP occurred in any of the sediment cultures examined, while

TCP was dechlorinated to 3,5-DCP and 3-CP in VL sediment cultures, and to 3,5-CP only in RH sediment cultures (Tab.1). Dechlorination activities were extensive also on TCE on both VL sediment cultures, which accumulated equimolar quantities of *cis-* and *trans*-DCE, and RH sediment cultures, only accumulating *cis*-DCE (Tab.1).

Table 1: Concentrations of chlorinated compounds in sediment cultures during incubation

		Venice Lagoon		**Ravenna Harbor**	
		Week 0	Week 13	Week 0	Week 13
HCBe	(μmol/l slurry)	91.92 ± 10.81	0.92 ± 0.20	85.73 ± 1.22	0.93 ± 0.25
1,3,5-TCBe	(μmol/l slurry)	0.03 ± 0.01	5.91 ± 0.22	-	65.28 ± 0.70
1,3-DCBe	(μmol/l slurry)	0.35 ± 0.05	41.32 ± 3.47	0.03 ± 0.08	0.81 ± 0.05
TeCBe	(μmol/l slurry)	22.73 ± 6.23	1.68 ± 0.28	86.47 ± 2.46	1.16 ± 0.03
1,3,5-TCBe	(μmol/l slurry)	0.02 ± 0.00	14.70 ± 5.74	-	96.54 ± 5.66
1,3-DCBe	(μmol/l slurry)	0.30 ± 0.02	9.14 ± 0.19	-	1.31 ± 0.21
		Week 0	Week 24	Week 0	Week 24
PCP	(μmol/l slurry)	66.53 ± 0.07	55.85 ± 4.27	82.71 ± 19.81	70.74 ± 16.45
-	(μmol/l slurry)	-	-	-	-
2,3,5-TCP	(μmol/l slurry)	101.18 ± 0.39	24.81 ± 32.70	138.22 ± 1.04	30.44 ± 50.70
3,5-DCP	(μmol/l slurry)	0.03 ± 0.01	20.57 ± 27.57	0.38 ± 0.01	88.77 ± 82.80
3-CP	(μmol/l slurry)	-	53.91 ± 5.83	0.36 ± 0.06	1.73 ± 0.64
		Week 15	Week 17	Week 15	Week 17
TCE	(μmol/l total vol)	245.23 ± 18.53	88.35 ± 59.65	196.36 ± 9.64	8.36 ± 10.92
cis-DCE	(μmol/l total vol)	2.06 ± 0.20	32.49 ± 2.35	55.42 ± 83.07	235.60 ± 75.57
trans-DCE	(μmol/l total vol)	1.18 ± 0.30	54.77 ± 40.72	0.20 ± 0.05	1.01 ± 0.52

Microbial community composition evidenced the development of peculiar species in correspondence to dehalogenating activities. In particular, different Chloroflexi could be detected at the end of the dechlorination phase in VL and RH sediment cultures, having 88% to 100% sequence similarities to known organohalide respirers of the non-*Dehalococcoides Dehalococcoidia* subclass. Moreover, two of those phylotypes (VLD-1 and VLD-2) were previously associated with PCB dehalogenation activities in the Venice Lagoon and were detected in all VL dehalogenating cultures, while VLD-1 was the main Chloroflexi enriched in dehalogenating RH sediment cultures.

Microbial reductive dehalogenation activities were already known in VL sediment cultures against PCBs. These findings show that dehalogenating activities of both VL and RH sediment microbial communities are instead efficient over several harmful compounds. The presence of the same dehalogenating phylotypes in different sites suggests a more widespread presence of organohalide respires in the Adriatic Sea and the differences in terms of dehalogenation efficiencies and specificity might depend from peculiar conditions such as the availability of substrates. The isolation and characterization of these phylotypes could be useful to design effective bioremediation approaches for the several polluted portions of the Adriatic coast.

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A LIFE CYCLE APPROACH ON FOOD WASTE MANAGEMENT IN THE FRAME OF CIRCULAR ECONOMY

Cristina Ghinea[1,2], **Elena Diana Comanita**[2], **Maria Gavrilescu**[2,3,*]

[1] Stefan cel Mare University of Suceava, Faculty of Food Engineering, 13 Universitatii Street, 720229 Suceava, Romania
[2] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. dr. doc. Dimitrie Mangeron Street, 700050 Iasi, Romania
[3] Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
*: *mgav@ch.tuiasi.ro*

Large amounts of food are wasted each year: only in Europe almost 88 million tonnes of food waste were generated in 2012, which means that, of 865 kg food produced per person, an amount of 173 kg per person were wasted. In other words, 20% of the total food produced is practically wasted by EU population. The sectors with relevant contribution to food waste are: households (53%), processing industry (19%), production sector (11%), food service (12%), wholesale and retail (5%). There are different reasons for food waste generation like: limitations of agricultural techniques, transportation and storage infrastructure, production surpluses, deterioration of products and packaging, excess purchases, excess portions prepared and errors in food storage etc. It can be observed (Fig. 1) that the main waste categories generated in the EU28 by households are mixed wastes (64%), recyclable waste (17.5%) animal and vegetable waste (13%), while in Romania mixed waste represents 80%, recyclables 18% and animal and vegetables waste only 0.62%. The alternatives applied for solid waste management differ in EU countries. In Romania landfilling is the main elimination method, while composting and recycling is applied in a lower degree (Fig. 2).

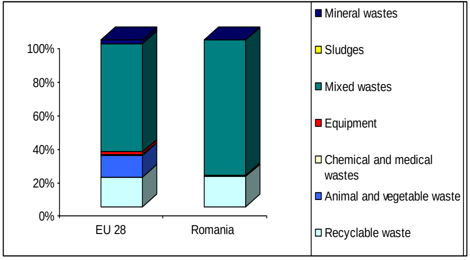

Figure 1: Waste categories generated by households in 2012

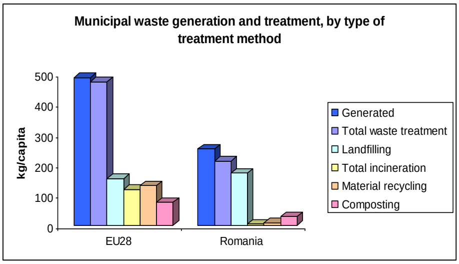

Figure 2: Municipal waste generation and treatment by type of treatment method in 2012

The solid waste management, in general and food waste management, in particular is closely linked with environmental, economic and social impacts. In the last years, a food waste hierarchy has been developed, which includes options for preventing food to become waste (preventable food waste and redistribution to humans and animals) and waste management alternatives as recycling through anaerobic digestion and composting, recovery of valuable fractions, while disposal in landfills continues to be an unfavorable option.

The European Commission considers measures for tackling food waste as a central section of EC new Circular Economy Package entailing the reinforcement of Europe transition towards a circular economy "which will boost global competitiveness, foster sustainable growth and generate new jobs". Circular economy should involve: durability, substitution, standardization, eco-innovation, eco-design, waste prevention and reduction, high-quality waste separation by consumers, actions to minimise the costs of recycling and reuse, industrial symbiosis, new business models etc. The main incentives of the concept of circular economy are based on the current situation: natural resources are limited, resources are consumed too fast or used inefficiently, and large amounts of waste are produced. Moreover, only a small portion of waste produced is returned back to the economic cycle. Therefore, the link between food waste and circular economy (Fig. 3) implies first the reduction of waste amount generated, followed by food reutilization, avoidance of food waste, changes in consumers behavior etc.

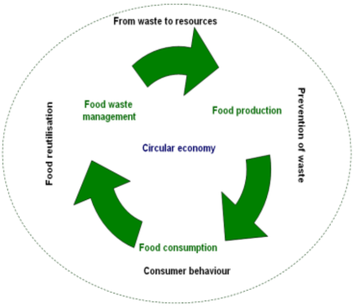

Figure 3: Food and circular economy

The main purpose of this paper is to analyze the food circular system in the context of circular economy, based on a life cycle approach. The following aspects are discussed: food production, consumption and waste generation with the environmental, economic and social aspects related at European and country levels. The research questions were: •*What is the connection between circular economy and food sector? •Could the circular economy be implemented in Romania and how? •Which are the main issues and opportunities related with food waste management? •What is the degree of knowledge of the population on food waste issues? •How diet and habits can influence the amount of food waste generated? •Which are the policies and solutions for food waste prevention and management? •May the following key actions of interventions be considered for waste prevention: education and training, communication and awareness campaigns, procedures for data collection, research and legislation, voluntary agreements etc. and how can be applied?*

Our analysis could offer the scientific support for decision making, planning and actions at national level, so as Romania to reach the targets imposed by EC policy and strategy on food waste management according to circular economy concept and package.

Acknowledgement

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PERSPECTIVES ON THE USE OF AGRO-FOOD WASTES AND GREEN SOLVENTS PRETREATMENT TO MEET BIO-BUTANOL DEMAND IN EUROPE

Alessandra Procentese[1,2,*], Francesca Raganati[3], Giuseppe Olivieri[3], Marco De La Feld[2], Maria Elena Russo[1], Antonio Marzocchella[3]

[1)] Istituto di Ricerche sulla Combustione Consiglio Nazionale delle Ricerche.
P.le V. Tecchio 80, 80125 Napoli, Italy
[2)] ENCO S.r.l. Engineering & Consulting – Via Michelangelo Schipa 115, 80122 Napoli, Italy
[3)] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II
[*]: procentese@irc.cnr.it

Introduction and study objectives

In the last years, first generation biofuels (FGBs) have been overtaken by second generation biofuels (SGBs). Among the difference between FGBs and SGBs, the severity of biomass pretreatment step has been addressed in order to design environmental friendly and energy saving processes aimed at the recovery of sugar fractions from the lignocellulosic feedstock. Moreover, the issue related to the biomass availability in European countries has been addressed by several reviews in the literature even though, to our knowledge, no studies related to the amount of organic waste coming from the food industrial sector have been published so far. Among the novel green processes proposed for biomass pretreatment, lignin extraction with Deep Eutectic Solvents (DESs) seems to be a promising alternative for biomass dissolution and fermentable sugars recovery thanks to their physicochemical properties similar to that of ionic liquids (IL). In addition, use of DESs is less energy consuming and they are more environmental friendly and inexpensive than ILs.

This paper reports a survey of several industrial Agro-Food Wastes (AFWs) available in Europe for the production of butanol as SGB. Data on biomass availability and composition were retrieved for each AFW and combined with experimental results reported in the literature on the butanol yield obtained after AFW pretreatment with DES and ABE fermentation of the sugar fraction. The results provided the potential butanol production rate for the whole set of AFW considered and were compared to the European biofuel demand.

Methodology

Eight industrial AFWs, potentially available for butanol production by biotechnological route, were taken into account: soft drink, grape marc, brewers' spent grains, coffee silverskin, wastes from the "fresh-cut" sector, apple residues, potato peel, sugar beet pulp. The listed industrial AFW were analyzed in terms of the following parameters: i) availability by country, ii) organic composition (hemicellulose,

cellulose, lignin content), iii) seasonal availability, iv) storage requirements, v) operational cost (transport and storage), vi) market price. The maximum butanol productivity ($W_{BUTANOL}$) for each feedstock was assessed as follows:

$$W_{BUTANOL} = W_{RESOURCE} * \Sigma_{FERM\ SUGARS} * Y_{B/Sugars} \quad (1)$$

where $W_{RESOURCE}$ is the annual availability of each waste, $\Sigma_{FERM\ SUGARS}$ is the amount of fermentable sugars in each feedstock, and $Y_{B/Sugars}$ is the butanol yield obtained during fermentation of DES pretreated biomass

Results and conclusions

Table 1 reports an approximate estimation of the maximum butanol productivity assessed with reference to the investigated AFW and butanol yield after DES pretreatment.

Table 1. Maximum expected butanol productivity from European AFWs treated with DES before fermentation process.

Feedstock	European availability (Mt y^{-1})	Sugars composition	Maximum expected butanol productivity (Mt y^{-1})
Soft drink	0.07	50% (mixture of glucose, fructose, saccarose,)	0.006
Grape marc	2	34% cellulose 35% hemicellulose	0.236
Brewers' spent grains	8	12% cellulose 18% hemicellulose	0.415
Coffee silverskin	0.1	10% cellulose 9% hemicellulose	0.003
Apple residues	0.1	21% cellulose 15% hemicellulose	0.006
Potato peels	0.6	8% cellulose 7% hemicellulose	0.016
Sugar beet pulp	7	23% cellulose 36% hemicellulose	0.702
Fresh cut vegetable	1.34	22% cellulose 28% hemicellulose	0.116

The assessed total butanol productivity was about 1.5 Mt yr^{-1} which correspond to $5.5 \cdot 10^{10}$MJ $year^{-1}$ (based on butanol heating value 36.6 MJ kg^{-1}). This value was compared to the European demand for transportation biofuels. Overall European fuel demand is about $1.4 \cdot 10^{13}$MJ $year^{-1}$. Assuming that the need for renewable transportation fuels in the EU will account for 20% of current total fuels demand, $2.8 \cdot 10^{12}$MJ $year^{-1}$ of renewable fuels are expected in Europe. The reported analysis suggests that about 2% of the European biofuels demand for transportation may be replaced by bio-butanol produced using AFWs as feedstock in biorefinery processes including pretreatment with DES and ABE fermentation.

Acknowledgements

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INTERFACIAL ADHESION IMPROVEMENT OF ”ALL WASTES” COMPOSITES BY INTERFACIAL FUNCTIONALIZATION

Mihaela Cosnita, Cristina Cazan, Anca Duta

Transilvania University of Brasov, RTD Dep. Renewable Energy Systems and Recycling,
Eroilor 29, 500036 Brasov, Romania
**: a.duta@unitbv.ro*

Introduction and study objectives

The paper investigates the increase of interfacial bonding in composite materials fully based on wastes of rubber, polyethylene terephtalate (PET), high density polyethylene (HDPE) and wood sawdust. The *interfacial adhesion increase* was controlled *by sodium dodecyl sulphate (SDS 1%) functionalization of composite components* and the composites water stability of was assessed by long term water immersion of composites.

In the actual context of natural resources shortage and sustainable development, the waste-to-products paradigm, has to become a viable strategy of waste management and product development. Globally, an important environmental issue is represented by the waste disposal of tire rubber and plastic. Every year, 1.5 billion tires are manufactured and millions of these are thrown away (500 million of tires are discarded to landfills, yearly) or buried, thus raising serious environmental threats. Additionally, PET and HDPE extensively used as packaging materials, leading thus to impressive annual waste amounts. Thus researches focus on the use of these wastes with addition of natural fibers, as lignocellulosic, in polymeric composite system; often they focus on replacing the synthetic reinforcing agents (eg. glass, carbon fiber, etc) with cellulose based reinforcement. This interest is increasing due to the advantages of natural fiber use: high mechanical performance, processing advantage, no abrasiveness to the manufacturing tools, low cost and density, low energy consumption and last but not least, being a renewable resource. The incompatibility of hydrophobic polymers and hydrophilic wood raises poor interfacial adhesion between fibre-matrix, decreasing the mechanical performance.

In this study, SDS interface functionalization was approached for interface strengthening and to develop novel composites for outdoor products applications.

The rubber-PET-HDPE-wood composites with functionalized components were obtained via compression molding method using a thermostat oven (type ECv 200-300). The processing duration was one hour at 150 ± 5 °C (samples 1), 160 ± 5 °C (samples 2), 190 ± 5 °C (samples 3). The anionic surfactant SDS with $CH_3(CH_2)_{11}OSO_3Na$ formula, mainly being used in the cleaning and hygiene products, was used in a solution of 1 % for components functionalization.

The FTIR data indicate that SDS did not significantly modify the ketone functional groups, but influences hydrocarbon groups, confirming the insertion and interaction between C12 hydrocarbon surfactant structure and composite components. Total absence of C-O-C peak of functionalized HDPE composite (corresponding to 1245 cm-1 wave number) may lead to the conclusion of a preferential adsorption of SDS on this type of functional group.

The SEM images, shown in Fig. 1, prove that the higher value of the curing temperature of composites, the higher mechanical and/or chemical adhesion between components; therefore 1% SDS functionalized HDPE composites obtained at 190°C (H - 3) exhibits the best interfacial adhesion, by comparing with those of lower obtaining temperatures 150 and 160 °C (H - 1 or H - 2), having a more homogeneous surface aspect.

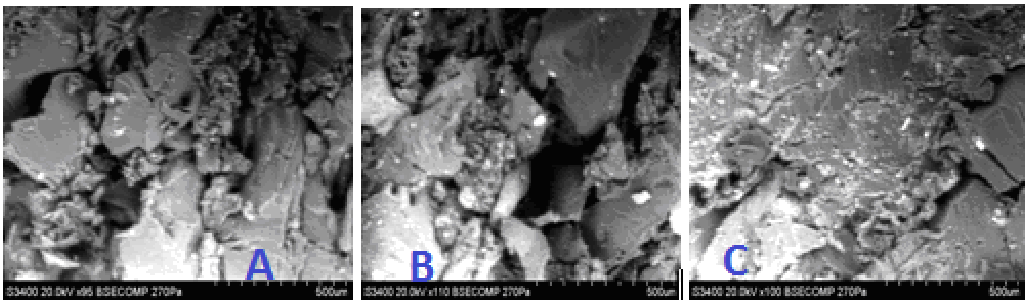


Figure 1: SEM images of HDPE functionalized composites: A) H – 1 ; B) H - 2 ; C) H – 3

These results are in good agreement with the mechanical test results, which recorded for H – 3 composite, the highest tensile strength and high Young's modulus value. The results showed that the composites processed at 190 °C with functionalized HDPE and wood exhibited the highest tensile strength (1.97 and respectively 1.95 MPa). Further water stability tests confirmed the best interfacial strength for SDS functionalized HDPE composite obtained at 190 °C, (2.05 MPa).

MODELLING OF BIO-HYDROGEN PRODUCTION IN STIRRED FERMENTERS BY COMPUTATIONAL FLUID DYNAMICS

Francesco Maluta[1], Giuseppina Montante[2],
Alessandro Paglianti[1]

[1)] Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, via Terracini 34, 40131 Bologna, Italy
[2)] Department of Industrial Chemistry "Toso Montanari", University of Bologna, via Terracini 34, 40131 Bologna, Italy

Introduction and study objectives

The dark fermentation of waste organics to hydrogen is a sustainable and environmental friendly process. It offers great potential and recognized advantages with respect to conventional methods for the production of hydrogen. Besides the biochemical and microbiological factors, the importance of fluid mixing and mass transfer for enhancing biohydrogen production is increasingly recognized. For moving from the laboratory to the production scale, the relationship between design, operating variables and performances of bioreactors should be predictable, since hydrogen productivity and energy efficiency might exhibit important variations depending on the process scale.

This work deals with the modelling of a stirred bioreactor for biohydrogen production from organic wastes. The attached-growth dark fermentation in a dual impeller vortex-ingesting batch stirred bioreactor is considered. The final goal of the vortex-ingesting configuration is to drive the stripping gas towards a membrane separation unit for pure H_2 recovery without adding any external device. The hydrodynamics and H_2 production features of this specific bioreactor were already investigated experimentally. It was proven that with the selected configuration, the process hydrodynamics requirements, such as effective fluid mixing and gas recirculation to strip the dissolved gaseous fermentation products, are fulfilled.

The objective of this work is to present a comprehensive modelling strategy for the prediction of fluid flow features, H_2 production and mass transfer in the bioreactor to be confidently adopted for scale-up. Computational Fluid Dynamics (CFD) has been recently identified as a viable approach for the design and the optimization of biohydrogen fermenters. It is adopted here as the modelling development framework. The modelling challenges for the reliable scale-up of the bioreactors are addressed. The issues which may arise from the adoption of standard CFD tools without proper verification and validation are highlighted.

Methodology

The model is based on the Reynolds Averaged Navier-Stokes equations (RANS) for each phase. The continuity and momentum equations in the RANS Eulerian formulation for a generic phase q, as implemented in the CFD software Fluent 6, are:

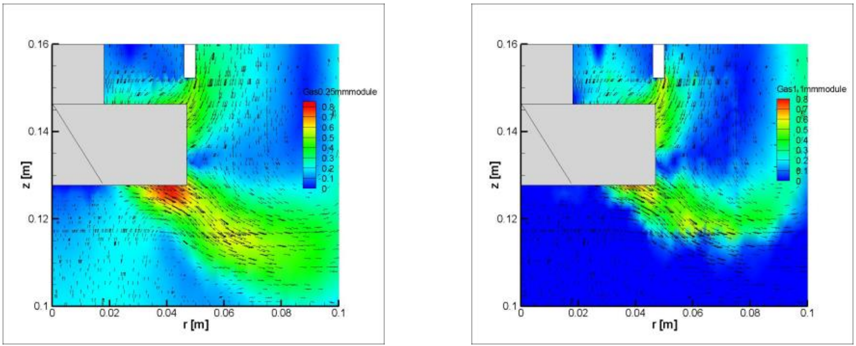
$$\frac{\partial}{\partial t}\left(\alpha_q\right)+\nabla\cdot\left(\alpha_q\mathbf{u}_q\right)=0$$

$$\frac{\partial}{\partial t}\left(\alpha_q\rho_q\mathbf{u}_q\right)+\nabla\cdot\left(\alpha_q\rho_q\mathbf{u}_q\mathbf{u}_q\right)=-\alpha_q\nabla p+\nabla\cdot\overset{=}{\tau}_q+\vec{R}_{pq}+\alpha_q\rho_q\left(\vec{F}_g+\vec{F}_{lift,q}+\vec{F}_{vm,q}\right)$$

where α_q is the volumetric fraction of the phase q, u is the velocity vector, p is the pressure, τ is the Reynolds stress tensor, F_g, F_{lift} and F_{vm} are the gravitational, lift and virtual mass forces, respectively. The inter-phase momentum transfer term, R_{pq}, is modelled via the drag coefficient, C_D, that is calculated by assuming the bubbles as rigid spheres of fixed diameter. The effect of the bubble size and of the Reynolds stress tensor modelling are evaluated by comparing the outcome of different alternatives. The model equations are solved in a computational domain that duplicates the bioreactor already adopted for the experimental characterization. The fluid dynamic equations are coupled with a kinetic model from literature and a mass transfer model to predict the complete bioreactor operative features and its production performances.

Results and conclusions

The effect of bubble size on the gas phase flow field predictions close to the lower impeller are shown in Fig. 1, as an example of the outcome of different modelling choices on the results.



(a) (b)

Figure 1: Gas velocity field close to the bottom impeller (a) db_1=0.25 mm, (b) db_2=1.10 mm.

Overall, the fluid dynamic and operating features of the bioreactor are correctly predicted. The results show that the CFD strategy already developed for simpler gas-liquid stirred vessels can be usefully applied to the design of bioreactors for hydrogen fermentation production, provided that reliable fermentation kinetics and mass transfer models are included. Due to the sensitivity of the results to a number of numerical and modelling parameters, extensive verification and validation are required and particular care is needed in the adoption of CFD for the bioreactors optimization and scale up.

CARBOXYLATES RECOVERY BY SOLID PHASE EXTRACTION AND THEIR EMPLOYMENT FOR POLYHYDROXYALKANOATE PRODUCTION

Salvatore Puccio, Gonzalo Martinez*, Davide Pinelli,
Dario Frascari, Lorenzo Bertin

Department of Civil, Chemical, Environmental and Materials Engineering (DICAM), University of Bologna, via Terracini 28, I-40131 Bologna, Italy
**: gonzalo.martinez3@unibo.it*

Introduction and study objectives

Polyhydroxyalkanoates (PHAs) are microbial polyesters with potential capabilities for substituting the petrochemical-based plastomers, elastomers, latexes or even high-performance polymers. In order to decrease PHAs production costs, several attempts to replace expensive carbon sources with biowaste-deriving ones have been carried out. Particularly, volatile fatty acids (VFAs), which can be produced by processing organic residues under anaerobic acidogenic conditions, were demonstrated to be feasible PHAs precursors. However, the relative low VFAs concentration in anaerobic effluents do not allow feeding such streams into fed-batch culture systems without causing cell dilution. Therefore, an integrated biorefinery scheme was proposed for the valorisation of organic fraction of municipal solid waste (OFMSW) through: i) their anaerobic fermentation for the obtainment of a VFAs-rich stream ($OFMSW_{Acid}$); ii) the recovery of the produced VFAs by solid phase extraction (SPE); iii) the production of PHAs by employing a pure culture of a halophile strain. This integrated strategy would potentially allow producing PHAs at high concentration using a cheap alternative carbon source and unsterilized conditions. All this considered, the aims of the present work were to study the feasibility of recovering the VFAs from $OFMSW_{Acid}$ using an ionic resin, and to utilize the recovered VFAs for PHAs production by employing a pure culture of a halophile strain.

Methodology

Preliminary SPE batch adsorption and desorption tests were carried out with VFA solutions in 2 mL-microplate-weld loaded with 1 mL of liquid and 0.04 g of dried-weak ionic exchange resin Amberlist 21 (Sigma Aldrich) at room temperature (21±1°C). Afterwards, a final batch process was carried out at a larger bench scale (2 L-becker, 100 g of dried resin and 2 L of $OFMSW_{Acid}$ including about 8 g L^{-1} of VFAs) to recover the target carboxylates for PHAs production. An alkaline ethanol solution (0.2 M NaOH, 2 L) was employed for the desorption tests. The powder obtained after ethanol evaporation was employed for the culture medium preparation.

Halomonas boliviensis (DSMZ 15516) was used as the PHAs producer strain. Pre-culture was started from agar plates and pre-grown within 24 h in 500 mL Erlenmeyer flask containing 150 mL of rich medium without any extra carbon source;

incubation conditions were 30 ºC, pH 7.5 and 200 rpm. The experiment was also performed in 500 mL Erlenmeyer flask (150 mL culture media), according to a dual-phase strategy: *i*) balanced growth using glucose (4 g L^{-1}) as the carbon source, and *ii*) PHAs accumulation using the recovered VFAs mixture (about 7 g L^{-1}). In particular, the culture medium consisted on (g L^{-1}): NaCl (45), NH_4Cl (1.5), MgSO4*7H2O (1.9), K_2HPO_4 (2) and yeast extract (2). The culture conditions were those mentioned above. An experimental control group was carried out in parallel to identify potential matrix inhibition from the recovered powder. To this aim, the actual powder was substituted with a VFAs solution prepared in the lab simulating the composition of the $OFMSW_{Acid}$ in terms of VFAs concentrations, also containing the corresponding amounts of inorganic ions such as PO_4^{-2}, SO_4^{-2}, Cl^- and NH_4^+.

Results and conclusions

SPE results using a laboratory prepared-VFAs solution allowed confirming the adsorption isotherm to be of Langmuir type (Fig. 1), with a high VFAs adsorption yield (100 % of the available specific sites). However, the yield diminished when the simulating solution also contained the actual $OFMSW_{Acid}$ inorganic ions (e.g.: PO_4^{-2}, SO_4^{-2}, Cl^- and NH_4^+), which interfered with the carboxylates recovery. Besides, in both previous experiments a physic-sorption was observed since the adsorbed VFAs mixture was much more rich in the VFAs with higher molecular weight. Regarding desorption tests, the process yields depended on the NaOH concentration in the ethanol solution. A complete desorption was observed by the occurrence of a stoichiometric ratio between the carboxylic groups attached to the resin and the OH^- ones. A yellowish powder was obtained when recovering VFAs from $OFMSW_{Acid}$. It contained only 0.12 g_{VFAs} g_{DM}^{-1} due to the presence of inorganic ions and other organic compounds original contained in the matrix.

PHAs were produced using the recovered VFAs-containing powder. Final cell concentration and PHAs content were 3 g L^{-1} and 42%, respectively. VFAs yielded 0.35 g_{PHAs} g_{VFAs}^{-1}, in agreement with the literature. No matrix inhibition was detected when using the actual $OFMSW_{Acid}$.

In conclusion, preliminary experiences demonstrated the overall strategy feasibility.

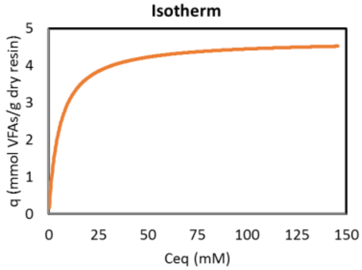


Figure 1: VFAs adsorption isotherm using Amberlist 21

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POTATO PEEL AS A FEEDSTOCK FOR BIOBUTANOL PRODUCTION

María Hijosa-Valsero*, Ana Isabel Paniagua-García, Rebeca Díez-Antolínez

Centro de Biocombustibles y Bioproductos, Instituto Tecnológico Agrario de Castilla y León (ITACyL); Polígono Agroindustrial del Órbigo, Parcelas 2-6, E-24358, Villarejo de Órbigo, León, Spain
**: hijvalma@itacyl.es*

Introduction and study objectives

The concept of biorefinery appeared during the 1990s as a result of the scarcity of fossil fuels and the growing trend in the use of biomass as a raw material. The purpose of biorefineries is the generation of biofuels, energy, biomolecules and non-food products from (preferably residual) biomass without competing with other sectors. Among these bioproducts, 1-butanol has awakened interest, due to its numerous industrial applications as solvent, extractant, base-product or biofuel. Nowadays, butanol is mainly produced via petrochemical processes, because the traditional industrial ABE fermentation employed expensive raw materials, like cereals, potatoes or corn. However, the use of residual lignocellulosic biomass could make the industrial biobutanol fermentation profitable again, provided that **adequate pretreatments** exist to release simple sugars from the complex lignocellulosic network.

In the present work, potato peels coming from a snack industry were studied as a possible raw material for biobutanol production. Five different soft physicochemical pretreatments (autohydrolysis, acids, alkalis, organic solvents or surfactants) were applied to potato peel. The pretreated biomass was subsequently subjected to a conventional enzymatic treatment to complete the hydrolysis. The main objective of the pretreatment step was to maximize the amount of simple sugars released and to minimize the generation of fermentation inhibitors. Finally, the fermentability of the obtained hydrolysates was assessed with the butanol-producing bacterium, *Clostridium beijerinckii*.

Methodology

Potato peel was dried, ground and sieved to a particle size of 0.5-1 mm before being subjected to each pretreatment. In a preliminary step, different acids, alkalis, organic solvents and surfactants were compared in order to choose the most suitable for potato peel hydrolysis. Finally, water (autohydrolysis), HNO_3 (acid), NH_4OH (alkali), acetone (organic solvent) and PEG 6000 (surfactant) were selected as reagents. Then, the physicochemical pretreatment process was optimised via response surface methodology (RSM) to determine the most appropriate values for operational parameters (temperature, time and amount of reagent) in a high pressure reactor; with a biomass-to-water ratio of 10 % (w/w). The next step consisted of an enzymatic hydrolysis to break down cellulose and hemicellulose with the aim of releasing simple fermentable sugars. The enzymatic hydrolysis was performed directly on the pretreatment slurry coming from the reactor (i.e. without separating the solid biomass and the liquid pre-hydrolysate), and it was carried out at pH 5.0 (50 mM citrate buffer), 50 °C and 180 rpm, during 72 h. The enzymes used were Cellic CTec2 (Novozymes, Tianjin, China) and Spirizyme Fuel (Novozymes, Bagsvaerd, Denmark). Once the experiments were finished, the RSM equations were calculated and values for temperature, time and reagent amount in the reactor were estimated and experimentally validated in order to maximise total sugar concentration and to minimise inhibitor concentrations in the final hydrolysates.

For fermentability tests, hydrolysates were supplemented with nutrients (NH_4Cl, K_2HPO_4, KH_2PO_4, $FeSO_4$, $MgSO_4$, yeast extract and cysteine), the initial pH was adjusted to 6.00 and the strain *C. beijerinckii* CECT 508 was inoculated. The fermentation was performed at 35 ºC and 100 rpm under anaerobic conditions. The pH was controlled by adding $CaCO_3$ to the fermentation media.

Sugars (glucose, xylose, cellobiose, maltose, rhamnose, arabinose) and some inhibitors (acetic, formic and levulinic acids, furfural and 5-hydroxymethylfurfural) were analysed by HPLC-RID. Other inhibitors (total phenolic compounds) were analysed by Folin-Denis' assay. Fermentation metabolites (acetone, butanol, ethanol) were analysed by GC-FID.

Results and conclusions

Optimal pretreatment conditions were 140 ºC and 56 min for autohydrolysis; 110 ºC and 83 min for 1.81% HNO3; 112 ºC and 29 min for 2.0% NH4OH; 128 ºC and 85 min for 10% acetone; and 146 ºC and 5 min for 1.92% PEG 6000. Nitric acid hydrolysis released the highest amount of total sugars (44 g/L), but also the greatest concentration of inhibitors (0.6 g/L formic acid, 1 g/L acetic acid, 0.02 g/L furfural, 0.06 g/L 5-HMF and 0.4 g/L phenolic compounds). For all the other pretreatments, the amount of released sugars ranged 35-39 g/L, with inhibitor concentrations about 0.1-0.3 g/L formic acid, 0.5-1.1 g/L acetic acid, <0.02 g/L furfural and 5-HMF and 0.4-0.5 g/L phenolic compounds. All the hydrolysates were tested for fermentability, obtaining the following butanol concentrations after 96 h: 3.7 g/L for autohydrolysis, 0.2 g/L for HNO3, 0.1 g/L for NH4OH, 0.1 g/L for acetone and 2.8 g/L for PEG 6000. Control fermentations attained 8.4 g/L butanol for HNO3 and 5.0 g/L for the other pretreatments. Currently, new experiments are being performed to improve butanol production by optimising nutrient addition, pH control and other operational parameters.

In conclusion, autohydrolysis followed by enzymatic hydrolysis could be a suitable pretreatment for potato peel, since it produces a fermentable broth which can be used for butanol production.

Acknowledgements

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TECHNICAL EVALUATION OF BIOGAS PRODUCTION FROM COSMETICS INDUSTRIAL WASTE

Francesca Demichelis, Maurizio Onofrio, Silvia Fiore*

DIATI, Department of Engineering for Environmental, Land and Infrastructures,
Politecnico di Torino,corso Duca degli Abruzzi 24, 10129, Turin, Italy
**: silvia.fiore@polito.it (S. Fiore)*

Introduction and study objectives

The extensive consumption of fossil fuels, the inflation of crude petroleum price and the environmental-political pressure drive industrial world towards green-resources, such as biomass and waste, and imply noteworthy environmental and social advantages.

This study is focused on anaerobic digestion (AD) of the waste (300 t/y in 2015) generated by a L'Oréal plant located in Turin area. Four residues, combined in a mixture according to their relative abundance, were considered: sludge from wastewater treatment plant (WWTP), residues of shampoo and conditioner, sludge from mascara production and food waste from the canteen. All waste is characterized by a low biodegradability and 44%-wt is classified as hazardous because of the high organic content (COD_{tot} 624÷1436 mg/g), and therefore it is now incinerated. The aim of the research is the evaluation of the technical feasibility of AD of unaltered and pre-treated (to enhance methane yield) waste mixture. The novelty of the approach is the implementation of AD in a usual industrial context (personal care and make-up production) as a key-practice to improve the sustainability of the overall productive process.

Methodology

The four wastes were characterised considering Total Solids (TS), Volatile Solids (VS), pH through GTM24 (pH340 WTM pH-meter), chemical oxygen demand (total and soluble COD) and elemental analysis (CHNSO Thermo Scientific Flash 2000). AD laboratory tests were carried out in 0.5 L Pyrex glass bottles (Duran, Germany) connected by 6 mm Teflon tubes (PTFE, Germany) to 2.5 L Tedlar gas bags with a push-lock valve. Biogas and methane measurement was performed through water displacement. Methane was measured inserting a 2L bottle (Duran, Germany) filled up with 1.8 L of water and phenolphthalein between the digester and the gas bag to remove carbon dioxide. AD tests were performed in batch mode feeding 5% TS and 1:1 inoculum to substrate ratio. Incubation was carried out in a water bath (Julabo Corio-C) at 35°C. AD batch reactors were manually shaken every 2h during daytime. 8 reactors were prepared for each trial: 3 replicates for biogas measurement and 3 for methane, plus 2 replicates for the inoculum alone (blank). AD tests were arrested when the marginal biogas production was below 1%. The investigated pre-treatment was a thermo-alkaline- sonication process carried out with 0.8%-wt NaOH at 80°C for 15 min at 45 KHz (WWR Ultrasonic cleaner USC 300^{TH}). Pre-treatment's performance was evaluated through disintegration rate (DR, the ratio between total and soluble COD after and before pre-treatment). Finally, first order kinetic disintegration constant (k_d) values were calculated.

Results and conclusions

Waste mixture was designed according to relative abundance of the single residues: 53%-wt sludge from WWTP, 31%-wt residues of shampoo and conditioner, 13%-wt sludge from mascara production and 2%-wt food waste. Before AD tests, the unaltered and pre-treated mixtures were compared about soluble COD (CODs) content and DR was calculated. CODs values were equal to 264.37 mg/g_{SV} and 497 mg/g_{SV} respectively for the unaltered and pre-treated mixture. Thus, the thermo-alkaline-sonication pre-treatment achieved a DR equal to 66.1%. AD tests accomplished net yields (Fig.1) equal to 0.10 Nm^3/kg_{VS} biogas and 0.06 Nm^3/kg_{VS} CH4 from the unaltered mixture and to 0.20 Nm^3/kg_{VS} and 0.14 Nm^3/kg_{VS} CH4 from pre-treated mixture, witnessing the efficiency of the proposed pre-treatment.

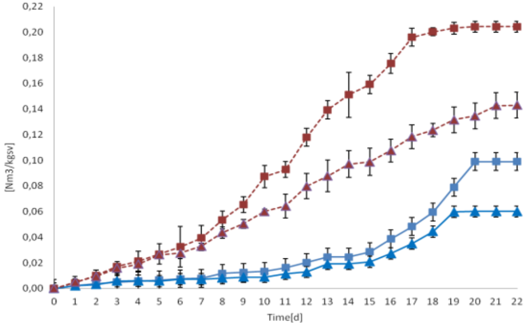


Figure 1: Biogas production gathered from unaltered (continue line, squares) and pre-treated mixture (dotted line, squares) and methane gathered from unaltered (continue line, triangles) and pre-treated mixture (dotted line, triangles).

k_d values equal to 0.11 d^{-1} for the unaltered mixture and 0.16 d^{-1} for the pre-treated mixture supported the improvement of hydrolysis, which represents the limiting-rate step of the overall process. Therefore, the achieved results assured undeniable evidence to the technical feasibility of the investigated chain (pre-treatment and AD) for the valorization of the considered industrial waste materials. Pre-treatment provided important and subsequent benefits: significant improvement of hydrolysis rate (45%) and thus of biodegradability, therefore biogas (50%) and methane (57%) yields were considerably enhanced.

Acknowledgements

The authors gratefully acknowledge L'Orèal Saipo Industriale SpA for the financial support to the research

SUCCINATE PRODUCTION BY ACTINOBACILLUS SUCCINOGENES: PACKED BED BIOREACTOR TESTS

Alessandro Ragini[1], Luca Longanesi[1], Cecilia Spagni[1], Heleen DeWever[2], Dario Frascari[1], Davide Pinelli[1,*]

[1) University of Bologna, Dept. of Civil, Chemical, Environmental and Materials Engineering, Italy.
[2) Flemish Institute For Technology – Mol, Belgium
[*]: davide.pinelli@unibo.it

Introduction and study objectives

Succinic acid (SA), an intermediate of the tricarboxylic acid cycle, was recently recognized as one of the top 10 building blocks according to the U.S. Department of Energy. It has a large number of industrial applications in the cosmetic, chemical, agriculture and food sectors. SA is traditionally manufactured from oil, but it can be easily produced by anaerobic fermentation. The SA biochemical production process fixes 1 mole of CO_2 for each mole of produced SA, thus providing a clear advantage in terms of carbon footprint of the process. Different microorganisms were recognized as natural high-yield SA producers. While most studies focused on SA production in suspended cell bioreactors, only few works report an effective biofilm–based SA production process, exclusively with *A. succinogenes*. The goals of this study were: i) to carry out a screening between 5 commercial carriers for *A. succinogenes* biofilm immobilization; ii) to scale–up the process to a 1 L packed-bed column bioreactor; and iii) to evaluate the feasibility of the process in repeated batch mode.

Methodology

Actinobacillus succinogenes (ATCC 55618) was obtained from the DSMZ collection. Five commercial biomass carriers with high surface area (250-900 m^2/m^3) were investigated: three are ceramic/glass carriers (Poraver®, Biomax®, Glaxstone®) and two are high density polyethylene carriers (Kaldnes K1® and Bio–Flo 9 Sinker®). The initial batch tests to select the optimal carrier were carried out in 116 mL glass anaerobic bioreactors, containing 60 mL of carriers. The bioreactors were incubated in an orbital shaker (at 37°C, 100 rpm). The headspace was flushed with either N_2 or CO_2. Two subsequent fermentation steps were designed and optimized to establish a reliable procedure for (i) microorganism growth and immobilization, in the absence of CO_2 (growth phase), and (ii) SA production in the presence of CO_2 (production phase). Glucose and lactose (LAC), the main component of cheese whey, were used as substrates. A packed bed bioreactor (PBBR) was used to study the feasibility of a repeated batch process. The main part of the plant was a 1.04 L glass column packed with 840 grams of Glaxstone®. The bottom of the column was connected through a peristaltic pump to a 2 L bottle used as a medium reservoir. The liquid, fed to the bottom of the column, was then recirculated into the bottle. The medium in the bottle was agitated with a magnetic stirrer at 500 rpm, to maintain a suitable gas–liquid mass transfer. Both the reservoir headspace and the top of the column were connected to a pure CO_2 bag. All the plant was kept at 37° and at constant pH=6.5.

Results and conclusions

Five triplicate tests were monitored for 30 hours using the same LAC concentration (7 g/L), under the same conditions, but using attached biomass grown on the five studied carriers. Poraver® and Glaxstone® showed the highest SA formation rates (0.4-0.5 g h^{-1} L^{-1}) and the highest final SA concentrations (4.7-5.9 g/L). Attached and suspended cell concentrations were measured at the end of the tests. Glaxstone® and Poraver® led to a similar biomass composition: 67% attached cells, 33% suspended cells. The specific rates were calculated by dividing the observed rates (initial slopes) by the total (suspended + attached) biomass concentrations. The specific rates observed with Glaxstone® were always higher than those obtained with Poraver®. Glaxstone® was thus chosen as the carrier for the following packed bed bioreactor tests.

The batch SA production tests by attached cells of A. succinogenes were carried out in a 1 L PBBR packed with Glaxstone® as biofilm carrier. Five tests were carried out at increasing initial lactose concentrations, to evaluate biofilm stability during SA production in a repeated batch mode. A first 48-hour growth phase was initially performed to establish the biofilm in the packed bed. Then two SA production tests were run at 8 and 12 g/L initial lactose concentrations. Finally, after another 48-hour growth step, three repeated bioproduction phases with 16 g/L of lactose were performed. The results are shown in Fig. 1. Low and similar SA final concentrations were detected in the first two tests at 8 and 12 g/L of initial lactose concentration suggesting that a thin biofilm had developed in the PBBR. Another 48h biofilm growth phase was carried out before the last three consecutive tests, conducted with 16 g/L of lactose. These tests showed a stable bioactivity. The final performance was comparable to that observed in the microcosm tests: final SA concentration = 8.0-8.7 g/L, SA production rate = 0.7-1.0 g h^{-1} L^{-1}, SA/LAC yield = 60-64%. At the end of the 16 g/L tests, some carriers were sampled from the inlet, middle and outlet sections of the packed bed and analysed for biomass concentration: the attached biomass resulted homogeneous (1.9 g$_{protein}$/kg$_{carrier}$), but lower than that measured in the small-scale batch bioreactor tests (2.6 g$_{protein}$/kg$_{carrier}$).

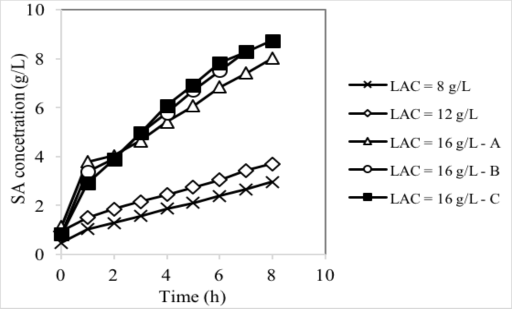


Figure 1: Succinic acid concentration profiles in the PBBR tests.

An innovative, efficient, reliable and effective method for A. succinogenes immobilization was developed on the selected Glaxstone® carrier. Satisfactory SA production performances were measured both in the small-scale batch bioreactors and in the 1 L packed bed bioreactor. The results indicate that a stable biofilm can be obtained also under flow conditions, with a homogeneous biomass concentration along the packed bed.

HIGH – PERFORMANCE THERMAL REMEDIATION OF PAH – CONTAMINATED SOILS BASED ON MICROWAVE IRRADIATION

Guido De Guidi[1,2,*], Pietro P. Falciglia[3], Alfio Catalfo[1], Federico G.A. Vagliasindi[3]

[1)] Dipartimento di Scienze Chimiche, Università di Catania, Catania, Italy
[2)] Centro di ricerca per l'analisi, il monitoraggio e le metodologie di minimizzazione del rischio ambientale (CRAM3RA), Università di Catania, Italy
[3)] Department of Civil Engineering and Architecture, University of Catania, Catania, Italy
[*]: gdeguidi@unict.it

Introduction and study objectives

Due to ecotoxicity and carcinogenicity effects of polycyclic aromatic hydrocarbons (PAHs), their presence in the environment is a major concern worldwide. PAHs are a group of organic compounds with two or more fused aromatic rings of carbons and hydrogen atoms, mainly generated by the incomplete combustion or pyrolysis of fossil organic matter. PAH high hydrophobicity and strong interaction with minerals and organic matter, make soils their ultimate sink. European Environment Agency (EEA) reported that more than 30,000 sites in Europe are affcted by PAH soil contamination phenomena.

Therefore, Remediation of PAH - contaminated soils is of great importance for the society, however, based on recent literature findings, it remains a great challenge for scientific and technical communities, due to PAH persistence, low solubility and biodegradability.

Microwave heating (MWH) remediation has recently been proposed as a high – performance treatment for the removal of several organic (i.e.: petrol hydrocarbons, diesel, PCB) contaminants from soils. The main driving force of MWH is their higher ability to heat the contaminated matrix very uniformly and rapidly than conventional thermal remediation. In situ MWH treatment mainly includes the irradiation of the contaminated soil by means of specific antennas, which results in a heat generation and, thus, in a vaporization of the contaminants (Figure 1).

The main goal of this study was the assessment of the potential of the MWH in situ application for PAH – contaminated soil remediation. Specific objectives were made investigating the effects of various operating conditions on contaminant removal kinetics and mechanisms.

Methodology

A model sandy soil was artificially contaminated with a solution containing 9 selected PAHs, namely Bph, Flu, Phe, Ant, Flt, Pyr, BaA, Chr and Per in dichloromethane. The solution - soil mixture was mixed for 1 hour. Afterward, the solvent was entirely removed from soil by means of a rotavapor system. After spiking procedure, soil samples were stored for six months before extraction and HPLC analysis for contaminant content and MW irradiation tests. Analysis showed an average initial total PAH concentration of 227 mg kg^{-1}.

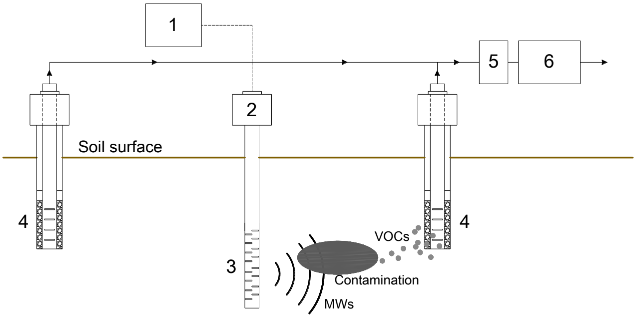


Figure 1: Schematic of in situ microwave plant for polluted soil remediation. 1) Power supply; 2) MW generator (magnetron); 3) antenna; 4) VOC extraction well; 5) water/vapour phase separation system; 6) water/vapour-treatment plant.

MW remediation application was simulated at the bench scale using a dedicated setup, able to generate a maximum MW irradiation power of 1.0 kW at the frequency of 2.45 GHz. The irradiation cavity was connected to an exhaust gas line for volatile organic compound (VOC) capture – treatment system. For each test, 20 g of PAH - contaminated soil were placed in the setup cavity and irradiated for a maximum time of 60 min, applying powers up to 1 kW. During the irradiation, the soil sample temperature (T) was measured with a type - k thermocouple system. At the end of the tests, PAH residual concentration in soil samples, as well as in the VOC capture line with generated byproducts were assessed.

Results and conclusions

Main results showed that the investigated treatment was very effective for the remediation of PAH – contaminated soils. In general, data showed that contaminant chemical – physical features, especially polarity, significantly influence the final temperature achievable and PAH contaminant removal kinetics. Specifically, a 70 – 100% removal range was observed within 10 min of MW irradiation, when a power of 1 kW was applied. Depending on the single PAH specific feature, different PAH removal kinetics were observed. Overall, four different PAH removal mechanisms were observed: (i) thermal desorption vaporization; (ii) molecular bond breaking; (iii) selective heating vaporization; (iv) contaminant stripping due to steam distillation processes. Obtained kinetics are useful for predicting the response of future remediation activities, as well as for guiding the design and the scaling-up of MW treatment systems. PAH removal mechanism results will also provide basic information and could be helpful in developing novel MW remediation technologies for soils contaminated with PAHs.

THE USE OF UP-FLOW PERCOLATION TEST TO ASSESS THE ENVIRONMENTAL PROPERTIES OF RAW AND TREATED FLY ASH

Vladana N. Rajakovic-Ognjanovic[1,*], **Milica Karanac**[2], **Jasna Smolar**[3], **Ana Petkovsek**[3], **Maja Đolić**[4], **Jovan Despotovic**[1]

[1] Institute of Hydrotechnics and Environmental Engineering, Faculty of Civil Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, 11 000 Belgrade
[2] Innovation Center of Faculty of Technology and Metallurgy ltd. In Belgrade, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia
[3] Chair for Soil Mechanics with Laboratory, University of Ljubljana, Faculty of Civil and Geodetic Engineering, Jamova 2, 1000 Ljubljana, Slovenia
[4] Vinča Institute of Nuclear Sciences, University of Belgrade, 11001 Belgrade, Serbia
**: vladana@grf.bg.ac.rs*

Introduction and study objectives

Thermal Power Plants (TPP) in Republic of Serbia produce annually app. 7 millions of tons of fly ash which has not been utilized yet as alternative material in civil engineering, hydrotechnics, agronomy, etc. Use of fly ash is has many benefits among which the most important are: saving natural resources from further exploitation, reduction of disposal areas and costs and sustainable management within the philosophy of circular economy.

The environmental acceptability of fly ash as alternative material can be controlled by different types of leaching tests. In this paper the results of up-flow percolation tests, performed on raw fly ash and lime and cement treated fly ash from the thermal power plant Morava are presented. The decision for using the up-flow percolation test was made on the basis of the previous research results, which proved that the up-flow percolation test correspond well to the results of field lysimeter test.

Methodology

Within the scope of environmental characterization of fly ash, the list of physico-chemical parameters which must be analyzed are given in procedures defined by European Commission. As the raw Morava fly ash exhibit excessive leachates of Sb, As and Se (Table 1), the lime and cement were used to study the possibility of reducing the environmental impact of fly ash.

Laboratory mixtures were prepared by using the 5% of hydrated lime (Ca(OH)2) and the 5% of cement (the composition is a mixture of CaO (stable) 62-67%, SiO2 19-25%, Al2O3 2-8%, Fe2O3 1-5%, SO3 3-4,5%, CaO (free) 2%, MgO 5%, Na2O and K2O 0,5-1,3%). Mixtures were statically compacted and aged in controlled conditions for 28 days. Aged samples were installed into the apparatus, presented in Figure 1, for up-flow percolation test according to CEN/TS 14405:2004. Eluates were taken in 7 sampling campaigns until the liquid to solid ratio (L/S) 10 was achieved. The eluates from each sampling campaign was analyzed and the decisive parameters are given for L/S = 10. Chemical analysis of eluates was made by using induced-coupled plasma-mass spectrometry (ICP-MS) and graphite-furnace atomic absorption spectrometry (GF-AAS) instruments.

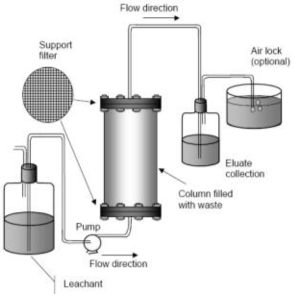


Figure 1: Equipment for up-flow percolation test.

Results and conclusions

The obtained results are presented in Table 1, along with the limiting values for inert wastes according to European regulations. Results show, that the release of heavy metals from the fly ash can be significantly reduced by the use of lime and/or cement. The optimal amount of stabilizing agents needs additional investigations. Future investigations have to include optimization of the amount of stabilizing agent in order to obtain all values of heavy metals below limiting values. Perhaps even extensive use of different agents has to be included in investigation. One of the options is to try to use gypsum (CaSO4), as a modifying and stabilizing agent, since it is one of the side-products of desulphurization process (operation performed within thermal power plants in Republic of Serbia).

Table 1: Up-flow tests result for heavy metals in raw and treated Morava fly ash (FAM)

The parameter	**Unit**	**Sample**			**Limiting values, mg/L**
		FAM	**FAM + 5% lime**	**FAM + 5% cement**	
		Measured values, mg/L			
Sb	mg/L	**0.32**	**0.10**	**0.53**	0.06
As		**2.16**	0.30	0.23	0.50
Cu		1.05	0.10	0.11	2
Ba		0.36	1.10	1.05	20
Cd		0.01	0.00	0.05	0.04
Ni		0.11	0.20	0.11	0.40
Pb		0.11	0.20	0.21	0.50
Se		**0.32**	0.10	**1.18**	0.10
Cr		0.12	0.50	0.19	0.50
Zn		0.74	0.50	0.53	4.00
SO_4^{2-}		**3212.54**	293.30	354.64	1000 (6000)
F^-		5.88	0.10	4.56	10

PHYTOREMEDIATION POTENTIAL OF *MISCANTHUS* X *GIGANTEUS* AND *SPARTINA PECTINATA* CULTIVATED ON SITES CONTAMINATED WITH HEAVY METALS

Krzyżak Jacek[1*], Pogrzeba Marta[1], Rusinowski Szymon[1], Hebner Anja[2]

[1)] Institute for Ecology of Industrial Areas, Katowice, Poland; 6 Kossutha St., 40-844 Katowice, Poland
[2)] Vita34 AG, Business Unit BioPlanta, Leipzig, Germany
[*]: j.krzyzak@ietu.pl,

Introduction and study objectives

Currently, the majority of biofuels originate from food crops grown on agricultural land, whereas most of the wooden biomass used for energy production are of forestry origin. In order to avoid tension between food and fuel production, energy crops should be grown on low quality agricultural land wherever possible. It makes marginal and degraded land a favourable place for cultivating energy crops. The cultivation of energy crops on heavy metals contaminated (HMC) areas offer opportunities, which combine site remediation with energy recovery. The aim of the study was to investigate the phytoremediation potential of two perennial energy grass species, *Miscanthus* x *giganteus* and *Spartina pectinata*, cultivated under different fertilisation on arable land (Bytom, Poland) and former sewage sludge deposit site (Leipzig, Germany) contaminated with lead, cadmium and zinc.

Methodology

Experimental trials were established in May 2014. At both of areas plots 16m2 each were established. Three representative soil samples were taken from each of the plots at 0-20 cm depth, to determine the basic parameters as well as heavy metal total and bioavailable fraction content. On each 16m2 plots, 49 seedlings were planted (3 plants per 1 m2). Both sites were treated as follows:

- K – Control, no treatment;
- NPK- NPK standard fertilization, applied to the soil before the experiment;
- INC - Commercial microbial inoculum Emfarma Plus®, ProBiotics Poland; 8L of 10% water solution was used to soak the roots of the seedlings and sprayed on the soil surface. Plant leaves were treated monthly during the growing season with 10% water solution of inoculum by aerosol treatment (8L per plot).

After the growing season plant material was sampled to determine heavy metal uptake and total biomass yield for each of the species and experimental options. Presented data were collected after third growing season. Amount of metals extracted per ha was calculated according to the following equation:

$$\text{HM extraction} = \text{Biomass yield (kg ha}^{-1}\text{)} \times \text{metal concentration (mg kg}^{-1}\text{)}$$

Results and conclusions

Total soil lead, cadmium and zinc concentration for Polish test site was 637 ±7.1, 26 ±0.38 and 2413 ±12 mg kg-1 d.w. respectively and exceed Polish limits for arable soil.

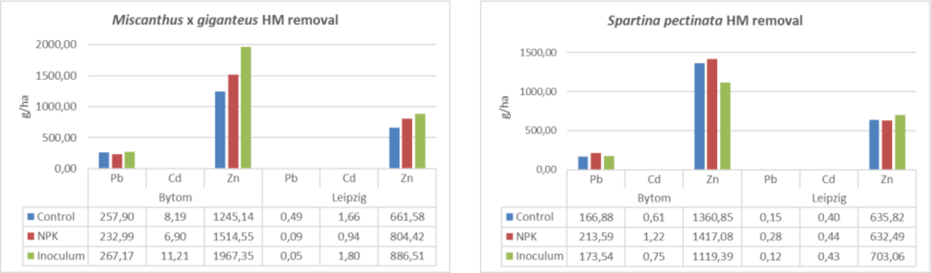
The pH value was almost neutral, followed by moderate content of organic matter (about 6%) and low electric conductivity. The level of bioavailable forms of cadmium and zinc was high (about 5% and 2.5% respectively). In case of German site, total lead, cadmium and zinc concentration in soil was 615 ±9, 34 ±1.45 and 3900 ±17 mg kg-1 d.w. respectively. The pH value was neutral, followed by high (35 %) level of organic matter and electric conductivity. The bioavailability of metals in the soil was very low, mainly due to high level of organic matter (Pb below detection limit, Cd 0.25 mg kg-1 d.w. and Zn 16 mg kg-1 d.w.). Differences in biomass production as well as heavy metal uptake between the sites were observed (Tab 1).

Table 1. Heavy metal accumulation and biomass production of *M.* x *giganteus* and *S. pectinata*

		Bytom (Poland)				**Leipzig (Germany)**			
		Pb	Cd	Zn	Biomass	Pb	Cd	Zn	Biomass
		mg kg^{-1}			kg m^{-2}	mg kg^{-1}			kg m^{-2}
Miscanthus x giganteus	Control	18.05 ±3.72	0.57 ±0.10	87.1 ±7.5	1.43	0.11 ±0.12	0.37 ±0.12	147.8 ±19.8	0.45
	NPK	16.89 ±2.22	0.50 ±0.17	109.8 ±38.8	1.38	0.02 ±0.03	0.22 ±0.20	187.6 ±60.2	0.43
	Inoculum	17.92 ±4.13	0.75 ±0.22	131.9 ±26.9	1.49	0.01 ±0.02	0.35 ±0.26	171.9 ±30.6	0.52
Spartina pectinata	Control	13.22 ±1.61	0.05 ±0.01	107.8 ±20.3	1.26	0.04 ±0.07	0.11 ±0.12	173.9 ±51.1	0.37
	NPK	15.55 ±2.46	0.09 ±0.04	103.2 ±27.7	1.37	0.07 ±0.07	0.11 ±0.06	159.6 ±29.6	0.40
	Inoculum	15.46 ±2.75	0.07 ±0.04	99.7 ±14.6	1.12	0.03 ±0.05	0.11 ±0.11	178.8 ±27.4	0.39

values are mean ± SD

About 3-fold higher biomass production was observed at contaminated arable land, regardless experimental option. Lead and cadmium uptake by plants was also higher for Polish site, while zinc plant uptake was higher for S. pectinata and M. x giganteus cultivated at sewage sludge deposit site. Based on the results of heavy metal uptake and biomass production, removal of contaminants per hectare was calculated (Figure 1). Used fertilization stimulate the zinc removal by M. x giganteus at both sites.



	Bytom Pb	Bytom Cd	Bytom Zn	Leipzig Pb	Leipzig Cd	Leipzig Zn
🟦 Control	257,90	8,19	1245,14	0,49	1,66	661,58
🟥 NPK	232,99	6,90	1514,55	0,09	0,94	804,42
🟩 Inoculum	267,17	11,21	1967,35	0,05	1,80	886,51

	Bytom Pb	Bytom Cd	Bytom Zn	Leipzig Pb	Leipzig Cd	Leipzig Zn
🟦 Control	166,88	0,61	1360,85	0,15	0,40	635,82
🟥 NPK	213,59	1,22	1417,08	0,28	0,44	632,49
🟩 Inoculum	173,54	0,75	1119,39	0,12	0,43	703,06

Figure 1: Calculated *M.* x *giganteus* and *S. pectinata* heavy metal removal.

Presented results showed potential of zinc phytoremediation by M. x giganteus and S. pectinata, especially at arable land, where higher biomass production could be reached. Based on the metal accumulation in plant aboveground parts those species could be used both for soil phytoremediation with the use of the biomass for energy production.

Acknowledgements

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FEASIBILITY STUDY OF INTEGRATING EAOP REACTOR AND MFC TO ACHIEVE SIMULTANEOUS EFFICIENT SLUDGE STABILIZATION AND DIRECT ELECTRICITY GENERATION

Hamed Rasouli Sadabad, Gagik Badalians Gholikandi*

Faculty of civil, water and environmental engineering, Shahid Beheshti University, A.C., Tehran, Iran
*: g.badalians@yahoo.com

Introduction and study objectives

In the last few years the circular economy has been received an increasing attention globally, as a solution to overcome the current production and consumption model based on continuous growth and increasing resource throughput. In this regard, various studies have been carried out to benefit the potential energy of waste materials such as sewage sludge into desired forms during management operations like disposal or digestion processes. Microbial fuel cells (MFCs), as tools for conversion of biochemical energy to electricity directly, are one of the relatively novel technologies that have attracted attentions noticeably in the waste management and the circular economy related criteria. Considering the unique properties of MFCs and circular economy concepts, we have focused on this technology to attain a novel package which would be able to generate electricity directly from sewage sludge in this study. Despite the great advantages, MFCs have various limitations that confine their utilization as a complete waste stabilization system. Also, their output contains noticeable amounts of pathogens and/or oxygen demanding content, which makes it impossible to safely dispose the effluents of these systems directly to the environment. In order to eliminate these limitations, we have integrated a two-chambered MFC with an electrochemical advanced oxidations process (EAOP) reactor (which has been taken into consideration in wastewater treatment, recently). The performance of EAOPs is closely related to the existence of very oxidizing and unstable species like hydroxyl radicals whose mean lifetime is estimated as only a few nanoseconds in water. In this study, we aimed to reach the suitable quality of sewage sludge for safe disposal into the environment and harvesting direct electricity from sludge simultaneously. In order to approach this purpose, we have designed a package which benefits a two-chambered MFC and an EAOP reactor integrated with each other.

Methodology

All of the investigations including experiments, pilot studies, and data collection were performed on the laboratory scale. The performance of the package has been investigated in various pH values, $[Fe^{2+}]/[H_2O_2]$ ratios, retention times and temperatures as operational conditions. The sludge samples have been provided from Tehran southern municipal wastewater treatment plant which treats about 400000 m^3

wastewater daily (Tehran province, Iran). Prior to the test, the feed sludge mixed by a low-speed mixer, in order to be uniform enough before being charged into the package parts (two-chamber MFC and EAOP reactor). Among the EAOPs, we have benefited the Fered-Fenton process in the package considering our previous studies as well as two-chamber MFC individually. According to the nature of the processes and the related reactions, the package has been designed in a way that the effluent of the MFC to be charged into the Fered-Fenton reactor. The effects of the mentioned operational conditions have been assessed on the VSS removal efficiency, pathogen removal ability and the generated electrical power density of the package. The reactors positions in the package structure were determined in a way that the influent of the package entered to the MFC chambers first, in order to generate electricity biologically and then the treated sludge inside of the MFC transferred to the EAOP reactor in order to be chemically stabilized. The MFC reactor contained three graphite electrodes in each chamber and a proton exchange membrane (PEM) which separated the chambers. Also, the EAOP reactor contained six graphite electrodes (as anodes and cathodes). The net volume of the MFC reactor was selected 5 times greater than EAOP, according to the difference of their retention times. Table 1 shows the operational parameters and their ranges.

Table 1: The evaluated operational parameters and their ranges in the current study

Parameter	Temperature, °C		pH		PS/TS, %		$[Fe^{2+}]/[H_2O_2]$	Retention time, h	
	MFC	EAOP	MFC	EAOP	MFC	EAOP	EAOP	MFC	EAOP
range	15-65	15-65	4-9	3-5	0-100	0-100	0.1-1	5-25	1-5

Results and conclusions

The results of the experiments showed that the best conditions of the novel package for the VSS removal efficiency, pathogen removal ability and the generated electrical power density are different from each other considering the nature of the processes which occur in each part of the package. The peak value of the generated electrical power density has been observed when the temperature and pH values were about 40 °C and 7 at the MFC reactor. In these conditions, the package generated about 8296.35 mW/m^3. On the other hand the VSS removal efficiency of the reactor and its ability to remove the pathogens have been observed when the pH value, temperature and $[Fe^{2+}]/[H_2O_2]$ of the EAOP reactor were about 4.5, 45 °C and 0.51, respectively, when the retention time was about 4 hours in the Fered-Fenton reactor. In this conditions, the package was able to remove more than 62% of the initial VSS content of the sewage sludge and >99% of the pathogens in the sewage sludge. Because the effluent of the MFC is entered into the Fered-Fenton reactor directly, to achieve the best results of the package, the pH value of the MFC effluent should be adjusted to the values near to 4.5. The results demonstrated that the package is capable of being utilized for sewage sludge stabilization and modified its quality to be disposed without any damage to the environment (after adjusting final pH value in the neutral conditions). Also, in this case, a part of the electricity which is demanded EAOP process can be harvested from the sewage sludge. Considering the negligible content of the pathogens and remarkable amounts of the Fe-containing complexes, the treated sludge is capable of being utilized as fertilizer in the agricultural lands.

INDICATOR MAPPING TOOL FOR THE COMPLEX KNOWLEDGE SPACE MODEL

Viktor Sebestyen[1,*], Jozsef Nemeth[1], Endre Domokos[1], Tatjana Juzsakova[1], Miklos Bulla[2], Akos Redey[1,*]

[1)] Institute of Environmental Engineering, University of Pannonia, 10 Egyetem St. Veszprém, 8200 Hungary
[2)] National Environmental Council, Budapest, Hungary
*: *redey.akos@gmail.com, sebestyenv@almos.uni-pannon.hu*

Introduction and study objectives

The complex knowledge space model (Fig.1.) is an expert system, that provides evaluation of relationships of environmental utilizations, changes of natural resource kits and evolution of the environmental state. For the analysis of environmental-, social- and economic relationships the system (environmental analysis) should have information on the actual state of the system, which is defined by the database of the different indicators.

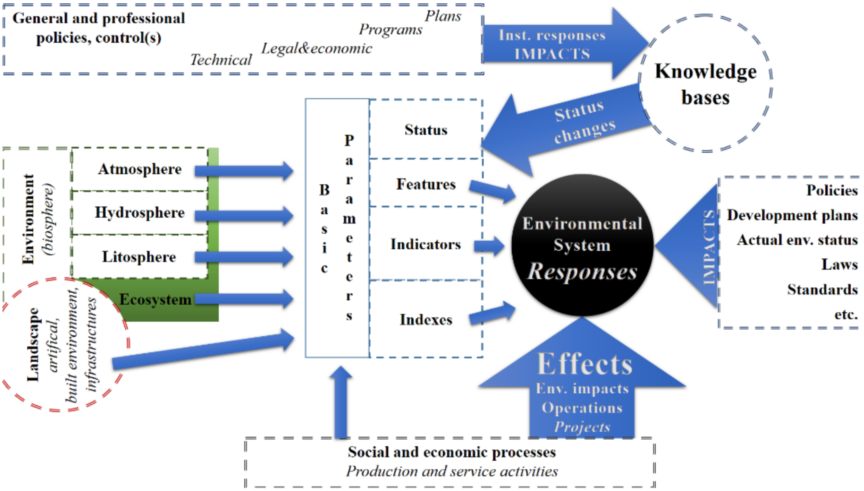

Figure 1: The Complex Knowledge Space Model (according to Bulla et. al; 2012)

The processes, which influence the environmental state, are executed in the economical-, social and environmental dimensions. The Environmental Impact Assessment (EIA) is the tool for evaluating the impacts of the different projects and investments. The tool for sorting the information for the national or regional environmental policies and controls the Strategic Environmental Assessment (SEA). is a distinguished tool.

Methodology

The complex knowledge space model uses the basic data that describe the environment, the general and professional policies and controls and the social and economic processes are taken into account. The environmental system gives responses depending on the changes of the mentioned processes, therefore such indicators should be chosen, which explain the economic and social interactions and also the pollution of the environment.

Some important criteria are the indicators and the measured environmental, social, economic, etc. figures should be available for defining the actual state, since the system undergoes a transformation from the basic state. The excessive numbers of indicators make it harder to overview the operation of the system (Complex Environmental Model), therefore special focus has to be put on the key indicators rather than the whole basic database.

Further criteria, that historical data should be available about the indicators, because the actual values of the indicators are not able to provide information about the direction and velocity of the changes (the derivates of the indicator values depend on time). The indicators were selected based on the national database of the Central Statistical Office, Hungary. The mentioned indicators fit in the CEM model's conception, at least data of 15 years must be available and should be able to be divided to basic data, for example the water production should be classified as surface water-, groundwater-, deep groundwater- and karstic water productions.

Results and conclusions

Altogether 70 indicators had been selected, like the energy production (primer and electricity), the unit prices of resources (drinking water, gas, electricity), the industrial production, the production of raw materials (coal, natural gas), the areas of the forests and agriculture, the emissions of air pollutants (transport, industrial, residential), the water production, the wastewater treatment, the amount of waste (landfilled, recycled, waste for incineration), the ratio of renewables, the environmental industry and investments, the available resources (oil, natural gas, coal, lignite), the R&D investments, the births and deaths (population), the GDP, etc. Correlation analysis and chi-squared test have been accomplished for independence to explore the different relationships of the system between the indicators. In case of 70 indicators, it is carried out with paired comparison, altogether 2415 relationships have been considered. In case of 100 indicators 4950 and in case 200 indicators 19900 calculations had to be made. The goal of the correlation analysis is the identification of the driving forces. If the paired correlation indices are cumulated, it results in the following: the main driving forces are the GDP, the landfilled waste, the gross average earning, the population and the poverty line. The least-related indicators are the biomass production, the irrigation water uses and the residential carbon-monoxide emissions. This approach of the Strategic Environmental Assessment (SEA) allows the logical describing of the environmental and socio-economical links.

Acknowledgement

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Cistus Ladanifer AS A FEEDSTOCK FOR THE MEDITERRANEAN BIOREFINERIES

Júnia Alves-Ferreira[1,2,3], Maria C. Fernandes[1,4,*], Luís C. Duarte[2], Alfredo Martínez[5], Helena Pereira[3], Florbela Carvalheiro[2]

1) Centro de Biotecnologia Agrícola e Agro-Alimentar do Alentejo (CEBAL), Apartado 6158, 7801-908 Beja, Portugal,
2) LNEG- Laboratório Nacional de Energia e Geologia, Unidade de Bioenergia, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal;
3) Centro de Estudos Florestais (CEF), Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal;
4) Instituto de Ciências Agrárias e Ambientais Mediterrâniças (ICAAM), Universidade de Évora, Pólo da Mitra, Ap. 94, 7006-554 Évora, Portugal
5) Departamento de Ingeniería Celular y Biocatálisis, Instituto de Biotecnología, Universidad Nacional Autónoma de México, Apdo. Postal 510-3, Cuernavaca, Morelos 62250, México;
**: maria.fernandes@cebal.pt*

Introduction and study objectives

Cistus ladanifer (rockrose) is a widespread shrub in the Portuguese territory and in other Mediterranean countries. This specie produces a sticky resin known as labdanum and is an important source of essential oils. Both products have been used in the cosmetics and perfume industry. The lignocellulosic residues obtained after the distillation process, the *C. ladanifer* distillery residues (CLR) are currently only used as solid biofuel for heating, although they present a favorable chemical composition for the production of biofuels and bioproducts, that is yet underexplored.

This work aims to develop an integrated process for the fractionation of CLR, which include the sequential separation of extractives, hemicellulosic sugars (as oligosaccharides) and lignin to yield added-value products. The cellulose enriched-solids obtained thereafter, will be used for the production of D-lactic acid using an *E. coli* transformed strain.

Methodology

Cistus ladanifer residues used in this work consist of 2 to 4-year-old plants previously extracted to obtain commercial essential oils. The biomass was milled and extracted successively in Soxhlet with ethanol and water. For the selective hydrolysis of hemicellulose, the raw material was treated with water (autohydrolysis process) in a temperature range of 130 to 230ºC. The effects of the operational conditions on the composition of the liquid and solid phases were evaluated using the severity factor (log *R*o). The remaining solids obtained in the previously optimized conditions were subjected to delignification treatments. These were carried out through mild organosolv processes using aqueous mixtures with ethanol or NaOH solutions. For ethanol/water delignification a temperature range of 170 to 220 ºC was tested. Alkaline delignification (2 and 4% NaOH) was carried out at 130 °C (1- 2 h). CLR and solid residues obtained after each fractionation process were chemically characterized after quantitative acid hydrolysis followed by HPLC analysis. Sugars, acids and degradation products were analysed using an Aminex HPX-87H column (Bio-Rad).

The enzymatic digestibility of cellulose-rich solids was also evaluated. The best condition was used for D-lactic acid production by *E. coli* JU15, through a sequential saccharification and fermentation process. A Doehlert experimental design was used to evaluate the effect of relevant variables (solid loading and enzymes loading) on D-lactic acid production. The fermentation was performed in mini-fermentors (200 ml total volume) at 37°C and pH 7.

Results and conclusions

Cistus ladanifer residues (CLR) contain an important amount of extractives, about 40 %, being polar extractives dominant over nonpolar extractives. Extractive free CLR are characterized to contain up to 32% lignin and 50% polysaccharides.

The upgrade strategy starts with extractives removal followed by hemicellulose fractionation using autohydrolysis. The hydrothermal process enables the production of oligosaccharides, mainly xylooligosaccharides that can reach a maximum concentration of 16 g/L. Under these conditions, the solids obtained contain 34.7% glucan. There was no apparent lignin solubilisation in any of the conditions, which is an advantage of this hydrolytic pretreatment

The results obtained for delignification indicate that aqueous alkaline treatments lead to both higher delignification and subsequent cellulose enzymatic saccharification yields, 87% and 89%, respectively, whereas organosolv delignification was much less effective.

Solid and enzyme loading has a marked effect in saccharification and fermentation. The higher saccharification yields occurred when solid loading was low and high enzyme loading. However, higher D-lactic acid concentrations were found with both elevated solid and enzyme loading, and, as expected, the highest concentration of glucose obtained, generated the highest concentration of lactic acid.

The results obtained in this work show that fractionation of *Cistus ladanifer* distillery residues using extraction, autohydrolysis and alkaline treatment is suitable for the selective separation of extractives, hemicelluloses, lignin and cellulose. Besides the production of oligosaccharides, hydrophilic and lipophilic extractives, as well as lignin-derivatives, can also be obtained and the glucan-rich solids can be efficiently used as a feedstock for the production of D-lactic acid by *E. coli* strain JU15.

Acknowledgements

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SORPTION OF LEAD ONTO CHEMICALLY MODIFIED BIOCHAR PRODUCED FROM URBAN ORGANIC WASTE DIGESTED SLUDGE

Suchanya Wongrod[1,2,3], Yoan Pechaud[1], Piet N. L. Lens[2], David Huguenot[1], Gilles Guibaud[3], Eric D. van Hullebusch[1,2,*]

[1) Université Paris-Est, Laboratoire Géomatériaux et Environnement (EA 4508), UPEM, 77454 Marne-la-Vallée, France
[2) UNESCO-IHE Institute for Water Education, P.O. Box 3015, 2601 DA Delft, The Netherlands
[3) Université de Limoges, Groupement de Recherche Eau Sol Environnement (EA 4330), Faculté des Sciences et Techniques, 123 Avenue A. Thomas, 87060 Limoges Cedex, France
[*]: E.VanHullebusch@unesco-ihe.org

Introduction and study objectives

Metal elements are known as toxic and persistent in the environment. Elevated concentrations of metals in the nature are the result of anthropogenic activities, *e.g.* discharges of wastewater from battery, mining, manufacturing processes and automobile industries into the rivers (Inyang et al., 2012). The exposure of metals to the ecosystem can lead to several adverse effects to the public human health. Lead is known as a carcinogenic metal, which can damage kidney and increase blood pressure in a long-term (World Health Organization, 2016). Thus, the development of strict environmental regulations is raising concerns by policy makers to increase environmental safety by reducing metal mobility and toxicity in surface water and groundwater. Generally, conventional water treatment technologies such as chemical precipitation, coagulation, ion exchange and packed bed filtration have been reported to effectively remove metal pollutants from wastewater (Inyang et al., 2015). However, these processes show less eco-environmental sustainability due to high costs for operation and post- treatment of the sludge. Thus, alternative environmental-friendly and cost-effective approaches are necessary to be sought.

The use of biochar as a filtration media is suggested for metal laden wastewater treatment (Mohan et al., 2014). It has been reported that biochar was effectively used as a low-cost adsorbent for contaminants removal in packed bed column since it generally requires less energy to manufacture compared to granular activated carbon (GAC) (Huggins et al., 2016). Biochar produced from by- product digested sludge generated after anaerobic digestion promotes the environmental sustainability for waste management to recycle back organic waste sludge, add more valuable to end-products (*i.e.* bioenergy), reduce waste quantity and costs for sludge disposal. Biochar is a black solid material derived from a thermal decomposition (*i.e.* pyrolysis) of bio-waste materials in a limiting oxygen environment (Inyang et al., 2015). Valorisation of the organic biomass through pyrolysis can eliminate pathogenic agents from the sludge, avoiding widespread of infectious diseases to the ecosystem (Seadi & Lukehurst, 2012). Recent studies show the potential application of biochar in metal-polluted water treatment (Mohan et al., 2014) due to its high specific surface area and surface properties (surface charge, hydrophobicity, etc.) (Liu & Zhang, 2009;

Zielińska et al., 2015).

The potential use of biochar converted from organic digested sludge has been reported to remove metals, including As(V), Cd(II), Cr(III), Cu(II) and Ni(II) from water (Inyang et al., 2012; Jin et al., 2014). However, low sorption capacities have been found in certain conventional biochar and thus activation of biochars have been recently studied to enhance metals sorption capacity (Rajapaksha et al., 2016). Treatment of biochar with KOH has been affirmed to increase surface hydroxyl groups and basicity on biochar surface (Fan et al., 2016; Li et al., 2014) as well as dissolve ash and condense organic matter (*e.g.* lignin and celluloses) in the biochar (Lin et al., 2012; Liou & Wu, 2009; Liu et al., 2012). In addition, modification of biochar with H_2O_2 helps to increase O-containing functional groups particularly carboxyl groups on biochar surfaces (Rajapaksha et al., 2016). This research work aimed to investigate the enhanced Pb(II) sorption capacity in aqueous solution with the application of biochars produced from different solid digestate, *i.e.* sewage sludge (SS) and organic fraction of municipal solid waste (MSW) digestates with different chemical modification (KOH and H_2O_2).

Methodology

Biochars were produced from SS and MSW digestates under slow pyrolysis at lab scale. Pyrolysis temperatures were optimized at 350°C for SS and 400°C for MSW with a residence time of 1 h and at 1 atm. Modified biochars were prepared separately by mixing biochar with 10% H_2O_2 solution (2 g :20 mL) (modified from Xue et al., 2012) and with 2M KOH (2 g : 100 mL) (modified from Jin et al., 2014). Important characteristics of biochar, including pH in water, metal and ash content, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were analysed. Batch sorption tests were performed to observe the interaction of Pb(II) with raw and modified biochars. The sorption experiments were operated at initial pH 5, initial Pb(II) concentration of 100 mg/L, and biochar dosage of 4 g/L (*i.e.* 250 mL of working solution per g of biochar) at 20 ± 2°C and at 180 rpm for 24 h.

Results and conclusions

The FTIR and XRD analyses of biochar showed O-contained functional groups (*e.g.* -OH, -COOH, C=O) and mineral phases (mainly SiO_2 and $CaCO_3$), respectively on its surface. This can influence the sorption mechanisms via ion-exchange or precipitation of metal on carbonate surface of biochar (Al-Degs et al., 2006). Significant enhancement of Pb(II) from 3.74 mg/g to 13.96 mg/g was observed on KOH-modified SS biochar (MSS350-KOH) compared to raw SS biochar (RSS350) and was 2 times higher in H_2O_2-modified SS biochar (MSS350-H_2O_2) than in RSS350. On the other hand, slight effect or no effect was found with H_2O_2-modified MSW biochar (MMSW400- H_2O_2) compared to its raw biochar (RMSW400). High correlation coefficients (> 0.99) indicated well-fitted of the pseudo-second-order kinetic model to Pb(II) sorption experiment. From the results, the biochar treated with KOH showed better Pb(II) sorption enhancement than biochar modified with H_2O_2 for both sewage sludge and organic fraction of municipal solid waste digestate –derived biochars. In addition, maximum Pb(II) sorption capacities of raw and modified biochars were observed at Pb(II) equilibrium concentration of 500 mg/L except RSS350 where the maximum sorption capacity occurred at 300 mg/L.

PERSPECTIVES ON WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT MANAGEMENT SYSTEM IN ROMANIA

Simona Cecilia Ghiga[1], **Raluca Maria Hlihor**[1,3*], **Isabela Maria Simion**[1,3], **Maria Gavrilescu**[1,4*]

1) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
3) "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine of Iasi, Faculty of Horticulture, Department of Horticultural Technologies, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania
4) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
**: raluca.hlihor@ch.tuiasi.ro, mgav@ch.tuiasi.ro*

Nowadays, the rate of waste electrical and electronic equipment (WEEE) is growing at an alarming rate, especially in countries where markets are saturated with huge quantities of new electronic goods. The large quantities of WEEE and the wide variety of materials they often contain - many of them with a potential harmful effect on humans and the environment - has focused the attention on how WEEE is handled, generated and on preventive actions. The complex structure of materials contained by WEEE, whether not properly managed could cause major environmental and health problems due to their hazardous content. On the other hand, even if in one way WEEE are characterized as hazardous materials at the same time these type of wastes are considered valuable, due to the content of precious and strategic metals.

The production of modern electronics requires the use of scarce and expensive resources (e.g. around 10% of total gold worldwide is used for electronics production). To improve the environmental management of WEEE and enhance resource efficiency according to circular economy concept, the improvement of collection, treatment and recycling of electronics at the end of their life is essential. Understanding the mechanisms and operational principles of WEEE management systems can only be possible after a careful identification and analysis of life cycle of EEE from production phase until final disposal phase of waste, considering sustainable preventive and control alternatives so as to close the loop (Fig. 1). In this framework, the present study is centered on the current situation regarding WEEE in Romania with a special focus on Iasi City. The analysis of WEEE management in Iasi City is carried out in the context of harmonizing national environmental laws with European Directives. According to the results of a collecting campaign carried during October 2015 in Iasi City, a total of 29,691 kg of WEEE of different composition were collected as indicated in Fig. 2. Considering the results in Fig. 2, this paper analyses the perspective of developing a sustainable management system for WEEE in the context of national environmental strategy and European Directives, entailing the improvement of environmental management of WEEE so as to enhance resource efficiency and contribute to a circular economy by closing one or multiple loops.

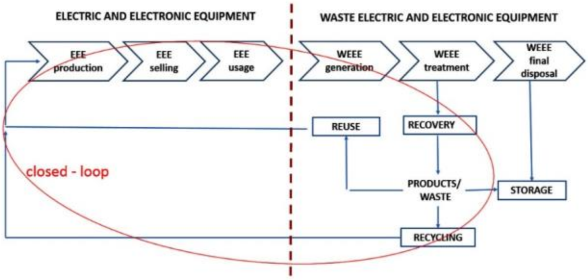

Figure 1: WEEE life cycle

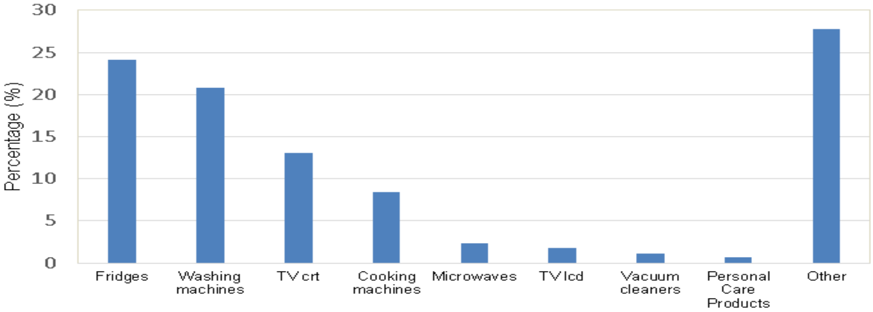

Figure 2: Percentage of different WEEE collected in Iasi City in October 2015

Our strategy is proposing three scenarios to be evaluated in the context of Life Cycle Assessment (LCA). The first scenario ***SW1*** - is based on the most simple way of WEEE managing (collection-screening-temporary storage-transport-recycling), the second scenario ***SW2*** - proposes a new step referring to population informing (population informing-collection-screening-temporary storage-transport-recycling) while scenario ***SW3*** – proposes skipping the stage of screening and temporary storage with the scope of reducing environmental impacts, costs and time (population informing-collection-transport with screening-recycling). The evaluation of environmental impacts according to LCA methodology revealed that the transition to a circular system needs the improvement of collection, treatment and recycling of WEEE to the end of their life, which is essential. Our analysis indicated that scenario ***SW2*** is the most suitable from the environmental and social points of view. This result is influenced by the population informing stage which improves automatically the collection step, overcoming with 70% the total quantity collected in the first scenario ***SW1***. Scenario ***SW3*** could work if the recycler receives and processes all WEEE transported. For the moment the recycler receives only sorted WEEE by category.

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SCREENING AND RANKING METHODOLOGY APPLIED TO BIOCHARS AIMED AT SOIL IMPROVEMENT

Mónika Molnár*, Viktória Feigl, Emese Vaszita, Katalin Gruiz, Éva Farkas

Budapest University of Technology and Economics, Department of Applied Biotechnology and Food Science , 1111 Budapest, Műegyetem rakpart 3,
**: mmolnar@mail.bme.hu*

Introduction and study objectives

Soil as the "biological engine of the Earth" is one of the most diverse habitats and contains the most diverse collections of living organisms. However soil management strongly influences soil biodiversity; different human activities or environmental factors cause shifts in habitat quality and in substrate availability, resulting in changes in abundance of individual species. The proper soil functioning is a key life support function, so there is a growing interest in the assessment of the quality and performance of soils that are or may be influenced and degraded by anthropogenic activities.

Biochar is produced from a wide range of organic materials by pyrolysis, specifically for improvement of poor quality soils. When biochars are applied to soil, it is aimed to have positive effects on soil properties and crop yields and carbon could be sequestered. Due to its many potentially advantageous properties biochar has been extensively investigated and the number as well as the quality of researches connected to biochar application have grown exponentially nowadays. It was demonstrated that both the pyrolysis technique and the feedstock affects the biochar properties with agronomic implications, such as pH, surface area, cation exchange capacity, the H/C ratio etc. However the fundamental mechanism of the direct biochar-based ecological effects is unexplored and poorly understood, particularly those on soil biota. There are only few studies describing the possible connections between biochar properties and the soil biota, and their implications for soil processes.

The principal aim of this research was to get a better understanding of biochar-mediated effects on soil chemical, physical and biological properties as well as to assess and analyse the direct and indirect interactions between biochar surface chemistry, physical properties and microbial colonization.

Methodology

In the first phase of our multistage research various biochar products were screened for their physico-chemical properties, biological activity and ecotoxicity with a test-battery developed by our research group to evaluate the possible applicability of the tested biochars to soil.

Ten biochars produced from various feedstocks such as grain husks, paper fibre sludge, wood screenings, manure, miscanthus, spelt mixed with paper, vine and natural biomass were investigated prior to a soil improvement study. The biochars were produced in PYREG® type pyrolysis reactors at different pyrolysis temperature (450 °C / 500 °C / 600–700 °C / 650–750 °C) and residence time (with 15 or 20 minutes). A complex methodology for the assessment and screening of biochars was developed and applied. In this screening study the biochars were tested both in their native form and mixed into sandy soil (from Hungary) at 10 weight%.

The physico-chemical methodology included measurements of BET surface area, porosity, particle size distribution, SEM analysis for surface morphology, surface chemical composition, pH, water holding capacity, electrical conductivity (EC), cation exchange capacity (CEC), NPK supply and toxic element content.

In the frame of the biological and ecotoxicological methodology the aerobic heterotrophic colony forming units of bacteria and fungi and bacteria/fungi rate was determined. Bacterial colonization studies were also carried out by plant growth-promoting rhizobacteria. Scanning Electron Microscope (SEM) was applied for the investigation of microbial colonization. Aliivibrio fisheri bioluminescence test, plant growth tests (mustard, wheat), and mortality test with animals (Folsomia candida, Panagrellus redivivus) were used for testing the potential toxic effects of biochars.

Results and conclusions

We developed a screening and ranking methodology applied to biochars aimed at soil improvement to assess the possible applicability of biochars to soil and to select the main influencing properties of the tested biochars as soil additive. The focus was on improving soil functions as habitat for soil biota.

For ranking of the biochar products and to select the best biochar(s) for soil improvement a complex multi-criteria evaluation system was developed based on scores (from -10 as the least appropriate to 10 as the most appropriate). The system took into consideration the suitable properties and effects of a soil amendment for improvement of various degraded soils. The greatest potential benefits and risks of biochars were evaluated. Biochar Quality Indices (BQI) were created by choosing appropriate indicators, indicator scores were determined; the indicator scores were weighted, combined and integrated into the Biochar Quality Index.

Our results suggest that a selected number of carefully chosen biochar quality indicators can adequately provide the information needed for selection of biochars prior to soil improvement and the developed screening and ranking system can be a practical tool for potential biochar users.

In the next phase of the multistage research we will assess in microcosms the biochar-mediated short- and long-term effects on soil chemical, physical and biological properties targeting improvement of soils.

Acknowledgement

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SYNTHESIS AND CHARACTERISATION OF FLY ASH-BASED GEOPOLYMER CEMENT USING A ROMANIAN BY-PRODUCT FROM THERMAL POWER PLANT

Men Fei Chok[1], Igor Creţescu[2,*], Carmen Teodosiu[2], Dorina Nicolina Isopescu[3,*], Maria Harja[2,*], Brindusa Mihaela Sluser[2], Mohamad Amran Mohd Salleh[4]

[1] Institute of Advanced Technology, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[2] "Gheorghe Asachi" Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, 73 Blvd. D. Mangeron, 700050, Iasi, Romania
[3] "Gheorghe Asachi" Technical University of Iaşi, Faculty of Civil Engineering and Building Services, 65 Blvd. D. Mangeron, 700050, Iasi, Romania
[4] Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra, Malaysia, 43300 UPM Serdang, Selangor, Malaysia
**: icre@tuiasi.ro; dorina_isopescu@yahoo.co.uk; mharja@tuiasi.ro*

Introduction and objectives

Thermal power plant using coal combustion produce substantial amount of fly ash during energy production process. Due to the mentioned aspect, the major environmental issued appear if the fly ash is not treated properly. Therefore a number of useful applications are found to cope with this industry waste stream, included construction industry. Fly-ash has been recognized as one of the potential precursors for geopolymers production. It can be used to produce new cementitious product with good workability and strength.

Synthesis of geopolymer uses alkali solution to dissolve the starting materials (precursors) by hydrolysis, followed by gel formation and polycondensation process. Generally, geopolymer refers to inorganic polymer which synthesized through a series of alkali-activation process using industrial waste that are rich in silica and alumina, forming three-dimensional amorphous alumino-silicate network with comparable properties to ordinary portland cement product. Fly ash is not a standard by-product world-wide, the chemical and physical properties varies according to source of collection. Thus, increasing researches are being carried out to understand the reaction mechanism of fly ash-based geopolymer material.

This experimental study aims to determine the effect of some important parameters on geopolymerization of low calcium fly ash in an effort towards achieving valorization of this locally available waste in Iași city, Romania.

Methodology

The fly-ash used in this study is collected from the nearest thermal power plant in Iași city and undergone chemical characterizations before usage. Some preliminary experiment is underway to determine the ideal mixing proportion while also familiarize with the mixing procedure. Basically, the fly ash will be mixing with prior prepared alkali solutions consist of NaOH and water, producing a mixture, which will be filtered and dried to produce GP cement. Poly (sialate-siloxo) which defines polymer with 2:1 ratio for Si/Al content is expected, based on the prior characterization result of the fly-ash chemical compositions. As such, the Si/Al ratio before and after geopolymerisation is to be observed, to ensure its suitability as potential cement product. The experiment is done according to standard procedure stated in ASTM to ensure quality of testing and result credibility.

Different geopolymers were fabricated according to experimental design matrix, which includes the alkali activation conditions (concentration of NaOH), solid to liquid ratio (aluminosilicate to alkaline solution) and curing temperature. For the geopolymerisation process, a polynomial model was obtained taking into consideration all three mentioned parameters. After the validation of mathematical model, the optimum parameters were determined tacking into consideration the above stated important ratio Si/Al.

The geopolymer cement produced are investigated using microstructural analysis (XRD, SEM, EDX, TGA and etc.), in order to understand the chemical composition of the raw material and chemical properties and microstructural changes before and after geopolymerization. The analysis is complemented with necessary mechanical testing such as compressive strength measurement. Mechanical testing is carried out after mixing the GP cement produced with water to form GP cement paste. The aforementioned testing is conducted on cube specimen using universal testing machine. Both chemical and physical characterization of the production provides more in-depth understanding of the inorganic polymer to support future study and commercialization.

Results and conclusions

Research studies shows that it is possible to produce geopolymer at ambient or slightly higher temperature. Knowledge of optimal alkali activation condition is important in producing environmental friendly products to set as the good alternatives to traditional cement materials.

The most interest in this research study was the geopolymerisation process which will determine the strength and durability of the produced material. Works are to be done to ensure completeness of the geopolymerisation in order to ensure it fits to the definition as polymer. Previous study has used metakaolin as one of the useful materials to act as the networking element that will interact with the N-A structure to form strong geopolymer, which is more environmental friendly and exhibit better carbonation result.

This experiment set as the important study towards realizing the application of fly-ash as alternatives construction material at industry scale in the city. Low calcium fly-ash geopolymer will soon provides the construction industry a second choice of materials for ensuring long-term sustainability of the resource usage during infrastructure development. It will also help to reduce the abundant waste produced by the neighboring thermal plant which continues to supply electric energy to the citizens.

MICROCOSM INCUBATION STUDY FOR MONITORING THE MID-TERM EFFECTS OF BIOCHAR ON ACIDIC SANDY SOIL

Éva Farkas*, Viktória Feigl, Éva Ujaczki,
Ildikó Fekete-Kertész, Mária Tolner, Emese Vaszita,
Katalin Gruiz, Mónika Molnár

Budapest University of Technology and Economics, Department of Applied Biotechnology and Food Science, Faculty of Chemical Technology and Biotechnology, Budapest, HUNGARY
1111 Műegyetem Rkp. 3, Budapest, Hungary,
**: farkas.eva@mail.bme.hu*

Introduction and study objectives

Biochar is charcoal produced from a wide range of organic materials by pyrolysis specifically produced in most cases for soil application with the aim of increasing C sequestration and improving soil fertility and crop yields. However, it is uncertain whether the same positive effects can be obtained in all soil types. According to the numerous references, the biochars and their technological and environmental performance need to be investigated on a "char by char" basis, to gain a detailed picture on the given biochar and its associated effects.

The objective of this study is to evaluate and compare the mid-term effects (11 months) of biochars from different feedstocks on the soil physico-chemical, biological and ecotoxicological properties. As part of a complete scale-up technology experiment aiming improvement of an acidic sandy soil, the biochars were pre-screened and a microcosm experiment was conducted with combined application of biochar types and amounts, compost and fertilizer. 13 biochars from different feedstocks were pre-screened to assess their applicability as soil amendment. Three biochars with the best technological and environmental potential were selected for the microcosm experiment.

Methodology

In the screening study the biochar products were tested both in their native form and mixed with sandy soil at 10w/w% concentration. Based on the comparative evaluation of the results, a priority list of biochars was created. The best-ranking three biochars were mixed into the acidic sandy soil (originated from Nyírlugos, Hungary) at 0 w/w % (control), 0.1 w/w %, 0.5 w/w % and 1 w/w % rate combined with fertiliser and compost in microcosms. The feedstock of the selected biochars was: grain husk combined with paper fibre sludge (A1, A2) and wood screenings (B1). For the monitoring of both the screening study and the microcosm experiment an integrated methodology was used. To assess the effects of biochars on the soil physico-chemical properties the pH, electrical conductivity, water holding capacity and ignition loss were measured. To determine the biological properties, the bacteria concentration and fungi number (CFU) were determined. For testing the potential toxicity of the amendments *Sinapis alba, Triticum aestivum* plant growth and *Folsomia candida* mortality test was applied.

All treatments were performed in three replicates. Soil samples were taken at the start, at the 6th and 11th month. To determine if the treatment had a significant effect, analysis of variance (ANOVA) was performed using StatSoft® Statistica 12.

Results and conclusions

According to the measured water holding capacity (WHC), electrical conductivity as well as the ignition loss A1 and B1 application had beneficial effect, while amendment with A2 biochar had no significant effect on these parameters. As expected, the biochars raised the pH of the acidic sandy soil (Fig 1). The highest pH was measured at the end of the experiment. Both the A1 and B1 biochars raised the pH by 1 unit, so we can predict that their effect on the soil pH will be maintained on the long term (1 year).

The results of bacterial and fungal cell concentrations presented different responses to the biochars, but clearly demonstrated that biochar treatment did not influence negatively the soil microbes. At 11th month the 0.5% A1 and 0.5 and 1% B1 had the most beneficial effect on the soil bacteria (10 times more than in the control) (Fig 2).

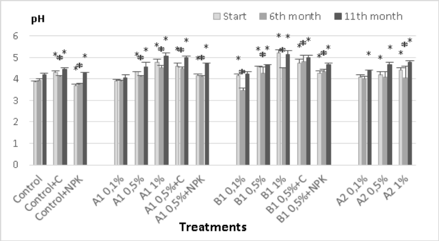

Figure 1: Changes in soil pH

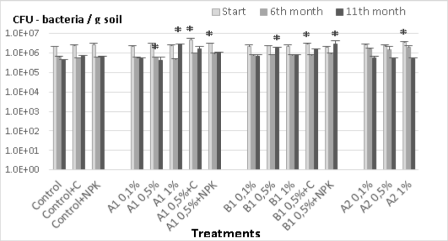

Figure 2: Changes in concentration of soil bacteria

The white mustard's shoot length could be a good indicator both of the presence of toxic substances and the habitat function of soil (Fig 3). At the beginning the biochars had no significant effect on this parameter, but after 11 months we found that 1% A1 biochar was the most effective treatment (~30% elongation), but all the other A1 and B1 concentrations enhanced the growth with at least 20%.

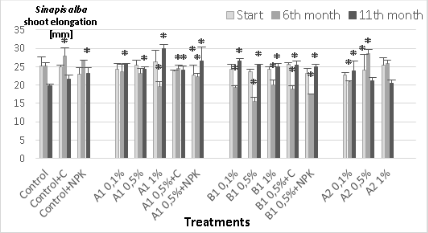

Figure 3: Changes in mustard shoot elongation

As a conclusion, although the B1 biochar (wood screenings) has had promising long-term effects, the 1% A1 biochar (grain husks and paper fiber sludge) was the most favourable treatment according to the comparative evaluation of the physico-chemical, biological and ecotoxicological results.

Acknowledgements

The work was supported by the EEA Grants and the Norway Grants within the "Green Industry Innovation Programme" (Terra Preta project, registration number HU09-0029-A1-2013).

MATHEMATICAL MODEL SELECTION FOR ABE FERMENTATION FROM GLUCOSE USING *Clostridium beijerinckii* ATCC 55025

Manuel Aguado Ramos, Yolanda Núñez Gutiérrez,
Elena Maganto Burgos, Daniel Hernández Mateo,
Daniela Zaharieva Petrova, Jennifer Doblado Ferrón

Tomsa Destil, S.L. Bahía de Pollensa nº 21; 28042 Madrid, Spain
**: manuel.aguado@tomsadestil.es*

Introduction and study objectives

During the ABE fermentatio a laboratory scale adjusting to a mathematical model to describe the process, some variables have been studied: pH, temperature, oxygen concentration. The essays have been carried out using a 5L bioreactor in batch working; the reaction volume was 2L. The bioreactor was inoculated 20% (v/v) with *Clostridium beijerinckii* ATCC 55025 strain and it was fed using 41 g/L of glucose. In order to describe the ABE fermentation, a mathematical model was set through process phenomenology analysis and using the experimental data.

One of the most relevant results is the adjustment of the fermentation model, which present hardness to consider the interaction between intermediary and final metabolites, but it confers a suitable prediction of all variables considered.

Methodology

Kinetic process. There are important troubles that avoid the scale change of the process to industrial level. Basically, the disadvantages are focused on the model proposed to the kinetic simulation of substrate conversion, cellular growth and butanol production. The knowledge about the enzymatic kinetic of the process (specially the metabolic route of *C. beijerinckii* for butanol production), is the key of the scale change. When the concentration profiles were experimentally obtained (substrate, biomass and metabolites), were obtained experimentally, the kinetic equations were chosen which better described their behavior. Several models were preselected for his capacity to express the phenomenology process. It was the starting point for the adjustment procedure. Figure 1 shows the statistical criteria of the kinetic equations corresponding to each base model. It also shows the inhibition terms about the cellular growth that includes to each one of them.

According to the information presented in the literature about the kinetic of the studied process, possible modifications were established on the base models. These changes were made in order to obtain systems with greater sturdiness, from the phenomenological point of view. The adjustment of each model to the experimental data and the estimation of the parameters were done through the iterative process of the Nelder-Mead algorithm for optimization of nonlinear systems, (using mathematical processing software MATLAB 7.0). In order to obtain a good estimation, estimated parameters are created close to the real ones. For this determination the linear least squaresmethod was used. The adjustment capacity of each model was evaluated according to the following criteria: Correlation Coefficient (r^2), Variance (^{2}) and Mean Square Error (MSE). The analysis of these three statistical indicators allowed to select an adequate model from the mathematical and phenomenological point of view to describe the fermentative process.

Results and conclusions

The statistical criteria were checked for the five considered models. Figure 1 shows the behaviour (experimental and predicted) of pH, the productivity of butanol, glucose and biomass through the time. In the graphics can be observed the reached level of correspondence with the model which was chosen and adjusted. During the simulation the same initial conditions of the experimental tests were used; the values were: glucose, 242.12 mmol / L; Biomass, 1.5236 mmol / L; pH, 5.20.

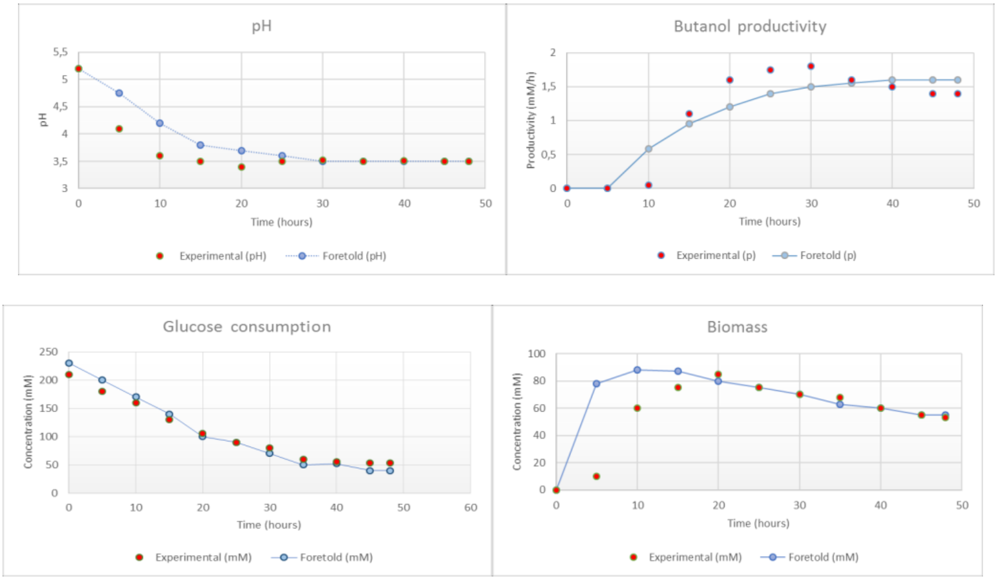

Figure 1: ABE fermentation variables

Acknowledgements

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TECHNICAL, ECONOMIC AND ENVIRONMENTAL ANALYSIS OF LACTIC ACID AND BIOGAS PRODUCTION FROM KITCHEN WASTE

Francesca Demichelis[1], Silvia Fiore[1,*], Daniel Pleissner[2], Joachim Venus[3]

[1)] DIATI, Department of Engineering for Environmental, Land and infrastructures, Politecnico di Torino,Corso Duca degli Abruzzi 24, 10129,Turin,Italy
[2)] Sustainable Chemistry (Resource Efficiency), Institute of Sustainable and Environmental Chemistry, Leuphana University of Lüneburg, C13, 21335 Lüneburg, Germany
[3)] Leibniz Institute for Agricultural Engineering and Bioeconomy Potsdam, Max-Eyth-Allee 100, 14469 Potsdam, Germany
[*]: silvia.fiore@polito.it (S. Fiore)

Introduction and study objectives

Nowadays, the concept of sustainable production and consumption is a key lever towards bio- based economy, which has biomass conversion into bio-products and bio-energy production as essential elements. In this study, a two-step bio-refinery process fed with kitchen waste was investigated for the sequential fermentative production of two added-value products: lactic acid (LA) and biogas. Organic waste, representing a massive social, economic and environmental problem, could be employed in bio-refinery processes with three important benefits: production of added value products (LA and biogas), decrease of bio-refinery process costs and reduction of waste amount. LA and biogas production through biological pathways is based on mature technologies, already implemented on pilot and full scale.

The aim of this research is the evaluation of technical, economic and environmental feasibility and sustainability of the proposed bio-refinery system, which is coherent with EU strategy on Circular Economy. The novelty of the approach consists of taking into account the conversion of kitchen waste into LA and biogas through two biological fermentative processes performed in sequence and combined into a value chain. The consistency of this study is verified by the implementation of the proposed value chain in areas with 2000 to 1 million inhabitants.

Methodology

Technical analysis defined LA production through simultaneous saccharification and fermentation (SSF) from kitchen waste and biogas generation from fermentative residues at 35°C. A bio-refinery plant made of the following components was hypothesized: blender tank, LA fermenter, downstream processing to obtain purified LA, anaerobic reactor, gasometer and CHP unit.

Economic analysis was performed considering three elements: investment costs (purchase and installation of equipment), operational costs (raw materials, reagents, utilities, maintenance service and operating labours) and profitability considering the current market values. The cost of land was not considered since the analysis was not geo-referred. A 5-years amortization with an interest of 3% is assumed for the investment cost. Environmental analysis is based on CO_2 equivalent emissions calculated with a conversion factor equal to 0.44 tons emitted per MWh produced and tons of petroleum equivalent (TEP) defined as 0.187 for each MWh produced.

Results and conclusions

Technical analysis estimated the feasibility of the two-step bio-refinery chain: LA production through SSF was investigated at laboratory (2 L) and technical (72 L) scales and scale effect was not detected. Whereas, anaerobic digestion of fermentative residues was carried out at laboratory scale (2L) and a 0.7 corrective factor was adopted for scale-up evaluation. Process yield reached 0.29 g LA/g dry organic waste with an optical purity of 97.9 % and 0.50 Nm^3 CH_4/kg organic dry matter.

Table 1: Economic and environmental analysis carried out for catchment areas of different sizes. Values are round off to the unit.

Inhabitants	2000	5000	10000	20000	50000	100000	200000	1000000
Organic waste [t/y]	286	715	1431	2862	7155	14310	28620	143400
Investment costs [€]	1335335	1374167	1479908	1609349	1997672	2670587	3964997	14403740
Amortization [€]	283302	291541	313974	341436	423822	566587	841207	3055874
Operational costs [€]	105495	122569	200171	264565	457744	825144	1469075	6634435
Profitability [€]	32915	82289	164578	329157	822893	1645787	3291574	16492374
Net incomes [€]	-355882	-331821	-349568	-276844	-58673	**254054**	**981291**	**6802064**
Net incomes after 5 yrs [€]	-72580	-40279	-35593	**64592**	**365149**	**820642**	**1822498**	**9857939**
CO_2 equivalent [t]	59	149	298	595	1489	2978	5956	29845
CO_2 produced [t]	6966	16800	33601	67203	1680079	336015	672031	3367202
TEP [t]	14	35	69	139	347	693	1386	6948

Economic analysis revealed the feasibility and sustainability of the proposed bio-refinery chain. Tab.1 shows the profitability of the investigated process for any catchment area. We found economic loss below 10000 inhabitants, cost-effectiveness after 5 years of amortization for catching areas between 20000 and 50000 inhabitants, and immediate profitability for catching areas up to 100000 inhabitants. Above 100000 inhabitants generated added value products became competitive on the market and the net income ranged between 17.75 and 47.43 €/t of organic waste.

Environmental analysis revealed CO_2 equivalent emissions equal to 208.13 kg CO_2/t waste for all catching areas, which may be compared to 420.88 kg CO_2/t waste ascribable to conventional organic waste disposal options (e.g. composting).

In conclusion, the proposed two-step bio-refinery value chain proved to be an immediately sustainable and profitable perspective, from technical, economic and environmental standpoints, for the valorization of kitchen waste for catching areas over 100000 inhabitants.

POPLAR-ASSISTED BIOREMEDIATION OF A MULTI-CONTAMINATED AREA IN SOUTHERN ITALY

Valeria Ancona[1,*], Anna Barra Caracciolo[2], Paola Grenni[2], Claudia Campanale[1], Ida Rascio[1], Martina Di Lenola[2], Martina Cardoni[2], Giuseppe Bagnuolo[1], Giuseppe Mascolo[1], Angelo Massacci[3], Vito Felice Uricchio[1]

1) Affiliation: IRSA-CNR of Bari
2) Affiliation: IRSA-CNR of Rome
3) Affiliation: IBAF-CNR of Rome
**: valeria.ancona@ba.irsa.cnr.it*

Introduction and study objectives

Plant-assisted bioremediation, the use of plants to promote the extraction, the sequester or detoxification of pollutants through biological processes is a green, effective, in situ, non intrusive, low cost, aesthetically pleasing and, socially accepted technology to remediate contaminated soil. Potential for plant-assisted bioremediation depends upon the interactions among, soil, contaminants, microorganisms (bacteria and microfungi) and plants occurring in the rhizosphere where, the release of root exudates and oxygen with circadian rhythm can stimulate the biodegradation activity of natural soil microorganisms. This technology has been applying for three years to a multi-contaminated (PCBs and heavy metals) area in Southern Italy using as plant a selected poplar clone (*Monviso*).

Methodology

At fixed times (0, 420, 900 days) the concentrations of 18 polychlorinated-biphenyls (PCBs) congeners and heavy metals (HMs: V, Cr, Sn, Pb, Zn, Ni, Sn) were evaluated on soil samples collected at different depths (0-20, 20-40 cm) and distance (0.25 m, 1m) from tree trunks inside some contaminated plots selected in the poplar treated area. The main soil properties (pH, moisture, organic carbon and available phosphorous content, etc.) were also investigated in order to assess the quality state of soil. At the same time, microbial analyses were performed in order to assess total microbial abundance, cell viability, dehydrogenase activity and the phylogenetic composition of the autochthonous microbial community. Finally, roots, trunk, branches and leaves were collected and chemically analysed in order to evaluate the possible contaminant bioaccumulation in plant tissues.

Chemical and microbial investigations were also carried out on soil "control" samples collected outside the poplar planting area in the survey site.

Results and conclusions

Three years after the poplar planting a significant decrease in overall PCB congeners and in most of HMs concentrations was observed. Currently, the values of all PCBs detected are under the Italian legislation limits (60 ng/g) in soils of all the planted plots investigated. Concentrations of both HMs and some PCB congeners were detected in the poplar tissues, with values generally higher in roots than in aerial plant tissues. In the soil samples collected from the non-planted area (*control*) at days 420 and 900 no significant decrease in pollutant (PCB and HM) concentrations was observed.

Poplar treated area

Analyses of the autochthonous microbial community at day 420 and 900 showed a gradual improvement in the soil quality in terms of both cell viability and abundance; in particular, microbial abundance and cell viability were always higher in the rhizosphere. Moreover, a soil quality improvement was observed also in terms of an increase in the organic carbon content, with the highest values in the rhizosphere at day 900 (11.36 g/Kg in the rhizosphere *vs* 6.21 g/Kg in bulk soil). The phylogenetical analysis of the microbial community performed on the same samples at day 900 showed a higher percentage of microbial taxa (*e.g. Actinobacteria, Firmicutes, Alpha- Gamma-Proteobacteria*) known for their ability to degrade PCB in the rhizosphere than in the bulk soil. Delta-Proteobacteria were found in a high percentage in soil samples far from the trunk. Finally, in the rhizosphere a higher evenness in taxa distribution (evenness index: 0.87) than in the bulk soil (evenness index: 0.30) was also observed. The plant-microbial interactions promoted PCB degradation and bacterial diversity.

Overall results show that the poplar-assisted bioremediation strategy using the *Monviso* clone was able to increase the soil quality; at the same time the poplar-microbial interactions occurred especially in rhizosphere soil were useful to promote both the PCB degradation and the phytostabilization of the heavy metals.

Acknowledgments

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REVALORIZATION OF OLIVE OIL WASTES BY THE EXTRACTION OF BIOACTIVE COMPOUNDS

Guillermo Rodríguez Gutiérrez, Fátima Rubio-Senent,
Juan Fernández-Bolaños Guzmán,
Maria Africa Fernandez Prior, Alejandra Bermudez Oria

Instituto de la Grasa, (CSIC), ctra de Utrera Km 1, Campus Pablo de Olavide,
Edif. 46. CP 41013, Seville, Spain.
**: guirogu@ig.csic.es).*

Introduction and study objectives

New techniques for total utilization of olive oil wastes are required to solve the environmental problems of this industry. Olive oil wastes, like alperujo, are rich sources in bioactive compounds and they are appropriate substrates for conversion into useful products. The nature of alperujo make necessary to apply specific treatment to process it successfully. It is the case of a novel thermal pre-treatment (hydrothermal reactor) that hydrolyzes bioactive compounds to liquid phase getting a final solid rich in cellulose, oil and proteins in which the calorific value has been increased. The new technology is based on a novel design that allows to operate under pressure and temperatures commonly used in the industry (up to 10 Kg/cm^2 and 190ºC). The application at the first time and combination of this technology with energy valorization methods to alperujo could solve olive oil waste problems. The alperujo is partially autohydrolysed in the hydrothermal reactor and phases are easily separated by decantation, filtration or centrifugation. Alperujo has been studied as a semisolid with high humidity (70%), but never before it has been treated using its phases liquid and solid, separately.

The aim of this study is to evaluate the valorization of the olive oil waste, like alperujo, through the utilization of its phases, the liquid and the solid. The thermal pre-treatment allows the separation of both phases. The solid is concentrated in oil that could be extracted or use together or not with the rest of the solid for energy production. The concentration of organic compounds like sugars have been decreased by the thermal treatment, getting a final solid with lower problems for energy production (volatiles compounds formation or caramelization, beside others). New compounds are both formed or increased significantly in the aqueous and oil fraction after the thermal process application. Three fractions could be obtained after treatment, a liquid phase rich in phenols and new compounds, a new pomace olive oil rich in minor components and a final solid more suitable for energy valorization.

Methodology

The hydrothermal treatment used has been patented (PCT/ES2011/070583)). It was performed using a prototype designed by our research group at the Instituto de la Grasa (Seville, Spain). The reactor has a stainless steel reservoir (100 L capacity) that can operate at temperatures between 50 and 190 ºC and at a maximum pressure of 1.2 MPa.

The phenolic extracts were fractionated by both organic solvents and chromatofraphic systems. Analyses were carried out by HPLC–DAD and MS. The antioxidant properties were determined by different methods, the antiradical activity using DPPH and ABTS radicals, reducing power, inhibition of primary oxidation and the inhibition of secondary oxidation.

Results and conclusions

The effects of time (15-90 min) on the composition of the phenolic compounds isolated at 160ºC were evaluated. Phenols were extracted with ethyl acetate. The HPLC analyses of the extracts showed variation of the concentrations of phenolic compounds with time and the apparition of new phenols. The antioxidant activities of phenolic extracts was measured by various assays conducted *in vitro*: antiradical capacity, ferric reducing power, the inhibition of primary and secondary oxidation in lipid systems. The results show that the phenolic extracts inhibited oxidation in aqueous and lipid systems to a significantly greater extent than the untreated control, and they performed as well as or better than vitamin E in this capacity.

The results of the present work showed liquors obtained from a new hydrothermal process of alperujo and extracted with ethyl acetate that have higher phenolic content and stronger antioxidant/free-radical scavenging than the control obtained with conventional extraction method. In addition, the great diversity and complexity of the natural mixtures of phenolic compound in the extracts was indicated. This thermal treatment promotes the solubilization and/or formation of new compounds not present in untreated alperujo, such as 1-acetoxypinoresinol, pinoresinol and 1-phenyl-6,7-dihydroxyisochroman, that contribute significantly to the health benefits associated with the consumption of virgin olive oils. Of all treatments and compounds determined hydroxytyrosol was found in the highest concentration and it was the main responsible of in vitro antioxidant activity of the extracts. However, antagonist or synergistic interaction between phenolic components of extracts should be considered. In addition, the positive results prove this low-cost procedure could be an alternative to conventional extraction method for obtaining antioxidant phenolic extracts from alperujo. These antioxidants could use as food additives or for applications in the pharmaceutical and cosmetic industries, revaluing the by-products of virgin olive oil processing.

NUTRIENTS LIMITATION AND PERMANENT LIGHT AS STRATEGIES TO IMPROVE METABOLITES PRODUCTION IN WASTEWATER-BORNE CYANOBACTERIA

Dulce Arias[*]**, Enrica Uggetti, Maria Jesús García-Galán, Joan García**

GEMMA – Group of Environmental Engineering and Microbiology, Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya·BarcelonaTech, c/ Jordi Girona 1-3, Building D1, E-08034, Barcelona, Spain
[*]*: dulce.maria.arias@upc.edu*

Introduction and study objectives

Nowadays, increasing attention is focused on the use of sustainable methods to produce bioplastics and biofuels to replace petroleum-based products. Polyhydroxybutyrates (PHB) and carbohydrates are compounds with high potential for bioplastics and biodiesel production, respectively. While PHBs can be generated by some bacteria and carbohydrates are produced by certain green algae, cyanobacteria are able to accumulate both compounds as intracellular carbon storage.

However, PHBs and carbohydrates accumulation yields in cyanobacteria depend on cultural conditions such as nutrients concentration or light intensity. Thus, in this paper, we explore different strategies for PHBs and glycogen production from cyanobacteria, using wastewater as feedstock.

Methodology

A mixed culture mainly dominated by cyanobacteria *Oscillatoria* sp., *Aphanocapsa* sp. and *Chroococcus* sp. obtained from a 30L closed photobioreactor (PBR) treating secondary wastewater and digestate was used for a batch experiment. The culture was subjected to a 24h light incubation during a period of 2 weeks testing two different nutritional regimes: a) N-limitation b) P-limitation.

Cultures were carried out in two closed polymethacrylate cylindrical PBRs with an inner diameter of 11 cm and a working volume of 1 L. Both reactors were agitated with a magnetic stirrer (Selecta, Spain) set at 250 rpm. Temperature was kept constant at 27 (±2) °C with a water jacket around the reactor. Light intensity was set at 220 μmol m^{-2} s^{-1} and was provided continuously through two external halogen lamps (60 W) placed on the two sides of each PBR. One reactor was inoculated with biomass submitted to N-free growth medium while the other one was submitted to P-free growth medium. In both reactors, $NaHCO_3$ was used as the inorganic carbon source continuously added to the culture in order to provide enough carbon to be transformed into PHB/carbohydrate.

Results and conclusions

Initial biomass concentration of 0.42 g volatile suspended solids (VSS) L^{-1} reached values up to 2.5 gVSS L^{-1} and a production of 0.17 gVSS L^{-1} d^{-1} for N-limited culture, while the P-limited culture achieved a concentration of 4.5 gVSS L^{-1} and a production of 0.30 gVSS L^{-1} d^{-1}. Thus, in spite of the nutrients limitation, initial biomass concentrations were incremented by 5-10 times, as a consequence of the permanent light condition.

Figure 1 shows PHB, carbohydrates and volatile suspended solids (VSS) contents of both cultures. N-limited culture obtained a constant PHB content of 5% of dry cell weight (dcw) during most of the experimental time and reached a concentration up to 137mgL^{-1}, while P-limited culture reached a PHB content of 7% dcw and a maximum concentration of 217 mgL^{-1}. Such content, achieved with a wastewater-borne culture, are similar and even higher than the 6% dcw found in pure cyanobacterial cultures submitted to nutrients limited conditions with inorganic carbon as the carbon source (De Phillips, 1992 and Meixner et al., 2016). Concerning carbohydrates, N-limited culture accumulated 40-63% from day 6 to 15 with a maximum concentration of 1gL^{-1}, while P-limited culture reached contents of 40% and a concentration of 1.5 gL^{-1}. Results are comparable to the studies of Markou et al. (2012) and Markou et al. (2013) that reached values of 50-60%.

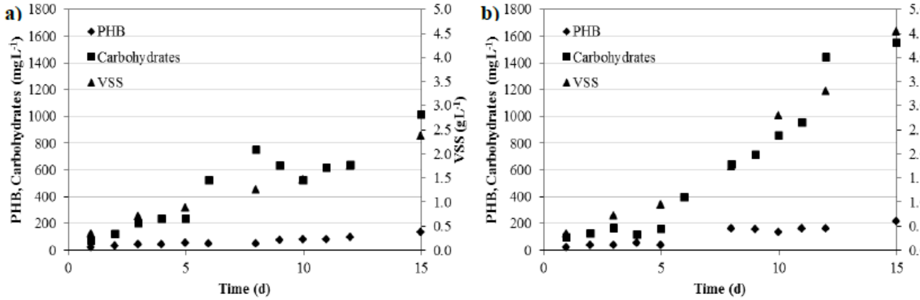

Figure 1: Volatile suspended solids (VSS), PHB, and Carbohydrates concentrations of a) N-limitation culture and b) P-limitation culture.

This study investigated the effect of starvation condition with permanent light on PHB and carbohydrates production from wastewater-borne cyanobacteria. In spite of nutrients limitation, results showed a high increase in biomass concentration. Regarding bioplastics and biofuel generation, this paper brings to the fore and demonstrates that the application of nutrients limitation could be a good approach to produce PHB and carbohydrates in wastewater-borne cyanobacteria.

Acknowledgments

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MICROBIAL POPULATION SHIFTS IN OZONE PRE-TREATED SINGLE-STAGE ANAEROBIC DIGESTERS

Asli Gumus, Bulent Icgen*

Department of Environmental Engineering, Middle East Technical University,
06800 Ankara, Turkey,
**: bicgen@metu.edu.tr*

Introduction and study objectives

Sludge treatment is commonly performed by anaerobic digestion process which leads to sludge stabilization by decomposition of its organic matter into biogas in a heated reactor and reduction of inorganic matter. Because of the emphasis on energy conservation and the desire to obtain self-sustainability in wastewater treatment plants, anaerobic digestion continues to be a dominant process for sludge stabilization. Therefore, significant effort has been focused on improvement of the performance of anaerobic digestion process such as use of chemical pre-treatments (i.e. ozonation). On the other hand, some reliable molecular methods such as fluorescent *in situ* hybridization (FISH) have gained interest for monitoring the bacterial population variation in the reactors during the performance improvement process.

In FISH experiment, rRNA molecule, which exists in multiple copies in the cell, is an excellent target for fluorescently labeled oligonucleotide probes which are directed against regions on the rRNA molecule specific for a bacterial group, genus or species. The small probes (16-20 nucleotides) cross the bacterial cell wall and hybridize with their complementary target sequence. In authors' previous work, the main step of FISH experiments included optimization of signal to noise ratios, performed by varying the *in situ* hybridization parameters for each targeted bacteria strain. Based on these systematic optimizations, direct quantification of specific groups of bacteria in fixed samples of anaerobic sludge reactors effluent was made possible, and information about microbial activities were obtained.

A partial ozone oxidation pre-treatment will be sufficient to render specific compounds more amenable to subsequent biological treatment. Ozone, as one of the strongest oxidizing agents, can be generated conveniently at treatment plants that use the high purity oxygen activated sludge process. The effect of ozonation on anaerobic digesters depends largely on the applied ozone doses. The aim of this study is determining optimum ozone dose by comparing the operational parameters of reactors and monitoring population shifts in FISH experiment during the anaerobic digestion process.

Methodology

Four semi-continuous feeding and completely mixed anaerobic reactors are set up with solid retention time/hydraulic retention time of 25 days. One of the reactors will be considered as the control reactor with no pre-treatment of its fed sludge. The rest of the reactors will be fed by different doses ozone pre-treated sludge (0.03 gO_3 $gTSS^{-1}$_

0.09 gO_3 $gTSS^{-1}$). Experiments are in mesosphere condition (35.5 °C) and pH will stay in appropriate range (6.5_7.5) using chemicals (NaOH, H_2SO_4). Anaerobic sludge culture of the reactors will be collected from Return Activated Sludge line of the Tatlar Wastewater Treatment Plant anaerobic digester located in Ankara, Turkey. Waste water used to feed the reactors will be obtained from a VRM wastewater treatment plant located in the Middle East Technical University (METU), Ankara, Turkey.

Results and conclusions

The reactors are currently in operating mode. Organic loading rate (i.e. COD) in kg COD/day, organic loading (i.e. VS) in kg VS/day, volatile suspended solid loading (i.e. VSS) in kg VSS/day, solids loading (i.e. TS) in kg TS/day, total suspended solid loading (i.e. TSS) in kg TSS/day, nitrogen loading (i.e. TN) in kg N/day, phosphorous loading (i.e. TP) in kg P/day and pH of the feed sludge are measured before feeding to reactor. The schematics of the experimental setup and preparing samples for FISH experiment can be seen in figure 1.

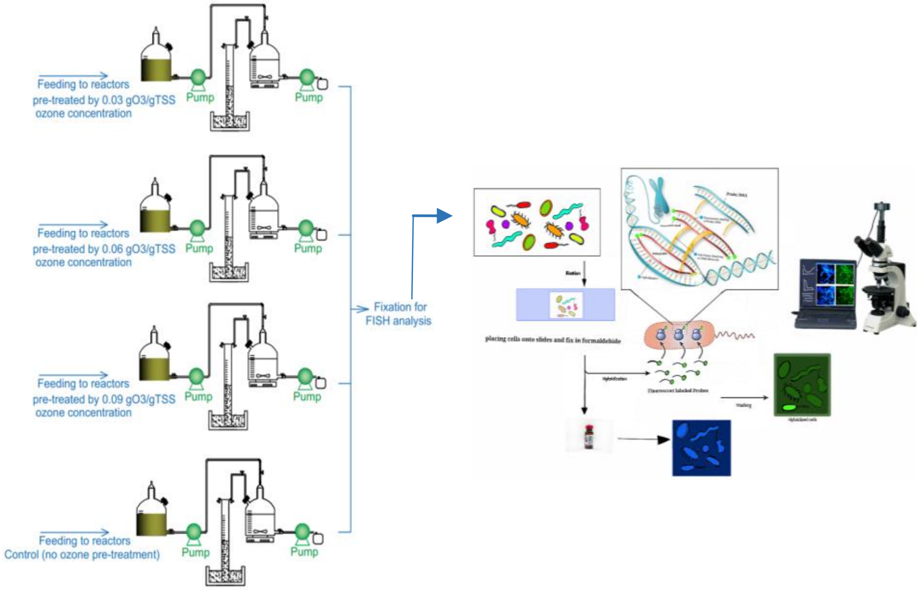

Figure 1: The schematic flow diagram of experiment

Corresponding operational data like total gas production (TGP) and its methane content, COD, TS, TSS, VS, VSS and alkalinity in effluent samples are measured three times per week. In the meantime, the dynamics of microbial consortiums in samples from control and pre-treated reactors are monitored and analyzed through FISH experiments.

Acknowledgments: This work was supported by The Scientific and Technological Research Council of Turkey (TUBITAK – 1001 Projects) under grant number of 116Y181.

HEALTH IMPACTS ATTRIBUTED TO THE OPERATION OF A MUNICIPAL SOLID WASTE-TO-ENERGY FACILITY IN THE GREATER THESSALONIKI AREA, GREECE

Christos Vlachokostas*, Georgios Tsegas, Charisios Achillas, Nicolas Moussiopoulos

Laboratory of Heat Transfer and Environmental Engineering, Aristotle University Thessaloniki, Box 483, 54124 Thessaloniki, Greece,
**: vlahoco@aix.meng.auth.gr*

Introduction and study objectives

Changing behavioral patterns and consuming habits of communities is the main reason that Municipal Solid Waste (MSW) is a very important pressure on the environment, especially in urban areas and megacities. Sustainable MSW management has become an issue of critical concern for public authorities/citizens over the past decades. This is also the case for Greece, where MSW is one of the most pressing issues facing responsible authorities in the midst of the financial crisis. A large number of unlawful landfills continue to blight Greece's beautiful countryside in breach of the Waste Framework Directive, for which Greece has been condemned by the European Court of Justice since 2005. Thus, the development of an optimal waste management strategy is not only more than urgent in the area, but will also create significant economic opportunities for businesses on a sustainable basis.

Greater Thessaloniki Area (GTA), is the second largest urban conurbation in Greece with a population of more than 1 million. Up to now, landfilling is exclusively adopted for waste management in the country. Waste-to-energy (WtE) is considered to be the only "competitor" to disposal in landfills. Public health and safety issues represent the main concerns of local communities against the development of WtE facilities. The study's main objective is to assess health impacts attributed to air pollution from the operation of a MSW WtE plant, as a future perspective in the outskirts of Thessaloniki. Three different alternative locations for three different emission scenarios are considered (Table 1). The corresponding externalities are also estimated to better demonstrate their significance to the local community. Air Quality Modeling is adopted to estimate concentrations of chemical stressors i.e. PM_{10}, NO_x, SO_2, CO, heavy metals (Cd+Ti) and dioxins-furans.

Table 1: Scenarios under study

Location	**Sindos**	Scenario 1 (S_1)	Scenario 2 (S_2)	Scenario 3 (S_3)
	Ag.Antonios	Scenario 4 (S_4)	Scenario 5 (S_5)	Scenario 6 (S_6)
	Mavrorachi	Scenario 7 (S_7)	Scenario 8 (S_8)	Scenario 9 (S_9)

Methodology

The methodological scheme follows a sequence of discrete steps. Firstly, the scenarios taken under consideration in the analysis (Table 1) and their corresponding assumptions are clearly defined and described. Secondly, the emissions from the WtE facility are quantified for each defined scenario (min, med, max). The emissions are the input to the Eulerian, three-dimensional chemical dispersion model MARS-aero, which is driven by the non-hydrostatic mesoscale meteorological model MEMO in a doubly nested configuration. The output is the concentration field of every examined pollutant in pre-defined zones in the area. The next step is the realization of Health Impact Assessment (HIA), using Concentration-Response Functions (CRFs) that correlate concentrations of the chemical stressors with specific health outcomes, i.e Years of Life Lost (YOLL) due to Chronic Mortality, Chronic Bronchitis (CB), Respiratory Hospital Admissions (RHA), Cardiovascular Hospital Admissions (CHA), Restricted Activity Days (RADs) and cases of cancers. This is followed by the monetary estimation of externalities that can be attributed to the operation of the WtE facility for each scenario.

Results and conclusions

The study presents the estimated external costs that can be attributed to the corresponding health impacts for nine (9) alternative operation scenarios in the GTA. The results clearly depict that even when taking into account the worst case scenario (maximum emission rates/worst meteorological conditions), the impact of such a facility to the public health is almost negligible, when compared to the impacts attributed to other sources of pollution. The worst case scenario for our case is approximately 3 YOLL when the total external cost of deteriorated air quality in the region is approximately 11,000 YOLL attributed to industrial activities, urban transportation and space heating.

The environmental impact in the case that the WtE facility is located in Sindos (S3) seems to be greater. However, this scenario can be considered as the optimal one. This is mainly due to the fact that Sindos is more densely populated compared to the other available locations, while also it is located close to the GTA’s industrial zone. Thus, the logistics costs for the transportation of the MSW will be minimized, while also the thermal heat that will be produced from the operation of the WtE facility will be exploited making the investment economically viable. It should be stressed out that Sindos is also grounded on the fact that the external costs attributed to the emission of air pollutants from the facility are negligible compared to the overall environmental load in the GTA.

As a final remark, comparison of the results with the overall environmental externalities assessed for the GTA allows to better understand and evaluate the order of magnitude and the severity of the environmental impacts attributed to the operation of a WtE facility in the area. Social acceptance is of vital importance in Greece in order to realistically and efficiently implement a MSW management strategy, considering that many MSW management plans were abandoned, mainly due to local community opposition and the “Not In My Back Yard” (NIMBY) syndrome. The low level of social acceptance becomes even lower when such facilities are located close to densely populated areas. Nevertheless, this study depicts that the severity of the environmental impacts of the operation of such a facility is very low, thus it could be located in a relatively short distance from domestic or industrial consumers so as to exploit also the co-generated heat from the thermal treatment. On this basis, this study hopes to contribute to better informed citizens and the maximization of public consensus in Greece, when these kind of projects are under consideration.

IMMOBILIZATION OF LIPASE FROM AGRO-FOOD BY-PRODUCTS ON GLASS WASTES AS ENVIRONMENTALLY SUSTAINABLE ALTERNATIVE IN HETEROGENEOUS BIOCATALYSIS

Luisa Barbieri[1], Isabel Belo[3], Leonardo Bertani[1], Elena Bursi[1,*], Luca Forti[2], Isabella Lancellotti[1], Felisbela Oliveira[3], Armando Venâncio[3]

[1)] Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Via Vivarelli 10, 41125 Modena, Italy
[2)] Department of Life Science, University of Modena and Reggio Emilia, Via Campi 103, 41125 Modena, Italy
[3)] CEB - Centre of Biological Engineering, University of Minho, 4710-057 Braga, Portugal
[*]: elena.bursi@unimore.it

Introduction and study objectives

Lipases (triacylglycerol ester hydrolases, EC 3.1.1.3) are a family of enzymes with great industrial potential, although they often involve high costs of production. A technique which allows to obtain low-cost lipases is the Solid-State Fermentation (SSF) of agro-food products in presence of appropriate microorganisms, such as fungi, bacteria and yeasts. The enzyme produced becomes more environmentally sustainable if it is immobilized on a solid support, in order to obtain a heterogeneous biocatalyst, easily recoverable at the end of the reaction and potentially reusable, since it retains its high catalytic power.

In this work we studied the activity of a lipase produced by SSF of olive pomace (OP) and wheat bran (WB) by *Aspergillus ibericus* and immobilized by adsorption on Pb-containing cullets from different chains as support for the catalyst. In particular, we used packaging glass from urban collection (PbO≈5 wt%) and funnel glass from cathode ray tubes (CRTs) with a high lead-content (from 12 to 25 wt% of PbO), that belongs to the Waste from Electrical and Electronic Equipment (WEEE) chain. Our goal is therefore to replace both the components of heterogeneous biocatalysis (enzyme and solid carrier) with materials of recovery, in a complete optics of circular/green economy.

Methodology

Waste glasses were firstly ground and sieved in order to obtain 180-300 μm and 300-500 μm particle sizes. Subsequently, they underwent a series of chemical treatments, which can be distinguished into surface cleaning by means of acidic and basic solutions (Treatment A and B) and silanization (C), performed in 0.3% $Cl_2(CH_3)_2Si$ in toluene at room temperature for 20 min under stirring with solid/liquid ratio of 1/10.

Lipase produced by SSF (whose activity is 20 U/mL) was diluted into phosphate buffer solution (pH=7), then absorption on glassy supports was carried out at 30 °C for 22 h.

The lipase activity was tested by UV-Vis spectrophotometric procedure using a typical lipase catalytic reaction, the hydrolysis of the *p*-nitrophenyl acetate in organic solvent. Results were compared with those obtained from semiquantitative and microstructural analysis performed by scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDS). The reuse of the immobilized lipase was also evaluated, testing the conversion efficiency of the abovementioned hydrolysis reaction up to four consecutive cycles.

Results and conclusions

The UV-Vis spectrophotometric analysis showed that the enzyme adsorption was successful on all the glass samples employed as supports. The particle size of the glass supports seems to have a key role in the effectiveness of the heterogeneous biocatalysis. In particular, higher conversion values (10-15%) were obtained for glass with 180-300 µm particle size, if compared to those obtained for 300-500 µm glass (4-8%). For the smaller particle size, the Pb content does not significantly affect the conversion. A more pronounced difference was instead obtained for the coarser particle size. A hypothesis could be that, while CRT glass is a Pb glass and almost glass beads contain Pb, glass deriving from urban collection contains both leaded and unleaded cullet. In the coarse grain size the presence of unleaded glass may have a greater influence.

The adsorption was confirmed by SEM images (Fig. 1). Dark-colored spots can be clearly observed on both types of glass. They are attributable to the adsorbed enzyme and can be identified as "lipase island". Indeed, in these areas EDS analysis detected the presence of phosphorus (deriving from the buffer in which the enzyme solution was diluted) and carbon (element due to the enzyme itself). Conversion data showed that the biocatalysts made with glass from urban collection can be reused for 4 cycles, while those made with CRT glass only for 3 cycles, gradually reducing their respective conversions efficiency, until exhaustion.

We are currently testing the same lipase adsorbed on waste glasses also to produce biodiesel by transesterification of waste vegetable oils. Contextually, we are testing silanizing agents with longer alkyl chains in order to investigate if it might produce an improvement in the adsorption step.

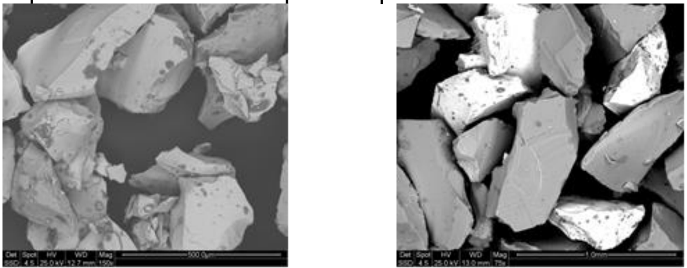

Figure 1: SEM images of glass beads from CRT (on the left) and from urban collection (on the right) with the adsorbed enzyme

PHYSICO-CHEMICAL FACTORS AFFECTING DARK FERMENTATION OF WASTE FROM CHEESE AND RICOTTA PRODUCTION

Ciro Vasmara[1], Rosa Marchetti[1,*], Anna Orsi[1], Lucia Monti[2], Giovanna Contarini[2], Riccardo Aleandri [3]

[1)] Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria (CREA), Research centre for animal production and aquaculture (ZA), Modena;
[2)] CREA-ZA, Lodi;
[3)] CREA Research centre for agricultural policies and bioeconomy, Rome
[*]: rosa.marchetti@crea.gov.it

Introduction and study objectives

Cheese whey (CW), that is, the milk whey resulting from cheese production, is still rich in lactose and proteins, and usually recovered for food and feed production. As lactose is a highly fermentable carbohydrate, CW is also more and more frequently considered as a substrate for hydrogen (H_2) and organic acid production in dark fermentation (DF). Scotta (SC) is what remains after protein recovery following cheese whey acidification for the production of ricotta, a typical Mediterranean dairy product. Scotta maintains the same amount of lactose as CW, with a much lower residual protein content. In recent years, the interest of the dairy industry has grown in the recovery of this residual amount of proteins. Proteins are removed from SC by ultrafiltration, leaving a lactose-rich, protein-free permeate (PE). As SC and PE are still rich in lactose, they could be suitable for H_2 production as well as CW. The aim of this work was to compare H_2 production by CW, SC and PE in in-batch laboratory conditions. As preliminary tests had shown that restoring the initial pH after acidification+centrifugation (AC) had a positive effect on H_2 production from cheese waste, an AC treatment was included in the comparison (Exp. I). A second experiment (Exp. II) was then carried out to identify the factors responsible for the results obtained in Exp. I.

Methodology

Cheese whey and SC where supplied by a large Italian dairy industry. Permeate was produced from scotta and supplied by the Bioproducts and Bioprocesses Laboratory of ENEA, Casaccia Research Center. Their average lactose content was 50 g L^{-1}. Exp. I: CW, SC and PE were used as they are, or after AC pre-treatment, which included: lowering the pH of the substrate at 3.2; leaving the substrate at this pH value for 3 h; centrifugation at 4000 rpm for 15 min. The AC treatment involved the formation of 3 physically separable phases: a supernatant (SU), a pellet (PL), and a floating white "cap" (FL). Separation phase was far less evident after centrifugation of CW as it is. Exp. I: Only the supernatant was used in DF. Compared treatments were: CW, CW+AC, SC, SC+AC, PE, PE+AC. Exp. II: H_2

production from SU, SU+PL, and SU+FL of CW was measured, in comparison with an untreated CW (Ctrl). Three replications were carried out for each treatment in both experiments.

Dark Fermentation was carried out at 35 °C, in 100-mL reactors, in strictly anaerobic conditions, at the pH starting value of 8.7. This pH has been demonstrated to be optimal for H_2 production from lactose containing substrates. In both experiments, each reactor was filled with 50 mL non-sterile substrate and 5 mL inoculum. The reactors were incubated in static conditions with occasional stirring.

Hydrogen volume was measured at 9 time intervals, during a 96-h incubation period. Hydrogen concentration in the reactor headspace was determined by means of a TCD-equipped gas chromatograph (GC). Total solids (TS), ashes, volatile solids (VS), chemical oxygen demand (COD), total N, fats, protein composition, and pH were determined in all substrates before and after pre-treatment. Residual lactose, pH, ethanol, volatile fatty acid and lactic acid concentrations were measured at the end of the incubation period. Volatile fatty acids were determined by means of a GC equipped with a capillary column and a FID. Lactose, ethanol and lactic acid concentrations were determined enzymatically. Total protein content was determined by the Kjeldahl method. Protein composition was determined by HPLC. Fat content was determined gravimetrically.

Results and conclusions

Exp. I: When waste as a whole was used, H_2 was produced in all treatments. The maximum H_2 production was 4 L L^{-1} substrate for SC and PE, with a production rate of 0.08 L H_2 h^{-1} L^{-1} substrate, whereas only 0.1 mL H_2 L^{-1} substrate were accumulated in CW at the end of the incubation period. After AC treatment, the maximum amount of 4 L H_2 L^{-1} substrate was obtained for all treatments, including CW. Exp. II: In SU+PL, SU+FL, and SU the H_2 production was similar in all these reactors and it was very higher than the Ctrl.

Even though the total protein content was much higher in CW (0.8%) than in SC (0.23%) and PE (0.1%), it was however not affected by the AC treatment. Soluble CW proteins were 10% lower in CW+AC than in CW, whereas they were completely lacking either in treated or not treated SC and PE.

In conclusion, SC and PE are more sustainable substrates in DF than CW, either because they allow higher H_2 production, and because the H_2 production phase sums up to a protein recovery phase, following a biorefinery approach. A H_2-production recovery is however possible from CW by an acidification + centrifugation treatment. The recovery effect in H_2 production seems due to changes in some CW physico-chemical factors, more than to protein removal. In fact the acidification treatment, while not modifying the total protein content of CW, induced changes in its physico-chemical state, as shown by phase separation in centrifugation following acidification.

Acknowledgements

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EVALUATION OF SRF PRODUCTION FROM BIODEGRADABLE MUNICIPAL SOLID WASTE: A METROPOLITAN CITY APPROACH-IZMIR-TURKEY

Ayşenur Bölükbaş[*], **Görkem Akinci**

Dokuz Eylül University Environmental Engineering Department Tınaztepe Campus 35390 Buca/IZMIR, TURKEY,
[*] *: aysenur.bolukbas@deu.edu.tr*

Introduction and study objectives

Municipal solid waste (MSW) production has been a significant problem for metropolitan cities because of the economic development, industrialization, and public practices. Global MSW generation rate is about 1.2 kg/capital/day with regard to the World Bank. This rate is averagely 1.3 billion tonnes per year and it is expected to be 2.1 billion tonnes/year in the near future. The changes in waste amount and composition are caused by the modern civilization, changes of consumption behavior and population increase.

As a developing country, Turkey, especially metropolitan cities of it, is face to MSW management problems. Improving industrialization and increasing living standards result in increase of waste amount and change in composition and properties of solid waste. The current solid waste management tools are inadequate and inefficient. There is a need to find new methods to treat municipal solid waste by meeting the requirements of the public.

While finding new disposal methods for biodegradable solid wastes, another aim is to produce eco-friendly energy as heat and electricity. The waste-to-energy conversion can be applied via combustion, gasification, pyrolysis, anaerobic digestion etc. Another promising method is producing solid recovered fuel (SRF). The household, industrial, commerce, forestry and agricultural solid wastes have a certain calorific value. Therefore, these wastes can be used in the Waste to Energy plants as waste fuel or solid recovered fuel (SRF). In basic, SRF can be explained as solid fuel prepared from sorted or mixed solid wastes such as municipality waste, commercial waste and production wastes. The properties of fuel such as moisture, heating value, particle size, chlorine and Hg content have important roles in the production of SRF.

There are a few researches about the calorific capacity of biodegradable solid waste in Turkey. The main aim of the study was to evaluate the thermal capacity of the biodegradable part of municipal solid waste in Izmir. Another aim is determining the composition and characterization of the municipal solid waste of Izmir in order to lead the thermal capacity evaluation. Finally the assessment of applicability of SRF production from biodegradable solid waste was aimed and with respect to results determining the most suitable pretreatment and production methods were planned.

Methodology

At the beginning of the project, solid wastes have been taken from three districts of each country; Mavisehir, Alaybey and Ornekkoy from Karsiyaka, Kizilay, Erzene and Naldoken from Bornova and Alsancak, Guzelyali and Basmane from Konak. After separation of recyclables, the remaining part (mostly biodegradables) of solid wastes was sieved from six different mesh size (10, 30, 50, 80, 100 and 120 mm). As a result, from 9 districts and 7 fractions 63 solid waste samples have been obtained. Various analyzes have been carried out to each of the particle size fractions. The parameters performed within the project are moisture (%w), calorific value (kcal/kg dw), organic matter (%dw), ash content (%),water soluble chlorine (%), total organic carbon (%w) and total carbon (%w).

Results and conclusions

The average biodegradable part of the solid wastes sampled from the regions was 60.9 % and the average moisture (in bulk and in fractions) was 62.6 %. The average organic matter was also found as 61.8 % dw. Moreover, the average ash content was 30.7 % dw. The water content should be less than 35 % with regard to Statement about SRF of Turkey. Furthermore, the calorific value has to be more than 2500 kcal/kg and the chlorine content should be less than 1 %. According to the water content limit, the wastes samples in the study should be dried in order to decrease the water content less than 35 %. Bio-drying can be used to dry the waste samples in a cheap and efficient way.

The maximum total carbon value is observed in Guzelyali-2 as 47.277 %, while the minimum total carbon value is seen in Kizilay-fine as 12.198 %. The biggest total organic carbon value can be observed in Naldoken-3 as 43.744 %. The smallest total organic carbon value is in Kizilay-fine as 9.27 %. The maximum total inorganic carbon value can be observed in Ornekkoy-1 as 20.832, as the minimum total inorganic carbon value is seen in Basmane-6 as 0.621 %. The maximum calorific value can be seen in Naldoken-3 as 4169.625 kcal/kg, while the minimum calorific value is observed in Ornekkoy-1 as 1393.739 kcal/kg. Exceptionally a few samples' chlorine contents are more than 1 % as defined in the statement; however, the general of the samples are proper with regard to chlorine content because the average chlorine content has been found as 0.86 %.

The calorific values of solid wastes in Izmir are sufficient and other parameters are appropriate with respect to the literature and Statement about SRF of Turkey, however; the water content has an important role and the moisture values are very high. Hence the water content should be handled properly to obtain efficient performance from the SRF. Therefore, according to the initial findings, if necessary sorting and drying experiments are conducted, the biodegradable part of the solid waste in Izmir is suitable for SRF production. SRF produced in the study can be used as fuel in the pre-calciner of clinker process in the cement industry or in the fluidized bed incinerator.

Acknowledgment

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REE4EU: INTEGRATED HIGH TEMPERATURE ELECTROLYSIS (HTE) AND ION LIQUID EXTRACTION (ILE) FOR A STRONG AND INDEPENDENT EUROPEAN RARE EARTH ELEMENTS SUPPLY CHAIN.

Patrizia Circelli, Silvia Colella, Nader Akil, Emanuele Festa, Valentina Cinti

CiaoTech PNO Group; Via Colajanni 4, 00191 Rome (Italy),
[*]: p.circelli@ciaotech.com , s.colella@ciaotech.com , nader.akil@pnoconsultants.com
emanuele.festa@pnoconsultants.com , v.cinti@ciaotech.com

Introduction and study objectives

The REE4EU project, funded in the frame of Horizon 2020 TOPIC SPIRE-07-2015 under Grant Agreement n° 680507, will realize a breakthrough innovation in the field of recovery technologies for metals and other minerals. It will make available Rare Earth Elements (REEs) and Rare Earth Alloys (REA) for magnet production by developing, for the first time at industrial scale, an efficient and cost effective method of extraction and a direct production route for REA which will be achieved /through in-process and End-of-Life (EoL) permanent magnets as well as Ni metal hydride battery waste. It started on October 2015 and it will last 4 years involving in its consortium 14 partners from 7 European Countries representing the full value chain and coordinated by SINTEF.

REEs are considered "key-enablers" of green technologies, as they are crucial in hybrid electric vehicles, wind mills and highly efficient electric motors. Additionally, they are necessary for many widely used hi-tech products such as computer memory, DVDs, rechargeable batteries, cell phones, fluorescent lighting to name a few.

The dependence on Chinese exports makes Europe, and western countries in general, extremely dependent to Chinese market control and REE are considered to be materials with the highest supply-risk. A recent study estimates the global trade in RE-containing products in 2010 at around €1.5 trillion, equivalent to 13% of the global trade but only 1% of RE waste is being recovered as no adequate process is currently available. To mitigate the supply risk, recently there have been a number of publically and privately funded initiatives in Europe investigating the recovery of REE. In order to have an overview on the European innovation landscape in this domain as well as the most relevant industrial actors who are active in the recovery of REE, value chains stakeholders analysis has been performed by PNO, as partner of the REE4EU project.

In this framework, the most relevant stakeholders (mainly European) have been assessed in a Value Chains Stakeholders Analysis Report. The aim of this report is, on the one hand, to help the consortium partners in setting up targeted dissemination and communications actions towards the relevant group of stakeholders from a specific value chain, and on the other hand, to provide information to the public at large on the relevant industrial and academic stakeholders that are connected to the topic of the recovery of REE. Furthermore a selected group of identified stakeholders are being interviewed to elaborate a market analysis on the most relevant EoL products containing REE. The market study and the reports will be available to the public by October 2017 and will be downloadable from the Innovation Place website of PNO (www.innovationplace.eu).

Methodology

The results presented in the REE4EU project have been acquired, based on a methodology elaborated by PNO, to determine the value chain needs analysis for the recovery of REE and the most relevant stakeholders that could benefit from the technologies developed in the project. The methodology is based on the following approach: a) Screening of the CORDIS database to identify the ***Innovators*** in Europe around the topic of recovery of REE; b) Screening of several patent databases such as WIPO or Espacenet to identify the ***Potential Investors*** in the topic of REE recovery; c) Desktop research, through associations and main reports to identify relevant stakeholders as ***Potential Business Drivers*** for the concept and technologies used in the REE4EU project.

The stakeholder analysis provides, therefore, relevant information on the most important industrial companies and research centers that are performing international innovation, research, and business activities within or around the value chain of the REE4EU project. In the report, the geographical characterization and the position of each industrial stakeholder in the value chains related to the recovery of REE are identified, websites and concise information about their activities, potential interests, and how they can be connected to the REE4EU project is also provided. Moreover, the analysis identifies and describes the stakeholders, representative of potential end users of the REE produced, connected to the 9 products/applications presented in the report of the "European Rare Earths Competency Network" (ERECON): hard disk drives, DVD and CD players, automotive applications, motors in industrial applications (e.g. servo motors from robotics), loudspeakers, air conditioning compressors, magnetic separators, mixed electronics, electric bicycles and wind turbines.

Results and conclusions

To summarize the main results, the Value Chains Stakeholders Analysis Report provides a helicopter view on the most relevant stakeholders who are connected to the to the REE4EU value chains.

Although the list of stakeholders provided in the document is by no means exhaustive, the study provides relevant information on more than 300 important stakeholders identified. Additionally, a market analysis is been developed by PNO and key partners of the REE4EU project, by exploiting the results of the stakeholders' analysis.

In particular, the market analyses will be carried out to develop a three-fold business plan strategy, 1) for the economic recovery and re-use of in-process permanent magnets, 2) related to the economic feasibility of collection, dismantling and recovery of EoL REE containing products and 3) for the investment in a new European RE-Alloy production plant, using multiple feedstock.

In parallel CiaoTech PNO is implementing also a communication and dissemination plan to underpin adequate involvement of all relevant stakeholders.

BIOCONVERSION OF CITRUS WASTES INTO LIPIDS BY *Zygomycetes*

Eleonora Carota*, Maurizio Petruccioli, Anna M. Gallo,
Silvia Crognale, Alessandro D'Annibale

Department of Innovation in Biological, Agro-food and Forest systems (DIBAF), Tuscia University, Via San Camillo De Lellis – Viterbo (Italy)
**: carota@unitus.it*

Introduction and study objectives

Zygomycotes are filamentous fungi able to convert a wide range of carbon sources into interesting industrial metabolites. Some species belonging to this class, have also been classified as *oleaginous*, being able to accumulate significant quantities of storage intracellular lipids, above the 20% of their dry weight. Among the lipids produced, ω-6 (linoleic acid) and ω-3 (eicosapentanoic and docosahexaenoic acids) could be valuable additive in the food industy, while others including palmitic, palmitolec, oleic and stearic acids could be used as renewable and sustainable feedstock for biodiesel production. Although the production of lipids from zygomycetes has been studied by several research groups, it still represents a challenge for different reasons. First of all, the fermentation must be performed on low-cost substrates, in order to reduce the costs and make the process economically feasible. Furthermore, the filamentous structure of these fungi might lead to the formation of large cell aggregates, which allow an easy biomass recovery by filtration, but represent a technical constraint for submerged fermentations, limiting mass transfer and negatively affecting sampling.

Orange peels is a solid waste widely produced in the Mediterranean area. Due to its low cost and scant valorization, it might constitute a cost-effective substrate for microbial bioconversions. For this reason, 6 oleaginous fungal strains, belonging to the genera *Cunninghamella*, *Mortierella* and *Mucor*, were evaluated in shaken flask for their abilities to grow on orange peel aqueous extract (OPE) accumulating lipids. Then, the lipid production process on OPE as the growth medium was transferred to the bioreactor level by using the most promising strain in order to assess preliminarily its upscaling.

Methodology

Microbial strains and inoculum production: Cunninghamella echinulata NRRL 3655, *Mortierella isabellina* NRRL 1757, *Mucor circinelloides* NRRL 3631, *Mucor miehei* NRRL 3169 and *Mucor racemosus* UCD 71-20 were obtained from the ARS and UCD Culture Collections (NRRL, Peoria and Davis, California), while *Mucor moelleri* was an environmental isolate. Pre-inoculum was prepared by growing 10^6 spores/ml in 250-ml flasks containing 50 ml of PDB medium, at 30 °C for 3 days in shaken culture (185 rpm).

Growth medium and culture conditions: Air-dried orange peels where crushed using a blender and then subjected to extraction at 100 °C in distilled water for 1 hour and then filtered through Whatman n. 41. The aqueous extract thus obtained, had a total sugar of 20 g/l and a very low nitrogen content (16 mg/l). For this reason, it was supplemented with $(NH_4)_2SO_4$ to reach a C/N ratio of 55 and adjusted to pH 5.5 prior to sterilization.

All experiments in shaken culture were performed in 250-mL Erlenmeyer flasks containing 49 mL of growth medium inoculated with 1 ml of pre-inoculum. Cultures were incubated in an orbital shaker (185 rpm) at 30 °C for 5 d. Samples were collected on a daily basis.

Batch fermentations were carried out in a jacketed 3-L stirred tank reactor (STR), with a working volume of 2 L, equipped with DO and pH probes. The agitation rate was set at 500 rpm, aeration at 1.5 vvm and temperature was maintained at 30 °C. Samples were collected every 12 hours.

Analytical methods: Biomass was determined gravimetrically after lyophilisation for 72 hours. Total sugars content was measured using the phenol sulphuric acid method. A sulfo-phospho-vanillin reaction was used for quantitation of lipid content. Nitrogen was determined by a modified Kjeldahl method. Fatty acid profiles were analyzed by gas chromatography after a direct transesterification on liophilised cells, followed by extraction with hexane.

Results and conclusions

Table 1 reports values of biomass and maximal lipid content with respect to dry biomass.

Table 1. Biomass, lipid productions and time of maximal lipid accumulation obtained for the strains tested

Strains	Biomass (g/l)	Lipid content (%, w/w)	Time (h)
C. echinulata	4.08±0.03	19.14±0.71	48
M. isabellina	11.21±0.35	27.63±2.28	72
M. circinelloides	8.63±0.14	21.02±1.79	72
M. miehei	11.05±0.11	20.15±0.23	72
M. moelleri	5.45±0.14	18.31±0.49	72
M. racemosus	2.59±0.23	20.86±1.84	96

Among the strains tested, *M. isabellina* and *M. miehei* showed a remarkable growth, demonstrating their capability of efficiently metabolizing sugars present in orange peels, including mainly glucose, saccarose and fructose. The first strain was also able to accumulate the highest lipid percentage, amounting to 28% of dry weight. GC analysis showed a predominance of oleic, linoleic acid and palmitic acid, amounting respectively to 36%, 27% and 20% with respect to total FAME. Among them, linoleic acid is of interest as a food additive in both enfants and adult formulations.

Transfer to bioreactor scale of *M. isabellina*, thanks probably to the high agitation rate, was not so problematic as expected, even if the lower biomass obtained (9.9 g/l) was probably due to the stress caused by mechanical agitation, as already observed in other studies. On the other hand, the reduced biomass was offset by a higher lipid content, amounting to the 37.5%, showing that the transfer to a bioreactor scale, albeit needing some improvements, it is certainly feasible.

Aknowledgments

We thank the ARS Culture Collection (IL) for providing some of the strains under study.

EFFECT OF ULTRASONIC IRRADIATION IN IMPROVING DELIGNIFICATION OF OIL PALM FRONDS TOGETHER WITH THE USE OF DEEP EUTECTIC SOLVENT

Ta Yeong Wu[1,*], Eng Kein New[1], Yu-Loong Loow[1],
Cornelius Basil Tien Loong Lee[1], Nicholas Wei Ren Cheong[1],
Luther Yang Wei Foo[1]

1) Chemical Engineering Discipline, School of Engineering, Monash University, Jalan Lagoon Selatan, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia.
**: wu.ta.yeong@monash.edu*

Introduction and study objectives

In recent years, intense development in the industry sector has resulted in an increasing demand for global energy which includes fossil fuels. This, in turn, causes excessive amounts of non-renewable fossil fuels being utilized at an alarming rate. With the aim of creating a more sustainable global environment for the present as well as the future generations, the depletion of crude oil and rise of carbon footprint resulted from the usage of fossil fuels serves as a major hindrance to achieving the goal. Due to rising concerns over the stagnant sustainable growth, researches have been conducted on alternative biochemical methods to substitute the long established petrochemical processes in the field of fuel and chemical productions. One of the promising methods is biorefinery which involves the utilization of biomass or other forms of renewable resources to produce high-value products. Global production of lignocellulosic biomass is extremely high which makes it the most abundant feedstock on earth. Most common method of removing excessive biomass is incineration as fuel which in turn causes the release of greenhouse gasses to the environment. Instead of waste disposal, it can be transformed into useful materials. The sophisticated structure within lignocellulosic biomass has caused problems in the process of digestibility and component extraction. Therefore a pretreatment stage is mandatory. Deep Eutectic Solvents (DESs) have been proven to be relatively effective in lignin removal as lignin serves as a protective barrier from chemical or solvent attacks. The study objective was to further enhance the functionality of DESs by incorporating energy irradiation namely ultrasound (US).

Methodology

Oil Palm Frond (OPF) was used as a lignocellulosic biomass in this study. Chemical based materials, namely choline chloride and urea, were used to synthesize Type III DES. In this study, only Type III DES was considered. It can be formed by mixing choline chloride and urea in a molar ratio of 1:2. The mixture was then heated to an elevated temperature of 90 ^{o}C and stirred at a rate of 200 rpm using a magnetic stirrer in an hour until a homogeneous colorless mixture was formed. OPF was treated using DES with a solid to liquid ratio of 1:10. 3.0 g of OPF and 30 ml of DES were mixed in a 50 ml Schott bottle. Two different concentrations of DES were prepared, namely 100% DES and 50% DES. 100% DES was pure DES whereas 50% DES was prepared via dilution using distilled water with 50% of its volume made up of distilled water. Ultrasound-assisted OPF and DES pretreatment was carried out indirectly in an ultrasound bath using a cup horn at 80% amplitude (20 kHz) with a pulsation of 3 s on and 1 s off for 40 minutes. The mixture was then heated in an oil bath to an elevated temperature of 120°C for 4 h at 1 atm. The treated OPF was undergone qualitative lignin content analysis by utilizing Fourier transform infrared spectroscopy (FTIR). The spectra obtained via FTIR was studied to conclude the initial findings of this experiment.

Results and conclusions

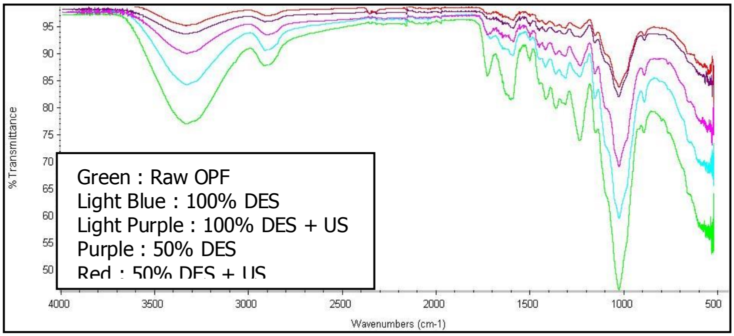


Figure 1: Effect of ultrasound-assisted DES pretreatment on different DES concentrations at 80% amplitude (20kHz) for 40 minutes

The ultrasound-assisted DES pre-treated OPF were analyzed, and the contents of lignin after treatment was determined based on the peaks obtained via FTIR. Specific wavenumbers on the spectra represent different functional groups which in turn provide information regarding the amount of lignin exist within the structure of OPF after pre-treatment. In this case, two different concentrations of DESs were applied, namely 100% DES and 50% DES, both undergone with and without ultrasound incorporation. Based on the results obtained (Figure 1), the effect of ultrasound impregnation was seen to be improving the overall effectiveness of DES pre-treatment. The peak at 1508 cm^{-1} was reduced from raw OPF (Green) to 50% DES with US (Red), implying that the aromatic skeletal C=C vibration from the lignin aromatic ring structure has been reduced. Another evidence that can further justify the claim is the reduction of intensity at peak 1235 cm^{-1} which represent the disintegration of C-O-C aryl-alkyl ether that presents within the structure of lignin. Ultrasound-assisted pretreatment portrayed a more prominent effect on lignin removal when 100% DES (Light blue) and 100% DES with US (Light purple) were compared whereby peaks were seen to be less steep as compared to the pre-treatment without ultrasound. The identical phenomenon could be observed at 50% DES with and without US. In conclusion, ultrasound-assisted DES pre-treatment was proven to be more effective in delignification of OPF.

POTENTIAL USE OF PURE AND DILUTED CHOLINE CHLORIDE-BASED DEEP EUTECTIC SOLVENT IN DELIGNIFICATION OF OIL PALM FRONDS

Eng Kein New[1], Ta Yeong Wu[1,*], Yu-Loong Loow[1], Zi Yet Poon[1], Luther Yang Wei Foo[1]

[1)] Chemical Engineering Discipline, School of Engineering, Monash University, Jalan Lagoon Selatan, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia.
[*] : wu.ta.yeong@monash.edu

Introduction and study objectives

One of the most prominent challenges facing humanity in contemporary society is to enable and envision a transition from the non-sustainable present to a more sustainable future. The main hindrance towards a more sustainable development is the depletion of remaining reserves of fossil fuel as well as emissions resulted from the combustion of fossil fuels. Recently, the focus of the study is shifting towards the utilization of plant biomass as it is regarded as the central and intermediate in a world substantiated by natural resources. Unfortunately, the complex chemical structure within lignocellulosic biomass, namely lignin has caused the extraction or transformation of biomass to be sophisticated. The existence of deep eutectic solvents (DESs) has improved the process of biomass valorization due to its ability on breaking down the recalcitrant structure in biomass which in turn producing higher value products. DES is considered to be sustainable as its production is simple and inexpensive, low environmental impact as well as minimal toxicity towards human health. The objective of this study was to provide information regarding the effectiveness of Type III DES on the reduction of lignin content. To further scrutinize its functionality, different concentrations of DESs were applied and the results were provided in this paper.

Methodology

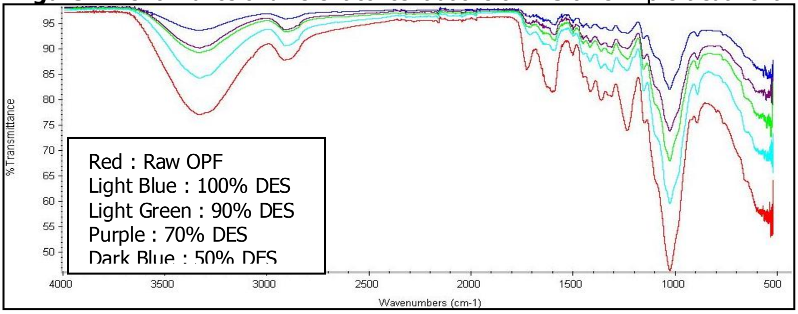
Oil Palm Frond (OPF) was used as a lignocellulosic biomass in this study. Choline chloride and urea were used to synthesize Type III DES. In this study, only Type III DES was considered. It can be formed by mixing choline chloride and urea in a molar ratio of 1:2. The mixture was then heated to an elevated temperature of 90^{o}C and stirred at 200 rpm using a magnetic stirrer for an hour until a homogeneous colorless mixture was formed. OPF was treated using DES with a solid to liquid ratio of 1:10. 3.0 g of OPF and 30 ml of DES were mixed in a 50 ml Schott bottle. Dilution was carried out by adding distilled water into DES, whereby 50% DES was a mixture of water to DES in a volume ratio of 1:1. The mixture was then heated in an oil bath to an elevated temperature of 120 ^{o}C for 4 h at 1 atm. The treated OPF was undergone quantitative lignin content analysis via acid hydrolysis adapted from NREL and qualitative lignin analysis via Fourier Transform Infrared Spectroscopy (FTIR). 3 ml of 72% of H_2SO_4 was added into 0.3 g of OPF. The mixture was then incubated at 30 °C and 150 rpm for 1 hour. 84 ml of distilled water was then introduced into the mixture and sent for autoclave at 121 °C for 1 hour. The filtrate obtained via vacuum filtration was used for acid soluble and insoluble lignin test. Acid soluble lignin was determined by using the liquid hydrolysate after acid hydrolysis and examined using UV-Vis at 320 nm. As for acid insoluble lignin, it could be calculated by referring to the difference in terms of weight of the filter paper before and after vacuum filtration.

Results and conclusions

Table 1 Performance of each DES concentration

	Raw OPF	100 % DES	90 % DES	70 % DES	50 % DES
Weight before hydrolysis (g)	0.3016	0.3022	0.3034	0.3030	0.3020
Weight of Filter Paper (g)	0.1122	0.1184	0.1166	0.1144	0.1180
Weight of AIL and Filter Paper (g)	0.1783	0.1817	0.1807	0.1783	0.1755
Acid Insoluble Lignin (g)	0.0661	0.0633	0.0641	0.0639	0.0575
Acid Insoluble Lignin (%)	21.92	20.95	21.13	21.09	19.04
Acid Soluble Lignin (%)	0.790	1.11	0.851	0.812	0.937
Total Lignin Content (%)	22.710	22.06	21.98	21.90	19.977

Figure 1: Performance of different concentrations of DES on OPF pre-treatment via FTIR



In this study, different concentrations of DESs were investigated. It was evident that diluted DES performed better in terms of delignification (Table 1) due to better mass transfer resulted from a reduction in viscosity of DES. The total lignin content of OPF after pre-treatment using 100% DES was 22.06% whereas the later resulting in only 19.977 % of lignin. The FTIR spectra shown in Figure 1 includes both raw and pre-treated OPF. The peak at 1508 cm^{-1} decreased from raw OPF (Red) to 50% DES (Dark blue), implying that the aromatic skeletal C=C vibration from the lignin aromatic ring structure was reduced. The result indicated that partial amounts of lignin were removed upon an addition of DES in different concentrations. The reduction of intensity at peak 1235 cm^{-1} also represented the destruction of C-O-C aryl-alkyl ether that existed within the structure of lignin. The preliminary finding showed that 50% DES was the most efficient concentration during the pre-treatment of OPF.

THE EFFECT OF RED MUD ON THE SOIL BIOTA IN SANDY SOILS – A MICROCOSM EXPERIMENT

Viktória Feigl*, Ivett Kerekes, Éva Farkas, Mónika Molnár

Budapest University of Technology and Economics, Faculty of Chemical Technology and Biotechnology, Department of Applied Biotechnology and Food Science; 1111 Műegyetem Rkp. 3, Budapest, Hungary,
**: vfeigl@mail.bme.hu,*

Introduction and study objectives

Red mud is the alkaline by-product of the alumina production from bauxite by the Bayer process. An estimated 2.7 billion tonnes of red mud is produced worldwide every year and this amount will be increasing probably by approximately 120 million tonnes per annum. Red mud can be re-used in construction, chemical, environmental, agronomic and metallurgical applications. In particular, sandy soils, with little or no nutrient or water holding capacity could benefit from the application of bauxite residues, as red mud could improve water and nutrient holding capacities by improving soil structure. Studies investigating the effects of red mud as soil ameliorant for acidic and/or sandy soils were only focusing on the changes in the soil physical and chemical characteristics and on the effect of red mud on the crop yields, but not on the soil's microbiological activity. There are also limited number of studies on the effects of red mud on soil's flora and fauna. The objectives of our work was to study the effects of red mud in low amounts (up to 10 w/w%) on the microbial activity and community structure of an acidic and a carbonated sandy soil, and to assess the effects of red mud on the soil as habitat for plants and animals.

Methodology

Red mud (RM) from Ajka, Hungary (from the red mud deposit, pH=8.9, water content=36%) was mixed into an acidic sandy soil (ASS, pH=4.9, sand=85%) and a carbonated sandy soil (CSS, pH=8.2, sand=81%) in 3 kg microcosms at 0, 1, 2,5, 5, 7,5 and 10 w/w% in three replicates. The microcosms were incubated at room temperature (22±2 °C) and irrigated to 60% water holding capacity every 2 weeks.

The microcosms were sampled at the beginning of the experiment and after 2 months. The short term effects of red mud was measured by an integrated methodology combining physical, chemical, biological and ecotoxicological methods. Water holding capacity (WHC), pH, electrical conductivity (EC), total (aqua regia extract) and water soluble (distilled water extract) metal content, plant available P and K content, NO_3^-, NO_2^-, NH_4^+, PO_4^{3-} and SO_4^{2-} content was measured as background parameters. The study was focusing on the microbiological effects:

living cell numbers (bacteria, fungi, Actinomycetes, phosphorous mobilizing bacteria, nitrogen-fixing bacteria; kopiotrophic and oligotrophic cell number), enzyme activities (dehydrogenase, invertase, β-glucosidase, phosphomonoeasterase, urease), substrate induced respiration and community-level physiological profile (BIOLOG EcoPlate). To ensure that red mud does not pose any risks to the environment by mixing it into soil ecotoxicity was assessed by *Aliivibrio fischeri* bioluminescnece inhibition test, plant elongation inhibition tests (*Sinapis alba* and *Triticum aestivum*) and earthworm (*Dendrobena veneta*) and Collembola (*Folsomia candida*) avoidance tests.

Results and conclusions

Red mud addition increased the pH and EC of both soils. For example in the case of the ASS (pH=4.9) 1% RM addition resulted in pH=7.3, 5% in pH=8.6 and 10% in pH=9.5. In the same soil EC increased from 63 µS/cm to 106 µS/cm, 245 µS/cm and 277 µS/cm, respectively. The WHC of the soils did not change significantly at these low RM doses. The bacteria living cell number measured by plate count method increased 3 times at 1%, 6 times at 5% and 15 times at 10% RM addition in ASS. The highest influence by RM addition was observed for Actinomycetes cell number in ASS: ~20 times increase was measured at 1–5% RM doses and ~60 times increase at 7.5–10% RM doses. Anaerobic cell numbers increased after the addition of 7.5–10% RM by 3–4 order of magnitude in both soils. Dehydrogenase enzyme activity increased 2 times at 2.5–10% RM dose in ASS and 1.2 times in CSS. Substrate induced respiration increased 3 times at 5–10% RM dose is ASS. *Sinapis alba* plant elongation was not influenced in the ASS soil at up to 5% RM dose, but decreased by 27–38% at 7.5–10% RM dose. The plant elongation was not affected significantly in the CSS soil at up to 10% RM. For the *Tetrahymena pyriformis* protozoon only 1% RM addition in ASS was favourable resulting in a 20% increase in cell numbers, but higher RM amounts caused 50–80% inhibition in reproduction. Based on the above presented selected results it can be concluded that red mud addition influenced the chemical composition of the sandy soils by increasing soil pH and mobile ion content. Red mud increased both aerobic and anaerobic cell numbers and overall microbial activity in both soils and the highest increase was observed at the highest red mud doses: 7.5% and 10%. However, the higher amounts caused inhibition for both plants and animals, so one should be careful when applying higher than 5% red mud in soils.

Acknowledgement

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EFFECTS OF SEWAGE SLUDGE BIOCHAR IN MIXTURE WITH TRADITIONAL ROMANIAN COMPOST ON SOIL PROPERTIES

Elena Goldan[1,*], Iuliana Lazar[1], Xavier Domene[2,3]

[1) "Vasile Alecsandri" University of Bacau, 600115, Romania
[2) CREAF, Cerdanyola del Vallès 08193, Spain
[3) Universitat Autònoma Barcelona, Cerdanyola del Vallès 08193, Spain
[*]: *goldanelena@yahoo.com*

Introduction and study objectives

Application of biochar can have a wide range of physical, chemical and biological effects on soil. These effects depend on the properties of biochar, which are determined by the method of production, type of feedstock and the pyrolysis temperature. Potential functions of biochar are: increase of the organic matter, carbon isolation, increased water retention, change of the pH of the soil, provision of nutrients available to plants. The positive effects on plant growth and nutrient content are usually observed using biochar in combination with other types of fertilizers. Mranita (traditional Romanian compost) is an organic fertilizer resulting from the decomposition of manure after a period of 1-3 years and is a product rich in organic matter and minerals. The manure is important not only as the amount of nutrients inserted into the soil, but also for improving the conditions for growth and development of plants. The sewage sludge biochar and traditional Romanian compost (mranita) were used in different proportions at two application rates of 5 t/ha and 30 t/ha on the yield barley plant. This study evaluated the effects of the mixture between sewage sludge biochar and traditional Romanian compost (mranita) on pH, conductivity and soil respiration.

Methodology

A greenhouse experiment was conducted in period August-November 2016 in Bacau, Romania, using barley like study plant. In this study two application rates were used, each with a control version and 11 different concentrations, each achieved in 6 repetitions. The application rates were of 5 t/ha with notations: 5/C, 5/M0-B100, 5/M10-B90, 5/M20-B80, 5/M30-B70, 5/M40-B60, 5/M50-B50, 5/M60-B40, 5/M70-B30, 5/M80-B20, 5/M90-B10, 5/M100-B0 and 30 t/ha with notations: 30/C, 30/M0-B100, 30/M10-B90, 30/M20-B80, 30/M30-B70, 30/M40-B60, 30/M50-B50, 30/M60-B40, 30/M70-B30, 30/M80-B20, 30/M90-B10, 30/M100-B0.

Materials used in this study are biochar obtained from sewage sludge at 500 °C produced by NovoCarbo Company from Germany and traditional compost (mranita) obtained from cattle manure. The manure was sitting in the stacks on the soil surface and covered with a thick layer of soil about 15-20 cm and left in natural conditions for 2 years. The soil used in the study was collected from the Bacau County, Romania in July 2016 from an area uncultivated for at least 5 years. After achieving the desired concentrations, in each pot were planted 25 seeds of barley and the number of germinated plants was daily monitored. After completion of germination period, the number of plants of barley has been reduced at two per pot. Monitoring of plant height and number of branches was done in the middle period and the end of the experiment. The duration of the experiment was 90 days, the days 40-44 were considered the middle period, and the end was days with number 85-90. At the end of the experiment, plants were collected and dried at 70 °C for 12 h. Soil samples were collected in three different stages of the experiment, namely the beginning of the experiment, middle and the end of the experiment period. The pH and conductivity were determined in aqueous suspension in the ratio of 1:5 soil:water. For measuring soil respiration the titration method with HCl was used.

Results and conclusions

The period of germination of the plants was carried out over a period of 7 days The daily number of germinated plants was higher in the first 2 days and in the next days, the number of germinated plants has decreased until in day 7. From the results of the study, is obvious that plant height and number of branches registered during the middle and end period of the experiment has achieved the highest values particularly in mixture biochar with mranita at application rate of 30 t/ha, especially in pots containing a higher concentration of mranita, between 50% and 100%. Plant dry weight obtained at two different application rates increased depending on increasing the concentration of mranita and with obvious differences between results obtained at 5 t/ha and 30 t/ha application rates. As a comparison between results obtained in pots with a big concentration of sewage sludge biochar and pots with a big concentration of mranita, the maximum value was obtained in pots where was applied a high concentration of mranita. From measurements was observed that pH and soil conductivity increased with increasing concentration of mranita in the case of the application rate of 5 t/ha and 30 t/ha, but a significant impact occurred in the case of application rate of 30 t/ha, where mranita has been used in high concentrations. Soil respiration is a process that releases carbon into the soil in the form of CO_2. Thus, from measurements recorded in soil samples collected in different stages of the experiment results that CO_2 recorded decreasing values according to the different periods of collecting soil samples. CO_2 values were higher in the initial samples in comparison with values from final samples. Between the two application rates, CO_2 recorded high values at 30 t/ha application rate in comparison with 5 t/ha application rate. Like a comparison between sewage sludge biochar and mranita, the lower value of CO_2 was obtained in samples where the concentration of sewage sludge biochar was very big, and in samples with a big concentration of mranita the value of CO_2 was higher. A strategy for promoting the biochar as sustainable waste management solution can be opportune for improving some of soil properties. The results will be useful for further research that may validate optimum application rates to modify characteristics of the soil as required.

Acknowledgements:

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EXPERIMENTAL INVESTIGATION CONCERNING EX-SITU BIOREMEDIATION OF PETROLEUM HYDROCARBONS CONTAMINATED SOILS

Valer Micle[1,*], Ioana Monica Sur[1], Adriana Criste[2],
Marin Şenilă[3], Erika Levei[3], Eugenia Gamenţ[4],
Carmen Cristorean[1,] George Călin Rogozan[1]

1) Technical University of Cluj-Napoca, Faculty of Materials and Environmental Engineering,
Department of Environment Engineering and Entrepreneurship of Sustainable Development,
28 Memorandumului street, 400114, Cluj–Napoca, Romania
2) University of Agricultural Sciences and Veterinary Medicine, Cluj-Napoca, Romania
3) INCDO-INOE 2000, Research Institute for Analytical Instrumentation,
Cluj-Napoca, Romania
4) National Research and Development Institute for Soil Science Agro-Chemistry and
Environment (ICPA) Bucureşti, Romania
**: valer.micle@imadd.utcluj.ro*

Introduction and study objectives

Soil pollution by petroleum hydrocarbons (PHCs) is one of the most obvious and important environmental issues faced by Romania. Pollution with PHCs occurs mainly as a result of extraction, processing, transport and storage activities. Rehabilitation of the sites polluted by PHCs is mandatory, considering the adverse environmental impacts and the large areas affected by this type of pollution.

Ex-situ bioremediation is a complex treatment process of contaminated soil that involves the use of microorganisms to biodegrade PHCs. The bioremediation process is influenced by several factors such as: soil moisture, pH, oxygen, mineral nutrient and microorganism's content. Biodegradation was found to be suitable for organic compounds or xenobiotics such as PHCs (gasoline, diesel, crude oil), polycyclic aromatic hydrocarbons (PAHs), chlorinated solvents and other compounds (alcohols, glycols, ketones, phenols, cyanides, polychlorobiphenyls (PCB), polychlorophenols, pesticides). Despite its applicability to a broad range of pollutants, the yield of bioremediation process may be limited by the selection and adaptation of suitable microorganisms to the contaminated environment, the existence of optimal conditions for the survival and growth of microorganisms and process parameters (oxygen concentration, soil temperature, soil moisture, pH, mineral nutrient and microorganism's content).

The objective of the study was determination of optimal parameters of the ex-situ bioremediation process for PHCs contaminated soils using an experimental set-up that controls the oxygen concentration, soil moisture and microorganisms content.

Methodology

An experimental set-up consisting of eight bioremediation tanks and aeration system provided with a compressor (Fig. 1) was used for the bioremediation of PHCs contaminated soils. Soil samples were taken from a former oil depot on the outskirts of Saint Gheorghe, Covasna County.

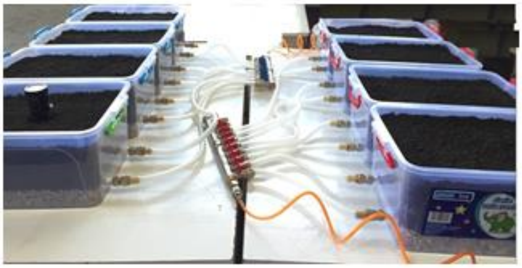

Figure 1: Experimental set-up

The soil texture, pH (1/5 soil to water extract), moisture, content of Kjeldahl nitrogen, organic carbon, available potassium, available phosphorus, micronutrients, metals and PHCs were determined. The consortium of the microorganisms was selected from indigenous species that proved to degrade the PHCs and was grown in the laboratory on culture media.

Each bioremediation tank was initially filed with 16 kg of PHCs contaminated soils. The initial content of PHCs determined by Fourier transformed infrared spectroscopy after extraction in tetrachloroethylene was 7600±760 mg/kg.

Experiments were conducted over 18 weeks at constant pH, temperature, nutrient contents and variable soil aeration time (1 hour/day and 2 hours/day), moisture (44% and 60%) and amount of added microorganisms concentrate (20 ml/kg and 40 ml/kg soil). From each bioremediation tank, samples were taken at 2 weeks interval for the monitoring of the PHCs and the microorganisms content.

Results and conclusions

In all cases a linear decrease of the PHCs content was found during the first 6 weeks of bioremediation, the most notable decrease appearing after 2 weeks of treatment. The PHCs decrease was higher in case of aeration for 2 h/day than in cases 1 h/day aeration. The amount of the used microorganism consortia also influenced the yield of bioremediation, more significant reduction of PHCs being observed in case of using microorganism amounts of 40 ml/kg soil. Moreover, important PHCs decrease was found at 44% moisture.

After 18 weeks of treatment, the obtained results show a bioremediation yield ranging between 20 and 70%. The highest yield was obtained at 2 h/day aeration, 44% moisture and microorganism concentrate of 40 ml/kg soil.

Acknowledgements

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THE ROLE OF *E. coli* IN THE UPGRADE OF LIGNOCELLULOSIC BIOMASS

Patricia Moniz[1,2], Talita Silva-Fernandes [1,2], Ivone Torrado[1,3,4], Júnia Alves-Ferreira [1,3,4], Maria C. Fernandes [1,2,*]

1) Centro de Biotecnologia Agrícola e Agro-Alimentar do Alentejo (CEBAL),
Apartado 6158, 7801-908 Beja, Portugal,
2) Instituto de Ciências Agrárias e Ambientais Mediterrânicas (ICAAM),
Universidade de Évora, Pólo da Mitra, Ap. 94, 7006-554 Évora, Portugal
3) LNEG– Laboratório Nacional de Energia e Geologia, Unidade de Bioenergia,
Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal.
4) Centro de Estudos Florestais, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal
*: *maria.fernandes@cebal.pt*

Introduction and study objectives

The biochemical platform of the biorefinery concept is mainly being developed aiming the use of cellulose and hemicellulose for the production of biofuels, *e.g.* bioethanol. Although this may be an advantageous strategy for providing environmental sound biofuels, it falls behind at economic terms when compared to the production of other, more valuable, bioproducts, e.g. precursors/or products for the chemical, food, feed or pharma industries.

Unfortunately, if bioethanol production using both cellulose and hemicellulose derived sugars is still a process under intensive development, the production of other added value products is presenting further difficulties, as typically, only a few organisms are available to be used industrially, due to many reasons, related from techno-economic to legal/safety constrains.

As such, many efforts have been implemented in the past years to develop robust microbial cell factories. Among these, *E. coli* is one of the most relevant and useful bacterial biocatalysts.

In this work, the role of *E. coli* in the upgrade of hemicellulose and cellulose derived streams to added-value products is reviewed and the future genetic engineering requirements for its further use is discussed, and put into perspective based on its utilization in relevant industrial media, namely (hemi)cellulosic hydrolysates, taking the D-lactic acid production by transformed *E.coli* as a model case-study.

Methodology

An extent bibliographic review was carried out in order to unfold studies using *E. coli* as bacterial biocatalysts. These studies were than interpreted and compared aiming the genetic transformation of *E. coli* to improve its role in the upgrade of lignocellulosic biomass.

Results and conclusions

The selection of a microbial host for the production of (added-value) bioproducts is typically based on either of two approaches: i) selecting based on a product-oriented strategy, which investigates the organism's ability to produce a specific product and further uses genetic engineering to make the organism utilize the required substrate(s); or ii) using a substrate-oriented strategy focusing on the capacity of an organism to utilize a wide range of substrates and then change the required metabolic steps by genetic engineering. *E. coli* is among the best hosts for the second strategy, and has been used in the past years for the production of several bioproducts in the biorefinery framework, among the most relevant, are second generation ethanol, D-Lactic acid, succinic acid, 1,4-Butanediol, etc.. In this work, special attention will be given to the discussion of the genetic transformations carried out to achieve the efficient production of several of these compounds, taking special attention on the production of D-lactic acid, as it is a commodity with a significant high market volume and relatively high market value.

The use of *E. coli* is typically justified by its high growth rate and productivities and particularly by its wide substrate range that includes both hexoses and pentoses that can be derived from lignocellulosic biomass. In *E. coli*, it was previously reported that the ability to metabolize pentoses is strain dependent and subjected to a complex sequential uptake chain that is initiated only at low glucose levels in the cultivation medium. For instances, the three most abundant sugars in straws are taken up by *E. coli*, in the order of glucose > arabinose > xylose. This is due to a combination of carbon catabolite repression, inducer exclusion and pentose uptake regulation. Previous studies have been carried out so that a simultaneous metabolism of glucose, xylose and arabinose under aerobic conditions without leaving any residual sugar in the cultivation medium could be accomplished. This was achieved by deletion of the ptsG gene (EIICBGlc), the preferred inner membrane transporter for glucose.

Unfortunately, the production of lignocellulosic derived sugars, will not only release fermentable sugars, but also substances with inhibitory effects. These toxic substances can be categorized into three major groups: furan derivatives, phenolic compounds, and weak organic acids. As compared to the studies on the genetic transformation for novel/improved bioproduct formation pathways or substrate uptake, the tolerance to these compouds is yet poorly understood.

As an example, the *Cistus ladanifer* residues were pretreated by autohydrolysis to produce glucose rich biomass that was used to produce lactic acid under SSF conditions. The maximum D-Lactic acid titer obtained was 370 mM and the highest productivity was 2.17 g L^{-1} h^{-1}. Although these results clearly indicate that this feedstock and process may be a future alternative for a bulk product route in the biorefinery framework, the impact of inhibitors must be clarified in order to reach better fermentative performance, by using also the liquid stream resulted in the pretreatment. Clearly, this points out to the need of further studies aiming the genetic transformation of *E. coli* in order to increase its inhibitor tolerance.

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SUSTAINABLE VALORIZATION OF BY-PRODUCTS FROM MEDICINAL AND AROMATIC PLANTS INDUSTRY INTO VALUE-ADDED PRODUCTS - SusMAPWaste

Alina Ortan[1,*], **Irina Fierascu**[1], **Radu Claudiu Fierascu**[1],
Daniela Ionescu[1,2], **Milen I. Georgiev**[1,3]

[1)] *University of Agronomic Sciences and Veterinary Medicine, 59 Marasti Blvd, 011464 Bucharest, Romania*
[2)] *S.C. HOFIGAL EXPORT IMPORT S.A., 2 Intrarea Serelor, 042124, sector 4, Bucharest, Romania*
[3)] *Group of Plant Cell Biotechnology and Metabolomics, The Stephan Angeloff Institute of Microbiology, 4000 Plovdiv, Bulgaria*
*: *alina_ortan@hotmail.com*

Introduction and objectives

Medicinal and aromatic plants (MAP) play a valuable and important role in economic, social, cultural and ecological aspects of local communities all over the world, as in excess of 80% of the population of developing countries relies on traditional plant based medicines for their health requirements. Moreover, in the present *eco* and *bio* rush, materials such as essential oils, pharmaceuticals, colorants, dyes, cosmetics and biocides are obtained from plants. All over the world, especially in countries with traditions in the cultivation of such plants (Romania being a country with a very strong tradition regarding the medicinal plants), production of bio-products based on natural compounds leads to the transformation of plants in large quantities of waste, mostly unexploited. Due to the *exponential increase* in the amount of *collected waste*, financial and environmental implications incurred by the economy and business units are significant. In this context, the project *SuSMAPWaste* is designed in order to close value chains in bio-economy, considering the principles of sustainable development and bio-economy. Plant waste constitutes strongly organic - enriched materials that can be further processed for environment reintegration in safe conditions. Research conducted in this direction will make significant contributions in areas like technology, methods of regeneration of natural resources, as well as storage, recovery and waste disposal management.

The *main objective* of the project is the development of an absolutely innovative technology for the sustainable valorization of by-products from medicinal, aromatic and oleaginous plants industry, with future market applications in obtaining value-added products. The project is developed in two main directions, namely: (a) The development of *green* technologies for obtaining a fibrous support material from oleaginous plants waste, enriched with a *penta-component formula* with *multi-target effect* (antioxidant, probiotic and detoxifying) from MAP waste, for *human consumption (process a)*; (b) Providing *innovative solutions* for the *complete exploitation of medicinal, aromatic and oleaginous waste* resulted after *process a*, by converting them into animal feed (*process b)*. The specific objectives are: 1. *Development of a technology* for obtaining a *penta-component formula with multi-target effect* (antioxidant, probiotic and detoxifying) from MAP waste; 2. *Development of a technology* for obtaining a *fibrous support material* from the edible oleaginous plants waste; 3. *Development* of *an appropriate formulation of a fibrous support material enriched with a penta-component formula with multi-target effect* (antioxidant, probiotic and detoxifying); 4. *Providing* innovative solutions for the *complete exploitation* of medicinal, aromatic and oleaginous wastes resulted from the experiments, by converting them into *animal feed*.

Results and conclusions

The *SuSMAPWaste* project is going to develop tools, methodologies and processes for the valorization of wastes through an *integrated bio approach,* using advanced biotechnological methods. Research and innovation actions are focused on the valorization of natural compounds with multi-target effect, which are essential for the development of a circular bio - economy and for the smart and efficient use of green resources.

From this perspective, the project proposes *an absolutely innovative and original* approach for valorization of MAP and oleaginous plants (OP) wastes *obtaining technologies* for enriching an fibrous support material from oleaginous plants, with natural compounds having triple action (antioxidant, probiotic and detoxification effects), produced from medicinal and aromatic plants waste, *for the first time in the world*, up to our knowledge.

The overall expectations of *SuSMAPWaste* are to support the transition towards a more efficient way of economic growth and employment, by developing sustainable and competitive bio-based industries, based on advanced biotechnological methods with sustainable use of biomass resource.

The project will increase the share of biomaterials produced in Europe by increasing the market share of bio-based materials, will allow improved management of renewable biological resources and the opening of new and diversified markets for bio – food and products, will contribute to the reduction of imports of feed.

The direct beneficiaries of the project are the companies - manufacturers of natural products based on medicinal, aromatic or oleaginous plants that are producing plants waste. For example, just one of the MAP Industry company in Romania produces annually about 30 tons of medicinal and aromatic plants waste, only by aqueous extractions and about 23 tons of oleaginous plants waste (in the form of pomace), that are no longer processed and thus become useless waste.

In conclusion, the *SuSMAPWaste* project shall offer a useful basis for a bio-economy approach, as it converts waste streams into value added products such as food, feed, bio-based products.

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POTENTIAL FOR CRITICAL RAW MATERIALS (BIO)RECOVERY FROM HUNGARIAN RED MUD

Éva Ujaczki[1,2], Yannick S. Zimmermann[1,3], Christoph A. Gasser[1,3], Mónika Molnár[2], Viktória Feigl[2], Markus Lenz[1,4,*]

[1)] Institute for Ecopreneurship, University of Applied Sciences and Arts Northwestern Switzerland, School of Life Sciences, Gründenstrasse 40, 4132 Muttenz, Switzerland
[2)] Department of Applied Biotechnology and Food Science, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, Műegyetem rkp. 3, 1111 Budapest, Hungary
[3)] Institute for Environmental Research (Biology V), RWTH Aachen University, 52074 Aachen, Germany
[4)] Sub-Department of Environmental Technology, Wageningen University, 6700 AA Wageningen, The Netherlands
[*]: Markus.Lenz@fhnw.ch

Introduction and study objectives

The world economy is confronted with an increasing supply risk of critical raw materials (CRMs). These are defined as materials with high supply risk and above average economic importance compared to other raw materials. Rare earth elements (REEs) have received considerable attention in the past years, partly as a result of the dramatic REE price surge when China – producing more than 95% of the annual world supply of REEs – had introduced tight export quota for REEs, because of the domestic demands. Though in 2011 the quotas and the export tariffs were eliminated, prices are still above pre-2011 values. The supply risk can be reduced, if so far untapped sources (primary, secondary) can be exploited in the future. One such untapped secondary source for CRMs is so called red mud. Red muds are the residues generated from alumina production where bauxite is digested in hot sodium hydroxide solution by the Bayer process. Currently, an estimated 2.7 billion tons worldwide is produced every year, and is expected to increase by approximately 120 million tons per annum. Alternative uses for red mud have so far not found an industrial application besides use in cement and ceramic production. Red mud can contain considerate amounts of CRMs and further raw materials with high relative economic importance. Extraction of such metals from red mud can be economically feasible. However, a detailed inventory of economic value in red muds of different origin does not exist so far. This research, therefore, discusses the possibilities to recover economically interesting elements from Hungarian red mud.

Methodology

Here, for the first time exhaustive inventory of valuable elements (CRMs including REEs) in Hungarian red muds was created using both X-ray fluorescence spectroscopy (XRF) as well as microwave assisted aqua regia digestion with subsequent Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis. Next, a number of conventional extracting agents (H2SO4, HCl, HNO3) were evaluated for their REE recovery potential. Small molecular weight organic acids (citric acid, oxalic acid) were benchmarked to evaluate the potential of heterotrophic bioleaching as green alternative to chemical leaching. Also, the optimal extraction conditions maximizing the overall economic potential of minor metals (and not mere metal concentrations of a limited number of elements) were determined using a design of experiment approach. Finally, a 2 step downstream purification (precipitation + LLE) of CRM (in particular REEs) from red mud hydrochloric acid leachates was developed. After initial evaluation of LLE efficiencies using four explanatory variables (i.e. LLE organic/aqueous ratio; D2EHPA concentration, stripping organic/aqueous ratio, HCl concentration) the optimal extraction conditions maximizing the economic potential of CRMs were determined using a design of experiment approach. The accuracy of design of experiment predictions was verified by laboratory tests.

Results and conclusions

Comparing different acids, hydrochloric acid (HCl) yielded the highest REEs efficiency. Increasing HCl concentrations from 0.5 to 6 M led to considerably increased extraction efficiencies of REEs. The best results regarding contact time were achieved at 3 hours. Significant ($p<0.05$) differences in the extraction efficiencies were observed between 22 °C, 50 °C and 60 °C for REEs. A slight but significant ($p<0.05$) decrease was detectable at increasing slurry concentration from 10 to 100 g L-1 for REEs. Regarding downstream processing, we could show efficient separation of Fe by pH induced precipitation and removal of Al with the raffinate during subsequent LLE. Ultimately, more than > 40% of the overall REEs (> 62% of the leachable REEs) in red mud could be purified using LLE, whereas Al + Fe were successfully rejected from the concentrate (~5% of the overall Al and 7% of the overall Fe present). Though less efficient for other CRM, oxalic acid yielded high (44%) Ga extraction efficiency with at the same time little extraction of Fe and Al, which may be explored for selective recovery of the latter.

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WINERY WASTE: A SOURCE OF HIGH ADDED VALUE BIOMOLECULES, EXPLOITABLE WITHIN THE H2020 NOAW PROJECT

Maura Ferri[1,2], **Micaela Vannini**[2], **Paola Marchese**[2],
Annamaria Celli[2], **Annalisa Tassoni**[1, *]

1) University of Bologna, Dept. of Biological Geological and Environmental Sciences, Via Irnerio 42, 40126 Bologna, Italy
2) University of Bologna, Dept. of Civil, Chemical, Environmental and Material Engineering
** : annalisa.tassoni2@unibo.it*

Introduction and study objectives

Nowadays only about 5% of chemicals and polymers are bio-based, while there is a strong demand to substitute petro-derived chemicals and building blocks by competitive sustainable equivalents in order to replace increasing scarce mineral oil as raw material and to develop more eco-friendly materials. In this context agro-waste represents a huge amount of biomass resources that could be converted into sustainable bio-products, according to the basic principles of the circular economy that aims to move towards a "near zero-waste society". However, energy consumption, degradation processes, complexity and variability in chemical composition of the waste feedstock, presence of contaminants, low quality and poor performance often characterize waste recovery and conversion products and make difficult the effective exploitation of waste.

NoAW project focuses a specific attention to winery waste and aims to develop an advanced chemical and biotechnological platform to convert waste into high value products. Through a multidisciplinary and multi-criteria strategy, including LCA methodology and territorial metabolism, which analyses environmental impacts of materials and energy flows in a geographic region, NoAW wants to develop some specific cross-chains of valorisation of winery waste.

In particular, one of the activities that will be developed at the University of Bologna will consists in the extraction of polyphenols and phenolic acids by chemical and enzymatic treatments from pomaces. These biomolecules will be exploited as building blocks for the production of new aromatic polyesters and copolyesters and as fillers for commercial biopolymers to provide them antioxidant and antibacterial properties. Moreover, starting from the solid residues of the extraction procedures, polymeric bio-composites will be prepared. Therefore, new fully bio-based materials, specifically addressed to packaging applications, will be developed starting from winery waste, contributing to implement the agro-waste conversion and valorization pathways.

Methodology

Within the NoAW project ("Innovative approaches to turn agricultural waste into ecological and economic assets"), financed by Horizon 2020, Waste work program 2014-2015 (WASTE-7-2015: Ensuring sustainable use of agricultural waste, co-products and by-products) (Grant Agreement n. 688338), wine pomaces were delivered (frozen at -20°C) by INNOVEN. Two kinds of pomaces have been analysed: white pomace, Garganega cultivar, that was pressed; red pomace, Merlot cultivar, analysed after pressing and wine fermentation.

The pomaces were subject to solvent extractions: 25% 50% 75% aqueous-ethanol, -methanol, -acetone and -acetonitrile were tested and compared to 100% water. Two different solid/liquid ratios (1:5 and 1:10) were assayed. Temperature (30°, 50°C, 70°C) and time (1h, 2h, 4h) of the process were optimised.

Total polyphenol, total flavonoid, total flavanol, total hydroxycinnamic acid, anthocyanin and tannin releases and total antioxidant activity were quantified by spectrophotometric assays. Specific compound presence and amounts were assessed by HPLC-DAD analyses.

Results and conclusions

Preliminary results indicated that best parameters for solvent extraction of polyphenols and phenolic acids from both white (cv. Garganega) and red (cv. Merlot) grape pomaces were 1:5 solid/liquid ratio, 2 hours incubation at 50°C. In these conditions, highest yield were obtained by 75% acetone processes, with increases of 4.7-times and 3.7-times in total polyphenol recoveries for white and red pomace, respectively. Other useful solvents were found to be 50% acetonitrile and 50% methanol for Garganega and 50% acetonitrile and 50% ethanol for Merlot. Extract antioxidant activities were in agreement with total polyphenol results.

Each selected solvent seemed to be more specific for different polyphenol families. Flavonoids and flavanols were more concentrated in 75% acetone extracts, both in red and white samples. Hydroxycinnamic acids were mainly extracted by 75% acetone from white pomace and by 50% ethanol from red ones.

Garganega and Merlot extracts had different composition, due both to the diverse phytochemical composition of the original grapes and to the different winemaking processes (pressing for Gaganega, pressing and fermentation for Merlot). In general, anthocyanins were specifically recovered in red pomace samples, while flavanols and tannins were mainly in white extracts.

In conclusion, 75% acetone seems to be the more useful solvent for high value biomolecules from winery waste. White and red pomaces are source of different ranges of polyphenols and phenolic acids. Moreover, the same pomaces will be further treated by enzymes (cellulase, xylanase, pectinase, etc; single or commercial mixtures) with the aim to recover specific compounds (such as vanillic acid), particularly suitable for exploitation as building blocks for the production of new aromatic polyesters and copolyesters.

HYDROGEN PRODUCTION AND NUTRIENTS RECOVERY FROM DIGESTATE USING MICROBIAL ELECTROCHEMICAL TECHNOLOGIES (METs)

Tommy Pepè Sciarria[1,*], Giovanni Vacca[1], Fulvia Tambone[1], Fabrizio Adani[1]

[1)] Università degli Studi di Milano-Disaa, Gruppo Ricicla Lab, Gruppo Ricicla,
Via Celoria 2, 20131 Milan, Italy.
**: tommy.pepe@unimi.it*

Introduction and study objectives

A key point to improve the sustainability of agriculture practices is the development of new technologies for nutrient recovery from biomass and agricultural wastes. Actually, the recovery of phosphorous from wastes, is considered crucial because the reserves of phosphate are mainly localized in few worldwide areas and the depletion of these reserves (expected before the 2100) could lead to geo-political crisis. In this scenario, it is clear the need to invest in innovative technologies for the recovery of phosphorous; within these, Microbial Electrochemical Technologies (METs) can provide a viable strategy in the near future. METs shares the principle of microbial catalyzed anodic substrate oxidation and can be addressed to different application: electricity production (microbial fuel cells, MFCs), hydrogen production (microbial electrolysis cells, MEC), bioremediation (nitrate removal either in MFC or in MEC mode) or Bio-electro synthesis (reduction of CO_2 in high value products). Moreover previous studies reported how to recover phosphorous and nitrogen from wastewaters through struvite crystallization/precipitation mediated by MET. Struvite ($MgNH_4PO_4 * 6H_2O$) is a crystal mainly composed by phosphorous and nitrogen commonly used as fertilizer.

The aim of this work has been conducted to evaluate the production of electric current, bio-hydrogen and the recovery of nutrients (PO_4^{3-} and NH^{4+}) from a digestate coming from an anaerobic digestion biogas plant. These results were achieved using a hybrid system composed by METSs bioreactors and chemical struvite precipitation process.

Part of the study has been also performed in order to reduce the costs of MET systems. For this reason, low cost cathode (stainless steel mesh) has been tested in comparison with standard carbon cloth cathodes with platinum as catalyst.

Methodology

Four single-chamber air-cathode MFCs were assembled; each reactor consisted of a liquid chamber 4 cm long by 5 cm in diameter, with a volume of 28 mL.

The anode was made of graphite fiber brush with titanium wire as core (Panex 33 160 K, Zoltek), 2.5 cm in both outer diameter and length. Two cell were equipped with carbon cloth platinum cathode (diameter 3.8 cm) while the other two with a stainless steel mesh cathode (diameter 3.8 cm). For the MFCs test, anode and cathode were connected with copper wire, and the voltage, across an external resistor of 1KΩ, was monitored every 900 seconds using a multimeter connected to a personal computer. For the MECs test, anode and cathode were connected with copper wire, and the voltage, across an external resistor of 10Ω, was monitored every 900 seconds using a multimeter (2700, Keithley, United States) connected to a personal computer. A power supply was used to add a little amount of voltage to the MECs bioreactors to produce H_2.

Results and conclusions

The first experimental phase, has been performed using synthetic medium, testing respectively microbial fuel cell (MFC) reactors and microbial electrolysis cell (MEC) reactors; moreover the MEC systems have also been tested applying different voltages to the reactors (0.75V, 0.9V, 1.07V). The knowledge acquired during the first phase have allowed the definition of the experimental design of the second phase, in which the bioreactors were fed with the digestate. The experiments carried out using the digestate as feeding, for both kinds of bioreactors (MFC and MEC), have shown a phosphate (PO_4^{3-}) removal between 21% and 30%, and an organic load (COD) break down between 27% and 44%. During the second step, the subsequent addition of solutions with a high amount of Mg^{2+} ($MgCl_2$ $6H_2O$ and seawater bittern) in the molar ratio of 1.6: 1 and 1.5: 1 (Mg: P), led to a further reduction of phosphate (PO_4^{3-}) between 66% and 87%. The performance of the MEC systems have been similar for each voltage applied, with an average hydrogen production of 1.90 ± 0:04 $LH_2\ l^{-1}d^{-1}$ with a hydrogen concentration of 85 ± 1.8% H_2 on the biogas produced. At the same time, the experiment conducted usingdetected Coulombic efficiency of MFC bioreactor has been 35 %, with a normalized power on the total volume of the bioreactor of 14.19 ± 0.15 W m^{-3}. These results shown how the MEC and MFC systems could be used both for the treatment (organic load reduction) and the valorization (H_2 and electricity production) of digestate. Moreover, the data obtained, have shown that, the MET systems, are able to promote the reduction and the recovery of phosphorus. One of the limitations of this technology is the high cost of materials; the tests conducted by comparing the low-cost cathode SSM with respect to the standard Pt cathode, have shown similar performance, which would allow a reduction in costs thanks to the hydrogen recovery and the electricity produced. In conclusion, the results showed that the MET systems can be integrated to the common anaerobic digestion and other wastewater technologies, to obtain a new kind of wastewater treatment system similar to a bio refinery process, to valorize biomass and livestock wastes not only producing energy but also recovering nutrients.

BIORIZON, THE WAY TO AROMATICS

Ludo Diels[1,2,*]

[1] VITO, Flemisch Institute for Technological Research, Mol, Belgium,
[2] Antwerp University, Belgium

Introduction and study objectives

The Shared Research Center, Biorizon, an initiative of TNO, ECN, VITO and the Green Chemistry Campus, develops technologies to produce aromatics derived from plant-based (waste) streams. Biorizon brings together global leaders (large industry and SMEs) in the fields of feedstock, conversion, equipment, building blocks, materials and end-products. Biorizon aims to be a world leader in the development of biobased aromatics to provide the chemical megacluster around the Netherlands, Flanders (Belgium) and Nordrhein Westfalia (Germany) with innovative, sustainable building blocks leading to many different applications in the products marketed by brand owners and small companies. The objective is to make commercial production feasible for industrial partners by 2025 at the latest.

Aromatics are among the most important resources for the chemical industry. Currently virtually all aromatic building blocks are made from fossil oil. Biorizon is anticipating the expected growing shortage of aromatics from the petrochemical industry and the widely shared ambition to green the chemical industry. On top of that one of the main drivers is to develop innovative molecules that are safer and more performing.

Biorizon utilizes plant-based streams such as wood or its fractions lignin and sugars to develop functionalized biobased aromatics for performance materials, chemicals & coatings. This diminishes the dependence on fossil fuel, it lowers CO2-emissions and it provides the chemical industry a profitable and sustainable perspective.

Biorizon is operated as a Shared Research Center, based on the open innovation methodology, bringing together collective intelligence of various industries, companies and knowledge organizations. The multi-disciplined technological need, as well as the long term roadmaps based on thermochemical conversion, sugar chemistry for furanes and lignin depolymerization-based chemicals for functionalized aromatics lead to a large network of applied research projects with more than 40 industrial partners, sharing research, intelligence, investments, risks and workload in different projects.

The presentation with give an overview of the Biorizon initiative and its projects. Special attention will be paid to the value chain approach including a strong downstream processing (use of membrane technology) in view of final industrial applications.

For partners and companies that are interested in the Shared Research Center, please join at: www.biorizon.eu/community

Methodology

The shared research center and its partners evaluate and develop several routes. 1) Thermochemical treatment via gasification or pyrolysis (all or not supported by catalysts) leading to pyrolysis oil containing still functionalized phenols or leading to benzene, toluene and xylene after hydrogenation. 2) Direct biomass solvolysis and catalytic stabilisation (Lignin First Process) followed by membrane-based fractionation of monomers, oligomers etc. 3) Biorefinery approach to separate C5-/C6-sugars polysaccharides and lignin followed by 3a) Sugar conversion into furans (acid catalysed dehydration) and further conversion into functionalized aromatic molecules (via Diels-Alder chemistry); 3b) lignin catalyst-based depolymerization followed by membrane-based fractionation; 4) Further studies are ongoing to make either new aromatic building blocks (e.g. for new polymers and materials) to support an innovative chemistry or to use the oligomers in coatings, emulsifiers, adhesives, glues, resins etc.

Results and conclusions

An overview will be presented on the different approaches to treat biomass in general and biowastes particularly to transform the sugars and lignins into new innovative chemicals being biobased aromatics with high functionality outcompeting existing molecules by performance and/or safety issues. It will generate new materials of the future leading to environmental more friendly materials with impact on the production process (e.g. no use of bisphenolA) and the use of the final materials (e.g. no formaldehyde emissions).

The pro's and con's of the different approaches will be presented as well as the challenges and opportunities for making an economic viable business from agriculture and forest rest streams as well as from the pulp & paper industry toward a new chemistry.

Up to recently most of the lignin application trials were based on the use of lignin as a polymer. As ligin is extracted it reacts during its extraction by forming no ether or ester bonds (as it is in nature) but by forming very stable carbon-carbon bonds. Breaking these bonds is very difficult. This makes the lignin relative unreactive allowing a use as filler or additive but in a limited way for integration into the new material matrix.

Several appraoches will be presented allowing to keep the reactivity high either by catalytic stabilisation, either by fractionation follwed by dealkylation and refunctionalisation. And indeed the lignin fractions (low and high molecular weight oligomers) are more reactive. This lead to a full new series of applications and new molecules. Key in this appraoch is the fractionation into monomers (even separation of monomers) and into low and high molecular weight oligomers. This will be shown by less energy consuming (e.g. compared to destillation) technologies like membrane separation. Special attention will be paid to these technologies allowing the use of more reactive lignini derivatives.s

Finally some ideas on integrated biorefineries, new material development and European initiatives will be presented.

OFMSW FOR BIOPLASTICS PRODUCTION (POLYHYDROXYALKANOATES)

Bianca Colombo, Barbara Scaglia, Francesca Favini,
Tommy Pepè Sciarria, Giuliana D'Imporzano, Fabrizio Adani*

Università degli Studi d Milano, DiSAA, Gruppo Ricicla labs,
Via Celoria 2, 20133 Milano, Italy
*: *fabrizio.adani@unimi.it*

Introduction and study objectives

Traditional plastics production is linked with high environmental pollution due to the dependence on fossil fuels and to the low biodegradability of this material. In recent years new kind of plastics have been produced in order to substitute common polymers, as they reduce the accumulation of non-biodegradable pollutants in the environment and can be produced from renewable sources.

Polyhydroxyalkanoates (PHAs) are bio-polyesters produced by different bacterial species from various carbon sources; these bio-polymers are accumulated in bacterial cells under the form of granules as carbon and energy storage. Among the common bio-polymers PHA are of particular interest because they are made from renewable sources and they are completely biodegradable, for these reasons they are considered as a class of eco-efficient bioplastics; moreover, with respect to common bioplastics they have thermo-mechanical properties similar to those of traditional plastics, that make them potential alternatives to plastics in the future.

Nowadays, PHA production is limited by high production costs due to the use of pure cultures and standard substrates. To reduce these costs liquid agro-industrial wastes (i.e. cheese whey, molasses, olive oil mill effluent) had started to be used as substrate to feed mixed microbial cultures (MMC). In this work the possibility to use more complex and solid wastes instead of liquid wastes using MMC was evaluated. The organic fraction of municipal solid waste (OFMSW), being largely ($5.7*10^6$ tons in 2014 in Italy), continuously produced and easily available, could be an interesting substrate for PHA production to sustain the high demand of plastics of the market.

Methodology

This work took part of the bio-refinery OFMSW-PHA, performing: 1) the optimization of the OFMSW percolate through treatments (35% of COD removal and 57% of NH_4 removal) to obtain a suitable substrate for PHAs production and 2) PHAs production. The enrichment of PHAs-producing bacteria was performed by using as inoculum an activated sludge. The enrichment was carried out in a Sequencing Batch Reactor (SBR) with a working volume of 800 mL, applying an aerobic dynamic feeding (ADF) strategy. In brief the SBR cycle length was of 12 h, with 1 day of Hydraulic Retention Time (HRT) and 5 days of Sludge Retention Time (SRT), keeping the temperature at 25 °C and the pH at 8.8. Aeration and agitation were provided by supplying air at 6 L min^{-1} and stirring set at 110 rpm. The selection process lasted three months.

The ability of the selected MMC to accumulate PHA was assessed by fed-batch assays carried out in a 300 mL working volume glass reactor, with continuous aeration and stirring. These assays consisted in feeding the substrate to the enriched culture adopting a pulse wise feeding method. For the accumulation tests, the operating conditions adopted were those adopted in the selection reactor.

Results and conclusions

In this work good results were obtained in both selection and accumulation phases. During the selection, in terms of average values, PHA content in dry cells was of 320 g kg^{-1} and the storage yield on COD was of 0.48 mg COD_{PHA} mg COD^{-1}. During accumulation process, in terms of average values, PHA content in dry cells was equal to 449 g kg^{-1}, PHA storage yield on COD was of 0.49 mg COD_{PHA} mg COD^{-1} and PHAs storage yield on organic acids was equal to 0.84 mg COD_{PHA} mg COD^{-1}. In terms of composition, the polymer produced during accumulation tests was a copolymer made of 56 % of HB and 44 % of HV, with a wide thermo-mechanical processability window. Moreover the total PHA production yield on OFMSW total solids was about 10 %; these results were well comparable with those obtained in literature using conventional agro-industrial wastes, making OFMSW a good candidate for a more sustainable and economical PHA production.

SYNERGISTIC EFFECTS OF THE MAJOR SIMPLE PHENOLS RECOVERY FROM OLIVE OIL WASTES AS AN ANTIOXIDANTS AND NEW PHYTO-REGULATION APPROACH

Guillermo Rodríguez-Gutiérrez[1,*],
Juan Fernández-Bolaños Guzmán[1], Baukje de Roos[2],
Garry G. Duthie[2], Antonio Lama Muñoz[1],
María África Fernández Prior[3], Juan Antonio Espejo Calvo[3]

(1) Instituto de la Grasa, Spanish National Research Council (CSIC), Spain.
(2) University of Aberdeen, Rowett Institute of Nutrition & Health, Aberdeen, UK.
(3) Tecnofood I+D Solution, Spain.
** : guirogu@ig.csic.es*

The olive oil industry produces different types of highly polluted wastes (OMW) depending on the olive oil extraction system. Nowadays, two main milling processes are applied to obtain olive oil: the three-phase system is used widely in most Mediterranean countries, while the two-phase system is mainly used in Spain. The production of any of these waste effluents constitutes a serious problem because they cannot be disposed to municipal sewage due to the recalcitrant character of its high organic content. The small producers have become especially economically vulnerable because of the stringent environmental regulations and sewage works enforcements. Hence, producers have to manage the waste and forward the environmental problem to the management companies, whose main solution today is usually the storage in atmospheric evaporation ponds, which is NOT an environmental good solution.

But at the same time, OMW are rich in bioactive compounds with proven excellent properties for pharmaceutical, nutraceutical and cosmetics application. In particular, the polyphenols of the olive have extraordinary antioxidant capacity, with positive effects on the cardiovascular apparatus, as well as anti-cancer properties. The most important simple phenols that can be isolated and purified from the olive oil by-products, in terms of quantity and bio-activity, are hydroxytyrosol (HT) and 3,4-dihydroxyphenylglycol (DHPG). HT is the most studied phenols in the olive, because its remarkable biological activities. The potential for hydroxytyrosol as a novel and bioactive ingredient in a functional food is high, because of its high anti-oxidant, anti-inflammatory and anti-platelet potency in humans. But the DHPG has still not been studied in deep. DHPG is a new phenol with high antioxidant activity, which is even higher than the one of hydroxytyrosol is known. The first studies about DHPG show interesting biological activities. Recentely this antioxidant has been obtained and purified by the first time, in spite of low concentration in the original source. DHPG is found in certain medicinal plants used in traditional Chinese, Japanese, and Korean medicine, and it could be interest in the fields of nutrition and pharmacology due to its powerful antioxidant properties. It is the main metabolite produced by deamination of the human neurotransmitter noradrenaline (norepinefrine). Therein, we demonstrated for the first time that DHPG possesses higher antiradical activity and reducing power than hydroxytyrosol (the main antioxidant present in the Virgin Olive Oil). It also displays similar activity to that of vitamin E in the inhibition of lipid oxidation, despite its high polarity.

Biological tests were carried out to assess the synergism between both phenols. An antioxidant test showed that HT and DHPG had high antioxidant activities, including lipid peroxidation, with DHPG having a higher antiradical activity than the potent HT and vitamin E. The cardiovascular benefits were assessed by measuring the anti-platelet activity of HT, DHPG, a mixture of the two and an extract rich in olive oil phenols. The results showed that HT and DHPG are for a large part responsible for the anti-platelet aggregation effects of olive oil, and possibly of table olives. Antioxidant assays to prevent the lipid oxidation in edible oils also showed the synergistic effect of these phenols in the proportion found in olive fruit. In addition the effect of both phenols as phyto-regulator was carried out showing the remarkable activity of DHPG to be used in organic and/or conventional crops.

REE4EU, INDUS3ES AND MEMERE INNOVATIVE PROJECTS

Patrizia Circelli, Marco Molica Colella, Andrea Rausa, Valentina Cinti*

CiaoTech PNO Group, Via Pacini 11, 20131 Milan (Italy
*: *v.cinti@ciaotech.com*

Introduction and study objectives

As Innovation and Technology transfer organisation, CiaoTech PNO Group is leading dissemination and exploitation activities in three EU SPIRE projects, ensuring the project impact among relevant stakeholders. **CiaoTech PNO Group is partner of Ree4eu, Indus3Es, MEMERE**.

The **"REE4EU project: Integrated high temperature electrolysis and Ion liquid extraction for a strong and independent European rare earth elements supply chain",** funded in the frame of Horizon 2020 TOPIC SPIRE-07-2015 under Grant Agreement n° 680507, will realize a breakthrough innovation in the field of Recovery Technologies for Metals and other Minerals. It will make available Rare Earth elements and Rare Earth alloys for magnet production by developing, for the first time at industrial scale, an efficient and cost effective method of extraction and a direct production route for Rare Earth Alloys which will be achieved through in-process and End-of-Life permanent magnets as well as Ni metal hydride battery waste.

The "**Indus3Es project New technologies for utilization of heat recovery in large industrial systems**" funded in the frame of Horizon 2020 TOPIC EE-18-2015 under Grant Agreement n° 680738 , will develop an innovative Absorption Heat Transformer (AHT) focused on low temperature waste heat recovery (below 130ºC, referred to a recovered waste heat source temperature), since large quantities of waste heat are continuously rejected from industries. Most of this waste energy, however, is of low-quality and is not practical or economical to recover it with current technologies.

"MEthane activation via integrated MEmbrane REactors (**MEMERE**)" responds to the EU Horizon 2020 call SPIRE-05-2015 and is a research and innovation project aiming at methane activation towards C2+, funded under the Grant Agreement n° 636820. It aims at the design, scale-up and validation of a novel membrane reactor for the direct conversion of methane into ethylene with integrated air separation. The focus of the project is based on the air separation through novel MIEC membranes integrated within a reactor operated at high temperature for OCM allowing integration of different process steps in a single multifunctional unit.

Methodology

REE4EU will open-up a fully new route bringing recovery of in-process wastes from PM manufacturing within reach. The REE4EU project will develop, validate and demonstrate in 2 industrially relevant Pilots an innovative Rare Earth Alloys (REA) production route from permanent magnets PM and Ni metal hydride (NiMH) Battery waste. The targeted integrated solution is based on recently developed lab-proven technologies for direct high temperature electrolysis of REA production. It will be combined in the pilots with an innovative and proven Ionic Liquid Extraction or tailored hydrometallurgical pre-treatment to demonstrate dramatic improvements in cost and environmental performance compared to state of the art technologies.

Indus3Es system will have a relevant impact making possible an energy efficiency increase and reduction of primary energy consumption of most energetic intensive industries in Europe. The embodied energy, the environmental footprint of the products and the manufacturing costs of energy intensive industries will be reduced, increasing the competitiveness of European products. Moreover, it will allow a sustainable economic activity for local "auxiliary" companies, usually SMEs, in high added value services related to the energy efficiency measures for industry.

MEMERE will develop new O_2 selective (supported) membranes for high temperature air separation and integrate these membranes in a novel membrane reactor for direct conversion of methane to C2. This new concept will thus combine the advantages of both high temperature membranes and membrane reactors resulting in a breakthrough technology in the field of methane activation to ethylene.

Results and conclusions

REE4EU will prove technical and economic viability on in-process permanent magnet waste, as well as end-of-life permanent magnets and NiMH battery waste. The targeted integrated solution will demonstrate dramatic improvements in cost and environmental performance compared to state of the art technologies. This includes avoidance of process steps, 50% energy savings, and 100% recycling of reagents as opposed to disposal of strong acid leaching agents in state of the art pre-treatment steps. REE4EU will also develop urgently required market data on EoL RE availability and a triple value-chain business case for a new European secondary rare earth alloys production sector.

For the **Indus3Es project,** different sectors were analyzed in depth to assess the applicability of the, focusing principally on temperature levels, capacities and possible heat sources and heat sinks, which can suit AHT requirements. Results showed that many industrial processes are suitable for integration of AHT technology. Sectors which are especially promising are the petrochemical, pulp&paper, and ceramics sector; followed by water and non-ferrous sectors, where it can be integrated in special applications. Cement and steel sectors showed too high temperatures for AHT integration.

This high temperature membrane reactor module developed by **MEMERE** will have an immediate result on the significantly increased C2 yields because of the distributive oxygen feeding and improved temperature control of the reactor, combined with improved overall plant efficiency and costs. MEMERE technology will deliver direct conversion of methane to C2+ with a reduced energy penalty in a much more effective way (target **C2 yields >30%**) as compared to currently available techniques.

SECTION IV

SUSTAINABILITY ASSESSMENTS AND ECO-INNOVATION

LIFE CYCLE EVALUATIONS OF PILOT-SCALE ULTRAFILTRATION FOR WASTEWATER REUSE

George Barjoveanu[1], **Carmen Teodosiu**[1,*], **Daniela Fighir**[1],
Dan Popovici[2]

[1)] Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73 Prof.dr. D. Mangeron Street, 700050 Iasi, Romania
[2)] SC APAVITAL SA Iasi, 10 M. Costachescu Street, Iasi 700495, Romania
[*]: *cteo@ch.tuiasi.ro;*

Introduction and study objectives

Relatively recently, the concept of the circular economy has been developed as a new paradigm for resources management, at European level. Thus, new legislation is currently developed and implemented with the scope of closing the life cycle of products by enhancing recycling and reuse to minimize resources use intensity and pollution. This paradigm applies also for water resources which face even higher risks, given the increasing pressures due to climate change and continuous quality deterioration. As a consequence, water professionals and service providers are constantly looking to develop and optimize wastewater treatment technologies that enable wastewater reuse. In general, additional wastewater treatment needed to increase wastewater quality to allow reuse is done by causing secondary environmental impacts mainly due to energy and chemicals consumption. In this context, developing and implementing efficient evaluation instruments is very helpful in finding the delicate balance between the needed pollutant removal for wastewater reuse and the impacts associated to these efforts.

The objective of this paper is to evaluate the performance of a pilot scale ultrafiltration system installed in a municipal wastewater treatment plant which was used as an advanced treatment stage to enable water reuse. The evaluation was performed by means of the life cycle assessment (LCA) and life cycle costing (LCC) methodologies. LCA is a standardized material and energy flow to identify and quantify environmental impacts throughout the life cycles of products and processes, while LCC evaluates the costs associated to processes.

Methodology

This study concerns the performance of a pilot scale ultrafiltration system (180 L/h, 1 m^2, 100 kDa polysufone membranes) used to polish the effluent of the Iasi wastewater treatment plant. The Iasi (MWWTP) consists of a conventional mechanical-biological wastewater treatment, and a newer second line which features a two-stage activated sludge process (first stage with very high organic load, second stage normal organic and sludge load). Recently, nitrogen and phosphorous removal was also implemented.

The technical and environmental performance of the UF system was evaluated by developing a life cycle assessment case study. The functional unit was 1 m^3 treated water which has enabled the comparison with the conventional wastewater treatment. The life cycle inventory included the electricity consumption and the operations and chemicals used for membranes cleaning. The life cycle impact assessment (LCIA) was carried out by using the Ecological scarcity at end-point, which is a modern LCIA method that enables the analysis of impacts related to resources consumption. The technical performance of the UF pilot system has considered the membrane system productivity defined as the ratio between the cleaning water volume and the permeate volume, as well as water quality indicators like: pH, conductivity, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), nitrates, Total Phosphorous (TP), Total Fe, Total Cr, Cu^{2+}, Ni^{2+}, Zn^{2+}. The UF pilot system was also evaluated for biological contaminant removal. Additionally an LCC analysis was performed in order to identify the cost structure of the additional wastewater treatment and to enable comparison with prices for potable/industrial water.

Results and conclusions

The UF system was used in UF tests, but also for membrane cleaning tests. The water quality results have demonstrated that this system may be successfully used for the advanced wastewater treatment for recycling, as it is possible to eliminate: up to 100% suspended solids, up to 75% organic compounds (expressed as COD) and up to 50% phosphorous compounds. More importantly for reusing purposes, the system is able to eliminate completely all the micro-organisms.

The life cycle impact analysis reveals that the results for environmental impacts are in general similar with other reports, and are especially due to additional electricity consumption. The study demonstrates that the LCA is useful in pinpointing the avoided impacts due to water reuse, but however, further investigation is needed to take into consideration aspects related to recycle water quality requirements (treatment requirements) and optimization of the UF pilot system.

Acknowledgment

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INTERACTIVE ASSESSMENT OF THE GOVERNANCE CONTEXT FOR SUSTAINABLE RIVER MANAGEMENT

Hans Bressers[1], Nanny Bressers[2]

[1) Environmental Policy Studies, University of Twente, The Netherlands
[2) Vindsubsidies, Water Board of Vechtstromen, 7500AE Enschede, The Netherlands
**: hans.bressers@utwente.nl; n.bressers@vechtstromen.nl*

Introduction and study objectives

Sustainability assessments are often concentrating on the technical aspects of eco-innovations, relating those to the economic, social and environmental perspectives of sustainable development. However, increasingly also the institutional aspects are included in the assessment. One may discuss whether these are part of the sustainability itself or a prerequisite for sustainable development. But even when one takes the second stance, it is implied that innovations that potentially contribute to sustainable development will not realize this potential unless nested in an appropriate institutional context. In this study, we concentrate on the interactive assessment of this context, enlarging it from institutions to the wider concept of governance. The "governance" of a certain part of society is the multiplicity of relevant private and public responsibilities and resources, instrumental strategies, problem perspectives and goals, actor-networks and scale levels that forms a context that enables and to some degree restricts actions and interactions in that part of society, for instance related to an eco-innovation.

The eco-innovation this study concentrates on is a long-term multifunctional and multi-stakeholder river restoration program. It concerns the River Vecht, often labelled the smallest of the Dutch main rivers and the largest of its small rivers. From its source in Germany at an elevation of 165 meters, River Vecht runs from source to mouth for 167 kilometers, of which some 60 kilometers in the Netherlands. At the beginning of the twentieth century this was still 85 kilometers, but during the first decades of that century many meanders were cut off. Since it's a rain fed river, this caused extreme low water levels in summer and as a result it was decided to build weirs, initially seven of them. This blocked most of the shipping that had taken place before. Natural meandering was blocked by reinforcing the riversides with stone. In the sixties, also at the German side such measures have been taken. All in all, the river was turned into a "heavily modified water body", geared towards efficiency for agriculture under stable hydrological conditions. At the beginning of the 21st century this dominant purpose has to share its position with many others from various stakeholder groups and climate change makes the hydrological conditions increasingly unstable. Already in 1996 a multi-stakeholder "area perspective note" called for a transformation towards a "living river", to serve better flood safety, spatial quality and biodiversity. In 2007 the initiative was taken to start a large scale multi-stakeholder program "Space for River Vecht", including more SD goals, with social aspects like community identity and economic aspects like recreation. The program is envisaged to run until 2050. Its governance conditions are however far from stable and need to be guarded as they change, in order to prevent them turning into a negative context. This is the purpose of the project reported here.

Methodology

As the study deliberately interacts with the field under study it can be labeled "action research". This by no means implies that it isn't theoretically and methodologically well-founded. The assessment methodology used is the Governance Assessment Tool (GAT), that in turn is rooted in Contextual Interaction Theory (CIT). In this methodology, four theoretically important qualities of the governance context are applied on fives dimensions of governance, in order to get a clear picture of the supportive and restrictive nature of the aspects of the governance context for the realization of a given program or project and its SD goals. The results are described in text, but can also be presented in overview tables with red, orange and green colors indicating the degree of supportiveness of the 4 x 5 different cells and the positive or negative dynamics observed in them.

The difference with previous applications of the tool is that in this project there is a very regular feedback of the analyses into the ongoing process, thereby involving the multi-stakeholder practitioners in the analysis and the researchers in the design of evolving governance arrangements. The interactive approach to the assessment leads to mutual awareness raising and creative solutions to weaknesses and threats.

Results and conclusions

The project runs from August 2016 to August 2018. The start-up analysis has been based on an internal evaluation study of the first phase (until 2015) for with 19 public and private stakeholders had been interviewed. This starting document revealed both a fairly supportive context for this phase, but also a number of alarming dynamics that could deteriorate this supportiveness in the near future. After an explanation of the Governance Assessment Tool to the program steering group, these initial results were presented. From there onwards the researchers were included in a task force to discuss the future of the program. There is an alternation between additional interviews with stakeholders that produce new insights on the SD challenges and opportunities for the program and its governance requirements and the meetings in the task force and sometimes the steering group where these options are assessed and elaborated. A main provisional result is that even though a substantial decrease of financial means for the program it to be expected, it is the continuity of the consensus oriented network relationships between the various public and private stakeholders that is most essential for future success of this long-term and thus complex and dynamic program. Revisiting and reformulating the blend of ecological, social and economic SD goals that is pursued by the program and the framing of this blend into new inspirational catchwords and narratives, seems most important for this purpose. The reformulation of the program's SD goals can also involve new actors that have hitherto remained somewhat in the back, like the general public and the recreation industry's entrepreneurs.

SUSTAINABLE ENGINEERING BY USING LIFE CYCLE ASSESSMENT (LCA) IN PROCESS DESIGN

Daniel Koch, Anton Friedl, Bettina Mihalyi

TU Wien, Institute of Chemical Engineering, Getreidemarkt 9/166, 1060 Vienna, Austria,
**: daniel.koch@tuwien.ac.at*

Introduction and study objectives

Process simulation tools in chemical engineering are used to develop and optimize processes in regard to technical and economic aspects. The usual procedure is to investigate the process or single process units and their parameters by recording data through systematic experiments, which are used to create a mathematical process model that covers the whole working area. The mathematical process model mainly consists of mass and energy balances that are solved by the process simulation tools. The developed process model can then be used to optimize the process parameters or the layout of the process in order to yield the highest efficiencies or the highest profits. However to meet the rising awareness of the need for sustainability, conventional simulation tools are quickly reaching their limits.

While small, concentrated frameworks are often sufficient in process design and optimization, it is imperative to expand the scope and to take the entire process life time chain, from cradle to grave, into account to analyse the influence on the environment. Therefore a new methodology, the ISO standardized life cycle assessment (LCA), with its own calculation tools was developed and has proven as a powerful tool to make a highly systematic and rational approach to entirely analyse the environmental impact of processes, services or product systems.

Until recent years LCA was focused on established systems but for the application of the precautionary principle it should already be implemented in an early stage process design phase, in addition to classic process simulation tools. It is essential for a sustainable development to include life cycle thinking in process design.

In trying to increase independence from fossil resources, biomass based refineries are the centre of interest for many research groups. This innovative technology also is intended to reach a sustainable development and to reduce the environmental burdens. There are already different concepts for biomass based refineries and even within one concept there is a selection of process paths to obtain the botanical ingredients in a certain quality.

This study investigates how LCA can help to find the most ecological respectively the sustainable process paths in an early stage of process design using a case study on the issue “lignocellulosic biorefinery”. To yield the different products in this biorefinery the lignocellulosic biomass has to be pretreated to provide the different fractions, cellulose, hemicellulose and lignin, for downstream upgrading (further refining procedures). Also two common research questions should be answered: "Is it possible to make profound decisions from an LCA documentation in the literature without conducting one exclusively with the specific application and frameworks?" and "How far are LCA results from different assessments about the same process principle comparable?"

Methodology

To find answers for the research questions LCA results from the current literature were studied, and the recently most assessed lignocellulosic biomass pretreatment method was selected. That is the dilute acid process, commonly used for second generation bioethanol biorefineries. Important aspects of the methodology were precisely investigated to have a good basis of comparison, including: goal and scope definition, functional unit, land use change, biogenic carbon sequestration, allocation of products and feedstock. All recognised obstacles and shortcomings were identified and documented.

Results and conclusions

Process development includes choosing one of many different paths to reach the desired outcome. The environmental impacts need to be included for a sustainable development.

Analysing the environmental implications for a specific process from different LCAs in literature comes with a large number of uncertainties and a high variation range. Comparing two different process path possibilities by merely literature LCA is hardly helpful. It is also unlikely to find life cycle calculations which investigate exactly the same two process paths, with the same goal and scope and the same data quality. Each process development has unique goals which cannot be ignored when trying to transfer a life cycle calculation result with different unique aspects onto it. Taking a selection of more life cycle calculation results from the literature into account, comes with a lot of detail work for each process. The variation in all steps, setting goal and scope, choosing the methodologies, data quality of the life cycle inventory (LCI), timeframe and more of the LCAs, leads to incomparability of the results. Trying to understand the variations and looking into the calculations in detail to take deviations in each level into account is a very high effort, even if it is done with ISO compliance there are certain presumptions, boundary conditions and calculations which are not exposed.

While it is already challenging to compare the environmental impact of different commercial processes by consulting the literature, it is even more increasingly unfeasible for processes in the design phase where even more uncertainties, flexible parameters and a larger number of assumptions are present. Therefore it is imperative to apply an exclusive LCA as decision support along with each process development. Ideally it is done together with the engineers developing the process.

SUSTAINABILITY OF THE PACKAGING WASTE MANAGEMENT SYSTEMS IN EASTERN EUROPEAN COUNTRIES

Daniela Cailean (Gavrilescu)*, **George Barjoveanu**,
Carmen Teodosiu*

Department of Environmental Engineering and Management, "Gheorghe Asachi" Technical University of Iasi, 73 Prof.dr.doc. Dimitrie Mangeron Street, 700050, Iasi, Romania,
**: dcaile@ch.tuiasi.ro; cteo@ch.tuiasi.ro*

Introduction and study objectives

Packaging waste (PW) is a waste stream that has been given special consideration at the European level, the generated PW in European Union accounting for approximately 80 million tons each year, with some variations in 2008-2009 due to the economic crisis. The PW legislation has been introduced since 1985, but over the decades, several amendments and revisions of Directive 94/62/EC on packaging and packaging waste have been implemented, to answer the societal, economic and environmental challenges of the member states and the extension of European Union. The main domestic packaging waste streams currently monitored in each European Union member states are: paper and cardboard; plastics; wood; glass; metals, with steel and aluminum as the most important fractions.

The main objective of this study is to assess the Packaging Waste (PW) management system profile and sustainability, in four European Union (EU) countries, which historically have been underperforming in the waste management sector due to various contextual factors: Bulgaria (BG), Hungary (HU), Poland (PL) and Romania (RO), in the period 2007-2014. In the interpretation of results, it must be mentioned that Hungary and Poland are member states of EU starting with 2004 and Bulgaria and Romania since 2007, a fact that influenced their performance in terms of PW and solid waste management in general.

The evaluation was performed in a coherent and unitary manner, following the life cycle stages of the PW: generation, collection, recycling for material recovery and thermal treatment for energy recovery (R1 type) and final disposal, based on national domestic PW indicators. To the best of our knowledge, this is the first study that assesses the sustainability of the domestic PW management system, based on the carbon footprint of PW, by using aggregated models and comparing the greenhouse gas (GHG) emission dynamics over the 2007-2014 period. Also, it provides results for the expected greenhouse gas emissions deriving from PW treatment options: recycling, thermal treatment and landfilling. Furthermore, by considering the concept of circular economy which strongly emphasizes the idea of material recycling, the study investigates the potential and dynamics of the secondary material markets, through the Secondary Material Price Indicator (SMPI).

Methodology

The selected data were collected from the Eurostat data base and National Environmental Status Reports and used in the framework presented in Table 1. The Carbon Footprint methodology applied to PW streams comprises calculations according to material flows and emission factors corresponding to waste treatment such as: recycling, composting, incineration and landfilling. The Carbon footprint analysis is based on 5 aggregated models found in the literature (Cifrian et al., 2013). In general, the carbon footprint (CF) of the PW systems is calculated (expressed as CO2e t/year), according to equation 1:

$$CF=\Sigma\ Qmi,j\ \times EFi,j \qquad \text{(eq. 1), where:}$$

Qmi,j – material flow i, which undergoes the treatment method j (tone of waste material/year);

EFi,j – emission factor of each material i, in each treatment j (kgCO2e/tone waste material).

Table 1: Sustainability indicators used in the characterization of domestic PW systems

Aspect	Indicator	Measurement unit
PW system profile (paper and cardboard; plastics; wood; glass; metals)	Generation, recovery, material recycling and incineration rates of PW per: year, country, treatment option, efficiency	Kg/capita
PW environmental performance	GHG emissions (Carbon Footprint Indicator, CF) per: year, country, treatment option, efficiency	CO_{2e} tones/year
PW economic value	Secondary Material Price Indicator (SMPI)	EUR/ton of recycled PW

Results and conclusions

The average composition (by weight) of PW, estimated in 2013, in European Union (EU 27) is: paper and cardboard (41%); glass (20%); plastic (19%); wood (15%) and metal (6%). The recovery shares in the domestic packaging waste stream are, in all studied countries, less than the EU27 average. A maximum of 20% increase is registered in the case of Bulgaria in 2011, and respectively Romania in 2014 (Table 2).

Table 2: Packaging waste recovery percentage of PW, 2007-2014

Country	2007	2008	2009	2010	2011	2012	2013	2014
Bulgaria	54.85	50.43	45.86	61.98	65.58	67.56	65.96	62.21
EU27	72.56	72.77	74.57	76.54	77.56	78.72	79.24	78.75
Hungary	54.58	56.53	55.00	62.30	62.93	60.12	60.29	59.73
Poland	60.04	50.60	50.26	53.68	55.85	57.09	50.35	60.01
Romania	36.62	40.74	46.75	48.31	54.41	57.46	54.46	56.42

The increasing recycling PW rates follow closely the corresponding recovery rates, which demonstrates that recycling is the most important waste valorization option that contributes to a diminished environmental impact. Also, this trend is linked to a market development for secondary material trade.

The CF indicator which considers the contributions of the CF for each PW category shows negative values for 4 out of the 5 models, irrespective of the year or country. The results present a decreasing CF trend which is correlated to increasing recycling rates (and not necessarily to improvements in PW management technologies) and indicate savings in the national GHG emissions.

URBAN LAND USE OF HUMOR CATCHMENT ROMANIA OVER THE LAST TWO CENTURIES AND ITS ENVIRONMENTAL IMPACT

Brindusa Mihaela Sluser[1,*], Mihai Gabriel Balan[2], Eugen Rusu[2], Catalin Balan[1]

[1)] Gheorghe Asachi Technical University of Iasi, Romania, Faculty of Chemical Engineering and Environmnetal Protection, Blvd. Prof.dr.doc. Dimitrie Mangeron 73, 700050 Iasi, Romania,
[2)] Al.I.Cuza University of Iasi, Romania, Faculty of Geography and Geology
[*]: brobu@ch.tuiasi.ro

This study aims to assess the impact of anthropogenic activities over a period of more than two centuries from Humor catchment (vegetation and fauna existing in forests, grasslands, meadows, and crops), deadwood, litter, soil and anthropized lands. The largest impact are recorded in the biomass and in the ecosystems forests soil. At the same geographic area, the impact varies in time and its evolution is determined by climatic fluctuations at different time scale, natural hazards (wind, fire, insect attacks, climatic excesses), but also to human interventions. The most visible changes in the Humor basin ecosystems were determined by large-scale changes in how the land was used. Deforestations and passing from lands with forestry use into agricultural use, or residential space, led to massive impact. Although the plantings, a sustainable management, and the forest rehabilitation could have a positive impact, but the deforestation of the large areas and the change of the purpose of land use, they led irretrievably to a negative impact. In period considered study to quantify the impact from 1778 to 1856, in case of change of land use from forest to grassland, loss of OCD are 60% (about 185 t/ha of 300 t/ha) and in case of change of forest in the urban area, are 79% (235 t/ha 300 t/ha). From 1856 until 1944, have doubled the areas cultivated, have decreased to third the surfaces occupied with shrubs and in their place reappeared the forests (Fig.1).

The oldest map that was used in the calculation of areas under different categories of uses dates from year 1778, before the colonization of Poles on Humor Valley (Fig.2). The territory was forested in the proportion of 9/10 and the pastures were limited around the locality Humor Monastery. A radical change in land use appears beginning with 1832 when it was colonized the poles of Pleșa village, and in year 1842, when the poles are brought to the Poiana Micului village. These colonization were accompanied by massive deforestation of more than 3000 ha, the purpose of obtaining areas for grazing and intended for the agricultural cultivation. From 1856 until 1944 have doubled the areas cultivated, have decreased to third the surfaces occupied with shrubs and in their place reappeared the forests. Between

1944 and 1982, have emerged some significant changes in land use through substantial diminution of the meadows covered surfaces and increasing the area covered by forests to their detriment. They have considerably increased the areas occupied with crops and it was extended well the urban area. From 1982 until 2012, except urban area that has stalled the other categories of use the other categories of use they met different developments: the forests have expanded slightly, meadows and crops has decreased significantly (Fig. 1). Diminishing of cultivated areas and pastures is explained by decreased interest of local people for agriculture, especially for zoo technical activity.

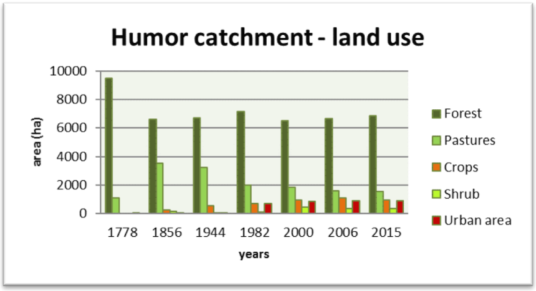
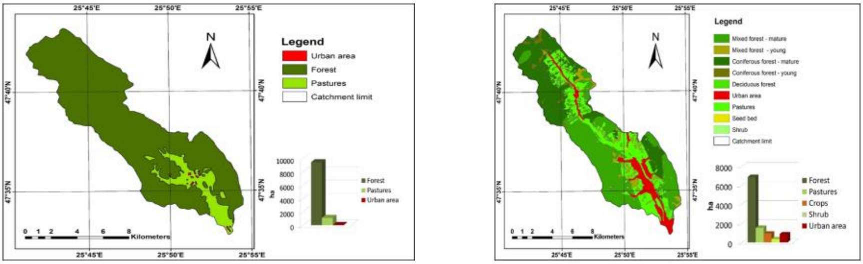


Figure 1: Humor catchment – land use evolution



(a) (b)

Figure 2: Evolution of landscape use in a) 1778 and b) 2015

The objectives of this work addressed to the following issues: quantification of the main recent changes regarding the land use and urbanization; analysis of the evolution of carbon stock after land use change; the current general trend of carbon sequestration stock and its environmental impact. The results of this study revealed the fact that anthropic activities considerably changed the land use and forest area lost more than 40% over 2 centuries, the associated impact is major negative reflected in landscapes views, less agricultural area and less forest. Due to high and rapid urbanization over the last 2 centuries in Humor catchment, Romania, the negative geomorphological processes were developed, such as: floods, landslides, soil de-structuring, soil erosion.

BRIDGING THE GAP BETWEEN ENVIRONMENTAL PRESSURES AND TOURISM DEVELOPMENT: AN APPROACH TO PROMOTE SUSTAINABLE TOURISM BASED ON LIFE CYCLE ASSESSMENT

Alexandra V. Michailidou, Christos Vlachokostas,
Nicolas Moussiopoulos

Laboratory of Heat Transfer and Environmental Engineering, Aristotle University
Thessaloniki, Box 483, 54124 Thessaloniki, Greece,
**: amichail@aix.meng.auth.gr*

Introduction and study objectives

The tourism sector is a key driving force for socio-economic progress on the globe; an enormous economic industry worldwide. Nevertheless, tourism is increasingly recognized as a significant resources' consumer at every scale of its activity i.e. local, regional, and global scale. This significant rate of resources use and consumption is mainly related to energy, water consumption, and waste generation via lodging and recreation activities. Undoubtedly, the rational use of resources is nowadays considered a main challenge for the decision makers in order to face environmental deterioration that can be attributed to tourism development and activity, face climate change impacts and future risks, and eventually put forward managerial approaches to promote sustainable tourism. Toward this direction, the paper presents the basic structure and components of a methodological scheme in order to combine environmental pressures that can be attributed to tourism areas and holistically characterize environmental sustainability in a Defined Area of Concentrated Tourism (DACT). The methodology is demonstrated for one of the prevalent Balkan tourism destinations Chalkidiki, located in the Region of Central Macedonia, Northern Greece.

Methodology

The generic methodological scheme is driven by the DPSIR framework and combines four discrete management and assessment tools in a toolbox: (i) Life Cycle Assessment (LCA) to estimate the environmental burned in DACTs (the "s" in the acronym is relative to areas), (ii) Environmental Indicators (EIs) via the use of Tourism Environmental Composite Indicator (TECI), which characterizes environmental sustainability, with the weighted average of key performance normalized sub-indices that express the relative weight of the levels of status of environmental pressures of tourism activity compared to a reference level, (iii) Carbon Footprint Analysis (CFA) embedded in the implementation of TECI and (iv) Multi-Criteria Decision Analysis (MCDA). On this basis the scheme is used to identify "hot spots", assess impacts of tourism activity and generate response for sustainability.

In brief, the main pillar of the methodological scheme is LCA which is essentially the "core" in order to combine efficiently all the other tools in the approach. In this light, LCA is adopted in order to (i) estimate the environmental load that can be attributed to tourism activity (i.e. hotels and other accommodation facilities, transport activities etc.) (ii) focus on accommodation "hot spots" in a DACT, (iii) take into account multiple impacts (impact-oriented approach), (iv) easily calculate and embed to TECI all direct and indirect GHGs' emissions as CO2-eq through CML 2001, by avoiding complex equations for each GHG, (v) identify the carbon intensive processes/services due to hotels' operation and thus introduce more effective practices for lower emissions and (iv) generate feedback to promote the implementation of realistic and effective mitigation measures that can be implemented on hotel premises and local transport sector.

Results and conclusions

An analytical "network of detailed activities" for each hotel under consideration was created to assess the overall environmental load via LCA. In brief, and according to the Eco-Indicator 99 impact assessment method, the operational use is for the most part responsible for the total environmental damage for all hotels under study, provided that the operation of hotels and road transport is taken into account (excluding air transport). The use of diesel and electricity for heating and the production of hot water is an important factor that contributes to the overall environmental load. In general, regarding the operation of the accommodation facilities, HVAC systems are the most energy intensive agents of environmental burden, followed by kitchen and production of hot water. However, when air transport is included in the LCA, it is prevalently responsible for the total environmental damage for medium to large-sized hotels of the case under study in comparison to the road transport, accommodation services and the hotels operational use and energy intensity. Based on the implementation of TECI and CFA a characterization of environmental sustainability of the DACT under study is realized. Last but not least, and based on MCDA, policy making should primarily put forward incentives in order to maximize the penetration of: (i) Renewable Energy Sources (RES) in hotels in the area, (ii) vehicles with biofuels in the hotels' fleet and (ii) local products in dining sector.

This work adds up to the considerably low number of respective LCA implementations found in the scientific literature and extents the scope of LCA application to a new tourism destination. Furthermore, the holistic approach adds scientific added value, since it provides a robust basis for the identification of environmental "hot spots" in order to highlight processes with considerable environmental impacts and promote the implementation of effective mitigation measures by hoteliers and public authorities. The work clearly depicts the fact that LCA can play a crucial role in decreasing the complexity in the strategic planning of tourism, especially in local-to-regional areas of concentrated tourism activities. The holistic approach presented provides a basis for policy insights that can lead to robust policy modeling and reliable national strategic governance since it provides a little stepping stone in characterizing environmental sustainability in areas of considerable tourism activity.

CHALLENGES OF CIRCULAR ECONOMY: ECO-INNOVATION AND ECO-DESIGN IN MANUFACTURING SECTOR

Teofil Câmpean[1,2], Raluca-Maria Hlihor[1,3],
Isabela Maria Simion[1,3], Elena-Diana Comăniță[1],
Petronela Cozma[1], Camelia Smaranda[1], Mihaela Roșca[1],
Dan-Alexandru Gavrilescu[4], Cristina Ghinea[1,5],
Maria Gavrilescu[1,6,*]

1) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
2) Rondocarton SRL, Cluj-Napoca, 2 Aviatorilor Street, 407042 Apahida, Cluj-Napoca, Romania
3) "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, Iasi, Romania
4) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Natural and Synthetic Polymers, Iasi, Romania
5) Stefan cel Mare University of Suceava, Faculty of Food Engineering, Suceava, Romania
6) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
**: mgav@tuiasi.ro*

The promotion of resource productivity along the whole life-cycle by waste minimization, pollution prevention together with resource conservation found their best place in the frame of circular economy, vital to convey the resource efficiency agenda according to Europe 2020 Strategy for smart, sustainable and inclusive growth. Circular economy is able to move the linear "take, make-consume, dispose" industrial processes toward closed-loop systems, by preserving the added value in products for an extended life - cycle and eliminating any waste, therefore facilitating the decoupling of economic development from resource use and its impacts.

This paper explores the opportunities to relate the principles and concepts of eco-innovation and eco-design in a logical succesion, applied in the revaluation of waste production resulted from corrugated board production and packaging manufacturing as solutions for extending their life cycle, in an industrial survey. Starting form the consideration that both production and recycling processes of paper and cardboard have their life-cycles, we will develop an analysis and workplan by following eco-design concept and principles in order to create environmentally friendly and sustainable product life-cycles, by applying an eco-innovative approach. The new ecological ideas and technology developed by eco-innovation and eco-design will promote significant directions towards the implementation of manufacturing with fewer wasted resources, by closing the loop in the production system according to the circular economy concept.

The experimental sequence of our work will include activities devoted to: the identification of a manufacturer which produces corrugated board and cardboard boxes for packaging purposes; the current situation and technological flowsheet (the

linear process); identification of other possible goals of the manufacturer; the potential of the existing technology to close the production loop by an efficient revaluation of recyclable materials represented by waste production. Also, the technological strategies and solutions which adhere to the principles of eco-innovation and eco-design will be inventoried.

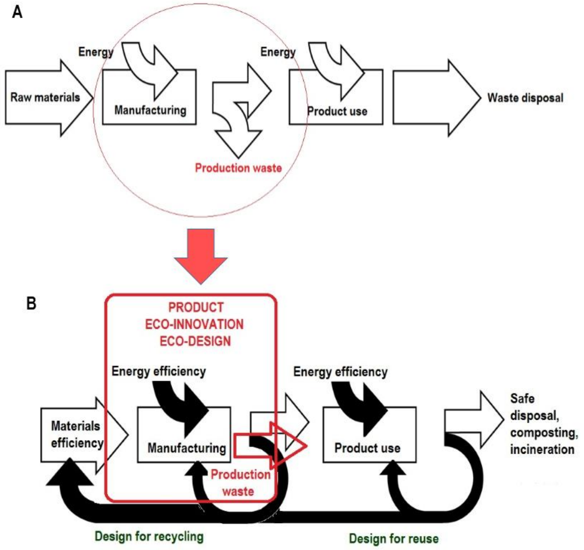


Figure 1: Changing linear production process to closed-loop by design for recycling, design for reuse and production waste revaluation by product eco-innovation and eco-design (the red rectangle)

Therefore, the waste production will be revaluated and re-engineered in a new product, required by the market, so as to solve the questions addressing natural resource protection and diminishing the greenhouse gas effects through the preservation of trees, currently used as wooden raw material. Moreover, the study will deliver knowledge transfer to the manufacturer for the assimilation of strategies and solutions for eco-innovation and eco-design in order to ensure the scientific support for technology and product design and development as well as to gain quantifying technical-economic and environmental performance for process and product. The paper will respond to the need to acknowledge and integrate economic and environmental performance in the manufacturing of a product by reusing waste production by applying strategies and solutions for eco-innovation and eco-design to exploit the technological potential and socio-enhancing economic and eco-efficiency in the context of circular economy.

Acknowledgement:

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EVALUATION OF ECO-EFFICIENCY BY MULTICRITERIA DECISION ANALYSIS. CASE STUDY OF ECO-INNOVATED AND ECO-DESIGNED PRODUCTS FROM RECICLABLE WASTE

**Elena-Diana Comăniță[1, *], Isabela Maria Simion[1,2],
Petronela Cozma[1], Camelia Smaranda[1],
Raluca Maria Hlihor[1,2], Cristina Ghinea[1,3],
Simona Cecilia Ghiga[1,4], Mihaela Roșca[1], Maria Gavrilescu[1,5]**

1) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof.Dr.Docent D. Mangeron Street, 700050 Iasi, Romania
2) "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, Iasi, Romania
3) Stefan cel Mare University of Suceava, Faculty of Food Engineering, Suceava, Romania
4) Romanian Association for Recycling, RoRec, Bucharest, Romania
5) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
**: ed.comanita@tuiasi.ro*

In order to become sustainable, the industry should achieve in the long run a balance between economy, ecology and community. Nowadays we witness a widespread recognition and integrative approach of economic and environmental aspects for production processes, products, services, business. This reality is more evident when new processes and products are created/innovated, designed and applied. It is largely recognized that ensuring economic efficiency simultaneously with reducing environmental impacts is promising in the early phases of any process/product synthesis and design. Therefore, it is unanimously accepted that eco-innovation and eco-design are tightly connected with process/product/service eco-efficiency. Eco-innovation is related to all forms of innovations (technologies, products, services) which are able to bring new and robust business oportunities and benefits for the environment in terms of resources and impacts. Eco-design (sometimes denoted as environmental redesign) is a fully integrated design activity in which the environmental impact is checked against targets for improvement. Both eco-innovation and eco-design contribute to sustainable manufacturing since new ideas are integrated into the manufacturing process by design so as to generate added value with less environmental impact, being therefore eco-efficient. This makes it possible to abandon the linear, *cradle-to-grave* production systems in favor of cyclical, *cradle-to-cradle* industrial metabolisms that support materials to preserve their status as resources and accumulate intelligence over time. This approach essentially causes a synergistic relationship between ecological and economic systems, leading to a constructive relationship between economy and ecology in an eco-efficient way. A more integrative and pro-active approach assumed as an important contribution to industrial eco-efficiency addresses the recycling of waste into new products based on eco-innovation and eco-design, entailing environmental concerns, but also the preservation of natural resources, industrial efficiency and economic development.

In this paper, we applied multicriteria decision analysis to develop an eco-efficiency evaluation for a redesigned product using waste production resulted in corrugated board and carboard box manufacturing as raw material, compared to the original which is made from corrugated board sheets. This analysis is useful in the decision making process in terms of the optimal allocation of resources to maximise the anticipated output for the given input. Two approaches will be considered: (i) the *classical* one, which assumes that accurate judgements exist on function values of certain attributes and their weighs (e.g. AHP method); (ii) the outranking approach, which considers weak preferences and incomparable criteria, assumes that the preferences for a certain solution are not obvious to the decision maker, so that the decision support aims at giving insights into the consequences of different weights (e.g. ELECTRE, PROMETHEE methods).

The results of our analyses based on various optimization algorithms will allow us to rank options, select a single optimal alternative or to differentiate between acceptable and unacceptable alternatives in product eco-innovation and eco-design, in order to make the best decision in the context of multiple assessment criteria. Here, Multicriteria Decision Analysis (MCDA) was proposed as a complete and complex methodological framework for conducting a sustainability-oriented design. The analysis will involve some basic steps, irrespective of the method applied (Fig. 1): (i) identification of objectives; (ii) documentation on the possible options for achieving the objectives; (iii) identification of the criteria used to compare the options; (iv) option analysis; (v) option ranking and selection; (vi) sensitivity analysis and validation of alternatives resulted from decision process; (vii) decision making and application; (viii) feedback from manufacturer. The study will provide basic information useful in recommending the application of eco-innovation and eco-design principles and practices to a Romanian manufacturer specialized in carboard packaging production, for the revaluation of waste production according to the circular economy concept, so as to increase production and product eco-efficiencies. Moreover, we will be able to perform experienced knowledge transfer based on well-documented scientific support, able to ensure a balance in economic, social and environmental trade-offs for the manufacturer by taking into account multiple goals related to the allocation of resources and investments, eco-efficiency, to avoid contradictory opinions among diverse stakeholders.

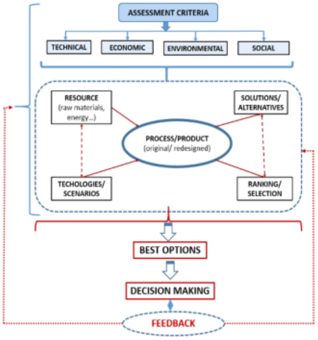

Figure 1: Steps in application of MCDA methodology for assessing eco-efficiency and adaptability of eco-innovated and ecodesigned process/products

Acknowledgement

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INDICATORS FOR KNOWLEDGE TRANSFER FROM UNIVERSITY TO INDUSTRY FOR LIFE CYCLE EXTENDING IN THE CONTEXT OF CIRCULAR ECONOMY

Petronela Cozma[1,*], **Teofil Câmpean**[1,2], **Ariadna Negruț**[1],
Mihaela Roșca[1], **Isabela Maria Simion**[1], **Elena-Diana Comaniță**[1],
Simona Cecilia Ghiga[1,3], **Camelia Smaranda**[1],
Raluca Maria Hlihor[1,4], **Maria Gavrilescu**[1,5*]

1) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
2) Rondocarton SRL, Cluj-Napoca, 2 Aviatorilor Street, 407042 Apahida, Cluj-Napoca, Romania
3) Romanian Association for Recycling, RoRec, 24 Sevastopol Street, 010 992, Bucharest, Romania
4) "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania
5) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
**: petronela_cozma@tuiasi.ro, mgav@ch.tuiasi.ro*

Knowledge transfer from research institutions - in particular from higher education bodies - to economic sectors is of growing worldwide importance, based on systematic policies, and monitored by means of suitable indicators, for the benefit of society as a whole. Three categories of activities are usually considered as involved in knowledge transfer, namely: research, knowledge transfer and economic activities (Fig. 1). Different categories of actors from both the academia and the industry, with different skills, goals, responsibilities, and inclinations, along with a host of other factors, contribute together to the transfer of research outputs as new knowledge, tailored to the needs of economic actors. Collaborative and contract research play a significant role in defining the research agenda since knowledge transfer goes hand in hand with knowledge production. Aside from research, licensing of the university intellectual property to the industry, teaching and continued professional development, consultancy and networking are components of knowledge transfer.

The present paper addresses the cooperation between university and industry in producing new knowledge, as well as in making recognized knowledge abide on problems and opportunities for exploitation, within a research and development cooperation based on both contract research and collaborative research. All these are obviously focused on the generation of economic benefits, environmental protection and social caution (Fig. 1). The knowledge transfer will focus on strategies and solutions for process and product eco-design and eco-innovation based on recyclable materials in the context of circular economy, by interconnecting the knowledge and expertise within a contract signed between the "Gheorghe Asachi"

Technical University of Iasi, Romania, as coordinator, and a Romanian corrugated board and cardboard packaging manufacturer (RM).

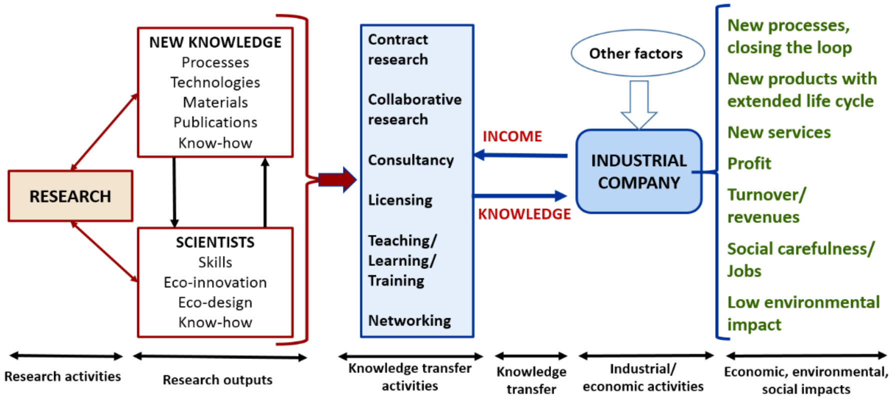

Figure 1: Model of knowledge transfer within the innovation ecosystem

The requisite for expertise and knowledge transfer to the economic agent arises from the necessity to close the production loop in the existing technology for corrugated cardboard and packaging manufacturing and to extend the life cycles by eco-innovation and eco-design for process and product according to circular economy principles so as to generate benefits for the economic agent by increasing its technical-economic and environmental performance. The knowledge transfer to RM will address process and product eco-innovation and eco-design, as well as the tools and methods for economic and environmental performance evaluation (Life Cycle Assessment, Cost-Benefit Analysis, Multicriteria Decision Analysis). Knowledge transfer will also include the dissemination of research and cooperation results for, and together with, the specialists of the industrial company RM (training, guides, patents etc.), as well as for other stakeholders (papers, conferences etc.).

In order to monitor and measure the performance of knowledge transfer, our study will consider the recommendations of the European Commission, Directorate General for Research and Innovation - Economic Analysis and Indicators Unit, in the sense that we will measure the results of knowledge transfer by means of three groups of indicators: (i) indicators for knowledge transfer through people (based on education and training); (ii) indicators for knowledge transfer through institutional cooperation in research, development and other phases of innovation; (iii) indicators for knowledge transfer through the exploitation of research results. Based on this analysis which involves multi-disciplinary and practical aspects, the links between university and industry in a national network for knowledge transfer will be strengthened.

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BIOLOGICAL REMEDIATION OF SOIL CONTAMINATED BY HYDROCARBONS

Spina Federica[1,*], Spini Giulia[2], Poli Anna[1], Romagnolo Alice[1], Zanellati Andrea[1], Bentivegna Giuseppe Nicolò[1], El-Nazhari Najoi[3], Regnier Tiffanie[3], Blieux Anne-Laure[3], Echairi Abdelwahad[3], Prigione Valeria[1], Puglisi Edoardo[2], Varese Giovanna Cristina[1]

1) Mycotheca Univeristatis Taurinensis, Department of Life Sciences and Systems Biology, University of Tuirn, Viale P.A. Mattioli 25 Torino Turin, Italy
2) Università Cattolica del Sacro Cuore, Piacenza, Italy
3) Satt Grand-EST, Dijon, France
**: federica.spina@unito.it*

Introduction and study objectives

Soil degradation is a serious problem all around Europe. It is usually driven or exacerbated by human activities such as inadequate agricultural or forest practices, industrial activities, waste disposal, oil spills, urban and industrial proliferation, and construction works. The main negative impacts of soil degradation are loss of fertility and biodiversity, reduced water holding capacities, impairments of biogeochemical cycles and a reduced resilience and buffer capacities. Soil pollution is one of the main causes of soil degradation and loss of terrestrial ecosystem services. In EU there are 42 potentially contaminated and 5.7 contaminated sites every 10,000 inhabitants, with approximately 340,000 sites that require remediation intervention. The most frequent contaminants are heavy metals, followed by mineral oils, polycyclic aromatic hydrocarbons (PAHs) and mixtures of benzene, toluene, ethylbenzene and xylene (BTEX).

Recently, there is growing interest in developing techniques to reduce levels of organopollutants from contaminated soils by means of selected microorganisms. Bioremediation is an alternative approach that has recently received much attention due to its potential as a cost effective solution and has been successfully applied in full-scale for the treatment of contaminated sites. Bacteria and fungi are the main protagonists of bioremediation. LIFE BIOREST (LIFE15 ENV/IT/000396, www.lifebiorest.com) aims to optimize a biomeredіation method where the transformation made by consortia of fungi and bacteria is finalized by the final step of re-vegetation. The first phase of the project is focused on the characterization of the microbial community that naturally populate this extreme environment and on the isolation of microbes capable of growing in the presence of pollutants as sole C source. The best performing strains will be used to set up consortia working in microcosms and mesocosms before up-scaling the process.

Methodology

The aim of the first phase of the action is the characterization of the microbial community of the contaminated site. The soil was collected at three different depths from -1 to -3 m. Different methodologies have been set up and carried out simultaneously in order to meet the objectives: i) total count for the quantification of the bacterial and fungal load of the contaminated area; ii) solid screening for the identification of the fungal and bacterial strains capable of growing in presence of target contaminants as sole carbon source; iii) enrichment in liquid cultures to favor the development of microbial communities adapted and capable of degrading specific target analytes.

The following contaminants were chosen because they represent the soil of interest has some predominant pollutants of the site: benzene as BTEX, naphthalene, phenanthrene and pyrene as PHAs, paraffin oil and heptadecane as alkanes.

Results and conclusions

Almost 300 fungal and 140 bacterial strains were isolated from the solid and liquid cultures. Fungi mostly belong to Ascomycetes even though few Basidiomycetes were found (i.e. *Phlebia tremellosa* and *Trametes gibbosa*). The main genera were *Cladosporium*, *Aspergillus*, *Penicillium*, *Fusarium*, *Scedosporium*, *Trichoderma* and *Epicoccum*. The bacterial isolates mostly belonged to the Gram negative genera *Pseudomonas*, *Sohingobacterium*, *Pseudoxanthomonas*, *Rhizobium* and *Acinetobacter*. A number of Gram positive *Bacillus* and *Paenibacillus* strains were also found. Phenanthrene and pyrene were the best substrates, easily used as sole carbon source, whereas few fungi were able to grow on the crude oil provided by Fidenza Municipality. Considering the very high content of hydrocarbons and the intrinsic toxicity of this oil that strongly limit the growth capability of microorganisms particular attention will be given to those isolates able instead to grow on it, indicating interesting adaptation features and great metabolic pattern.

Dereplication of fungal isolates was performed microsatellite area using M13 marker and, when necessary (GTG)5, while dereplication of bacteria was performed using both (GTG)5 and RPAD2 as single primers. Results indicate a great fungal and bacterial biodiversity with high intraspecific variability according to the soil depth (-1, -2, -3 m).

All the bacteria and fungi were then tested against all the pollutants of interest in an innovative miniaturized approach in 96 multiwell plates. Several strains were capable of growing on the pollutants (at 200 ppm and 1% v/v) as much as positive controls with glucose, highlighting their capability to exploit complex source of nourishment as far as simple and bioavailable ones.

The most performing fungi and bacteria are going to be used in microcosms singly and in consortia in order to evaluate their actual capability to transform the pollutants and survive in the extreme conditions of the contaminated soil.

SUSTAINABILITY ASSESSMENT OF URBAN WATER USE: FROM BUILDING TO URBAN SCALE

Emanuela Di Fusco, Giovanni Buroni, Giada Felisa,
Ilaria Lauriola, Tonino Liserra, Valentina Ciriello,
Vittorio Di Federico[*]

Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali (DICAM),
Università di Bologna, Viale Risorgimento 2, 40136 Bologna,
[*] *: vittorio.difederico@unibo.it*

Introduction and study objectives

Innovative solutions are needed to support a sustainable use of water resources in urban areas. Climate change and population growth may determine increasing scenarios of quantitative/qualitative impoverishment of water bodies and a contemporary difficulty associated with meeting urban water demand. In this context, technical solutions to increase water reuse and improve environmental awareness within the society are equally important.

Within a common framework of analysis, we assess the potentiality of both "green" solutions and ICT technologies to support the transition towards a smart use of water from the building to the urban scale. Analyses presented in this study are part of the GST4water project (Green-Smart Technology for Water) which aims at providing a set of hardware and software solutions to assess domestic water consumptions and suggest proper measures for grey water and rainwater reuse. In this context, the goal of our study is to provide to various stakeholders useful information to analyse domestic water consumptions at diverse scales and identify water reuse technologies to improve performances in terms of environmental sustainability.

Methodology

Real-time monitoring of domestic water consumption (including information associated with the different type of end user) and data transfer to cloud platforms are the basis to detect the behaviour of domestic users and to calibrate models to interpret this behaviour and return profitable information to stakeholders at different levels. Our approach aims at developing a suite of software tools working at multiple scales of analysis. Starting from the building scale and based on real time data and algorithms to mimic residential water demand, we reconstruct the behaviour of domestic users and return them back these information through a suite of indicators accounting for consumption performances and sustainability. Contemporary, suitable "green" solutions are suggested to increase water reuse, together with their potential environmental implications. At the district and urban scales, an evaluation of the impact of measures applied at local level is performed by analysing different scenarios within the context of an urban metabolic model. This accounts for water, energy and economic flows and returns indicators at the macroscale useful for policy makers and for the management of the integrated water system.

Results and conclusions

Our study provides analysis and modelling tools that are flexible enough to be applied in different contexts for the interpretation of the residential water demand and the analysis of urban water use under a general perspective provided by the metabolic approach. The employment of solutions for water reuse are compared, from a sustainability perspective, to current scenarios without reuse strategies, while accounting for economic and environmental implications. Results of our analysis may be used as a benchmark and support the employment of strategies to increase water saving and the environmental awareness within the society.

Acknowledgements

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USING ISO STANDARDS TO CREATING A RISK PROCEDURE, WHICH ESTABLISHES THE GOALS, LINKS AND COMPONENTS FUNCTIONING FOR INTEGRATED ENVIRONMENTAL MANAGEMENT SYSTEMS OF ROMANIAN INDUSTRIAL COMPANIES

Vasile N. Popa [1], Luminița I. Popa [2], Anca N. Iuga (Butnariu) [3]

(1) *Regional Department for Defense Resources Management Studies, Mihai Viteazul 130, Brașov, Romania*
(2) *Transilvania University of Brașov, Department of Automation and Information Technologies, Mihai Viteazul 5, Brașov, Romania*
(3) *Transilvania University of Brașov, Department of Engineering and Industrial Management, Mihai Viteazul 5, Brașov, Romania*
*: *vasilepopa2001@yahoo.com, mluminita2001@yahoo.com, ancadezv@yahoo.com*

Introduction and study objectives

For Romanian industrial companies, it is useful to use ISO standards to creating a risk procedure, which establishes the goals, links and components functioning for integrated environmental management systems. This procedure does not exist now in our country. The Integrated Environmental Management System is a set of interconnected processes that use the same resources - human, material, financial, informational - to meet a set of objectives related to the satisfaction of stakeholders. For the procedure realization, we must organize an Integrated Management Committee composed of the heads of departments in the organization. The head of this committee is Quality Risk Department Manager. For each department we shall appoint an employee who is responsible for establishing the links and functioning of the integrated management system components of industrial company. Taking in consideration the standards, the risks and the quality of the products and processes as subjects of the procedure achieved, a theoretical and applicative research was carried out within a comparative study between Romanian /European Union industrial companies regarding the circular economy principles applied in environmental management.

Methodology

Our first goal **i**s achieving integrated environmental management model structure following a collaborative study with specialists. The integration of all management systems mentioned in the procedure with current systems of organization, in an operational management system has a great significance for industrial company managers. The effectiveness of this management system is measured by the achievement of objectives. The goal of achievied management system is to define integrated management methodology to establish the following elements: policy and the own objectives of the system; risks affecting the objectives to be achieved; processes and appropriate resources to fulfill the requirements of stakeholders. The second goal was to analyze and conclude the results of comparative study between

Romanian /European Union industrial companies, regarding the circular economy principles applied in environmental management. Our working hypotheses of the comparative study were as follows:
Hypothesis 1: Taking in consideration the standards, the risks and the quality of the products and processes used within a circular economy , the knowledge level of the Romanian enterprises is lower than the level of EU enterprises.
Hypothesis 2: Taking in consideration the standards, the risks and the quality of the products and processes used within a circular economy, Romanian companies have not to much interest in applying these, unlike the EU enterprises.
Regarding with our research methods, the questionnaire-based investigation method was chosen. Subjects were provided with questionnaires in order to direct research to the objectives pursued. The methodological tool used to gather information was the opinion questionnaire. It has the advantage of providing complex information and the objective possibility of correlating the indicators, thus making it possible to obtain credible and easy-to-interpret results.The following data shall were used:
1. The data provided by the European Commission *„Published Results circular-economy"*:
after the public consultations starting with 04.06.2015;
2. The data provided by the questionnaire drawn up by the authors of the research and applied to a number of 25 industrial companies in Romania.

Results and conclusions

Using the standards listed above, the management of industrial company uses a unique methodology to increase the industrial processes effectiveness by balancing and interacting the three quality management system (ISO 31000 "Risk Management", ISO 9004 "The leadership of an organization to lasting success. An approach based on quality management "and ISO 26000 "Social Responsibility "). These three systems of management cooperate within industrial company, realizing an environmental integrated system. The quality and reliability standards need not only for goods but also for the management system itself.

The integrated environmental management model establishes the unique and balanced effectiveness of component management systems as a integrated whole, using standards for sustainable success, social responsibility and economic results of the industrial company.
This model was created as an open system in which industrial company specific performances and objectives could be included optionally.
The verification of the two hypotheses of the study
Hypothesis 1- it was not verified during the comparative study Romania / EU;
Hypothesis 2- it was verified during the comparative study Romania / EU.
Enterprises in Romania have positive concerns about the "development of standards for voluntary use" as a measure to promote the principles of circular economy in eco-product design.

Enterprises in Romania are aware of the importance of "ensuring access to finance for high-risk projects. EU Enterprises are not sufficiently concerned about the "development of standards for voluntary use" as a measure to promote the principles of circular economy in eco-product design.

SUSTAINABILITY AND QUALITY ASSESSMENTS REGARDING AN INNOVATIVE SEED DRYING METHOD WITH LESS NEGATIVE EFFECT ON THE ENVIRONMENT DUE TO LOWER ENERGY CONSUMPTION

Vlad Nicolae Arsenoaia*, Petru Marian Cârlescu, Radu Roșca, Ioan Țenu

[1] University of Agricultural Sciences and Veterinary Medicine, Iasi, Romania
Mihail Sadoveanu Alley 3, Iași, Iași County, Romania,
**:vlad_arsenoaia@yahoo.com*

Introduction and study objectives

Sustainable development is a long term strategy which involves among others, lower energy consumptions and the discovery of renewable energies. Currently, for drying of agricultural seeds, convective dryers are used worldwide, vertical and horizontal with continuous and discontinuous function, all with high energy demands, because they do not solve the problem of the distribution and the uniformity of both temperature and velocity in the drying seed layer.

Agricultural plant seeds are subjected to the drying process to extend the conservation and to maintain the quality and the nutritive value during the storage. The seeds of agricultural plants, which are subjected to the technological drying operation, behave differently depending on the physicochemical characteristics, and some of them do not support aggressive drying conditions, characterized by high temperatures and velocities of the air when passing through the product layer.

A cylinder drying unit was designed and built, provided at the interior with deflectors, to equalize the velocity and temperature gradients throughout the surface of the product. This unit not only reduces the energy demand but also increases the seed quality according to the obtained results.

Methodology

The experiments were conducted in the Department of Agricultural Mechanization of the University of Agricultural Sciences and Veterinary Medicine "Ion Ionescu de la Brad", Iaşi, Romania, using a laboratory drying unit for agricultural products. It allows control and monitoring of the drying process parameters that can be chosen by the user before or during the drying process. The dryer was equipped successive with a conventional rectangular box and the innovative cylindrical baffled box, both with 150 mm layer thickness.

Mathematical modelling was used in design, in the operational and optimization work for both drying boxes. The mathematical model of the convective drying process is based on the theory of fluid dynamics, mass balance and energy.

The experiments were conducted under the same conditions for the conventional variant with a rectangular drying box and the proposed cylindrical box by varying and monitoring the operating parameters of velocity and temperature of the warm air (1-2.5 m/s, respectively 40-80°C) and using corn seeds with three initial moisture contents 25, 22 and 19%.

Results and conclusions

The influence of heat can be favorable only if applied wisely regarding the correlation of the following three factors: the temperature of the drying agent, its speed and temperature of the grain seed. During the drying process, humidity vary continuously downwards after complex laws. In order to maintain a high proportion of the qualities as the initial seed, it is required a close correlation between the temperature and humidity of the drying agent. The air flow was numerical simulated in both the rectangular and the cylindrical drying boxes. Because the velocity profile doesn't cover corners, in the middle section of the air flow, for the rectangular box, turbulences occur both for low and high air velocities.

The air field lines obtained in the cylindrical case have a laminar flow at the entrance of the box and along the cylindrical sieve can be seen a uniform distribution of hot air throughout the surface layers of seeds subjected to drying.

Analyzing the results of the physical parameters obtained throughout the experiments, one can conclude that the best results concerning the drying time, the energy consumption and the protein content of corn seeds have been recorded for the variants in which the drying process was done by using the cylindrical box. The variant in which the recorded energy consumption was the maximum value was obtained at the drying of the corn seeds having an initial humidity of 25% in the rectangular box, at the air velocity of 1 m/s and at a temperature of 40ºC, and the minimum energy consumption was obtained at the drying of the corn seeds having an initial humidity of 19% in the cylindrical box, at the air velocity of 2 m/s and at a temperature of 80ºC.

After the drying process mathematical modeling, Computational Fluid Dynamics (CFD) simulations have been made in two variants for the cylindrical box with 150 mm corn seed layer.

By means of the Computational Fluid Dynamics simulation was optimized the construction of the cylindrical box and of the deflectors so that one could obtain a uniform distribution of the air currents and of the temperature fields in the seed layer. This leads to reaching a uniform drying and to reducing the energy consumptions.

Based on the drying experiments, it was obtained for the cylindrical unit compared to the conventional one, a reduction of protein loss of up to 1.81% and a decrease of the energy consumption of up to 15%.

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LIFE CYCLE ANALYSIS OF PROCESSES AND PRODUCTS MANUFACTURED FROM PRODUCTION WASTE BASED ON ECO-INNOVATION AND ECO-DESIGN PRINCIPLES

Isabela Maria Simion[1,2,*], Elena-Diana Comăniță[1], Petronela Cozma[1], Cristina Ghinea[1,3], Teofil Câmpean[1,4], Raluca Maria Hlihor[1,2], Mihaela Roșca[1], Simona Cecilia Ghiga[1,5], Camelia Smaranda[1], Maria Gavrilescu[1,6]

1) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
2) "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania
3) Stefan cel Mare University of Suceava, Faculty of Food Engineering, 13 Universitatii Street, 720229 Suceava, Romania
4) Rondocarton SRL, Cluj-Napoca, 2 Aviatorilor Street, 407042 Apahida, Cluj-Napoca, Romania
5) Romanian Association for Recycling, RoRec, 24 Sevastopol Street, 010 992, Bucharest, Romania
6) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
**: teslaru.isabel@tuiasi.ro*

The current production and consumption models continue to generate significant impacts on the environment, which must be reduced to secure the future. The main challenge addressing the pathway and development towards sustainable industrial production is thus to reduce environmental impacts, maintaining in the same time a viable economic life cycle and social well-being.

In the production of goods, for example, we need to take a look at the reduction of waste production impact. To answer the need of a Romanian manufacturer (RM) to close the loop by the revaluation of production waste, we found eco-innovation and eco-design principles among the most relevant answers to this challenge. RM has modern facilities and technologies to produce corrugated board and packaging. Corrugated packaging is environmentally friendly because it is manufactured from waste paper using starch as an adhesive, a natural biodegradable product. The entire manufacturing process is computer-aided, starting with the box design, ordering, manufacturing and packaging boxes.

Aside from cardboard boxes, RM manufactures various other related products for the construction and transportation industries, designed and produced using corrugated board sheets as raw material. The manufacturing process generates waste in the form of cardboard strips, edges andtubes from paper rolls.

We found that RM has a great potential to close the production cycle through the efficient reuse of recyclable materials resulted as waste in the two stages of the technological process (corrugated board and cardboard boxes manufacturing) to produce various subassemblies, in the context of existing modern technology. This way, RM can ensure a longer life cycle of production and products and can integrate advanced environmental strategies in its activities and decisions regarding production optimization and process development, leading towards the zero emissions target, in line with the principles of circular economy. This approach is facilitated by the fact that RM is open to progress, assigns great importance to the application of specific practices for reaching sustainable industrial production based on resource conservation, mitigating impacts in the environment.

In order to facilitate RM decision making process, we applied Life Cycle Analysis (LCA) to assess the environmental impacts generated by the current production pathway for subassemblies manufactured using corrugated board sheets, compared to environmental impacts potentially induced by the use of waste production as raw materials for these subassemblies, which are redesigned based on eco-innovation and eco-design concepts (*innovation of design*). Both incorporate new concepts, such as: new vision of a product-industrial system linkage, the concept of extended life cycle and integration of involved players (university, manufacturer, stakeholders). Also, we evaluated the environmental impacts potentially generated by recycling waste production for paper used in the manufacturing of corrugated board so as to demonstrate the environmental benefits of eco-innovation and eco-design. We performed a complete LCA analysis consistent with the ISO 14000 group of standards entailing four interrelated phases: (i) goal definition and scope; (ii) inventory analysis; (iii) impact assessment with four sub-phases: classification, characterization, normalization, weighting; (iv) improvement assessment. The system boundaries and the functional unit were selected. The evaluation was assisted by a dedicated software. We considered in our evaluation relevant impact categories (IC) such as: climate change ecosystems (CCE); climate change human health (CCHh); particulate matter formation (PMF) for the ReCiPe method and acidification potential (AP); global warming potential (GWP), photochemical ozone formation (POF).

The appraised eco-innovations interconnected with eco-design resulted in noteworthy progresses of the environmental performance of the analyzed process and components. Our results also highlighted the role of knowledge transfer from university to industry in promoting process eco-innovations and ecodesign and the increasing relevance of LCA as a tool to support decision making in manufacturing.

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RISK ASSESSMENT AND LIFE CYCLE ASSESSMENT APPLICATION FOR A SUSTAINABLE REMEDIATION OF CONTAMINATED SITES

Sara Zanni[*], **Alessandra Bonoli**

DICAM - Department of Civil, Chemical, Environmental and Materials Engineering, Terracini Street 28, 40131 Bologna, Italy,
[*]: sara.zanni7@unibo.it

Introduction and study objectives

When approaching the remediation of a contaminated industrial site, several aspects ought to be taken into consideration. Since the primary aims of a remediation are the safety of human health and the protection of the environment, sustainability, defined by the Brundtland Commission (*Our Common Future*) as development meeting the needs of the present without compromising the ability of future generations to meet their own needs, should be the driving concept for the remediation planning. For this reason, sustainability assessment tools and indicators must be applied, starting from the planning phase, in order to compare the different technologies and techniques available and choose among them the most suitable one for the specific application.

Two different tools have been applied to the case study of a former quarry site, where soil and groundwater contamination has been historically detected:

1. Risk Assessment, aimed to simulate exposure of possible human targets to pollutants and threads posed to their health in the short, medium and long term;
2. Life Cycle Assessment (LCA), applied to quantify environmental impacts and benefits deriving from different remediation options.

In this sense, Life Cycle Assessment represents a powerful decision supporting tool. Developed in compliance with UNI EN ISO 14040(44):2006, it is generally applied for the assessment of eco-efficiency and environmental impact of product and processes, allowing the quantification of environmental impacts generated throughout the whole life cycle already during the design phase. In the eco-design perspective, the implementation of LCA tool enables to tackle the 80% of the overall environmental impact of a product/process.

Methodology

A dismissed quarry site has been identified as case study for sustainability assessment tools application.

Following an extensive characterization phase on the case study site, i.e. repetitive monitoring of both soil and groundwater performed over 15 years on the area, Risk Assessment procedure has been implemented, as required by regulations (for Italy: D.Lgs. 152/06), in presence of chemicals exceeding the limit values. The conceptual model of the site has been elaborated and exposure pathways defined with the application of Risk-net software.

LCA has been only recently used to evaluate innovative remediation solutions proposed, due to difficulties, on one hand, in adaptation of software tools developed to evaluate product, rather than process, and, on the other hand, in quantification of environmental benefit granted by the clean-up intervention. Timing to meet the remediation goals and lifespan of the technique applied are other critical elements, strongly affecting the tuning of the model. Local framework should be considered, both for the sensitivity of the specific environment and depletion of resources, related to land transformation and energy consumption.

Results and conclusions

Results of the characterization phase showed the historical presence and evolution of heavy metals and chlorinated compounds in the site.

Chlorinated compounds (among which the most abundant proved to be Tetrachloroethylene, PCE), as dense nonaqueous phase liquids (DNAPLs), are xenobiotic compound, widely present in groundwater due to industrial solvents spill. Most of them may have carcinogenic effect on humans and are treated accordingly, into Risk Assessment procedure, resulting in specific prescription for site use. Where a microbial reductive dechlorination of TCE is naturally active, it proceeds via formation of cis-dichloroethene (cis-DCE), vinyl chloride (VC), and ultimately ethene and ethane. Only a combination of anoxic and aerobic conditions, together with proper bacteria consortium available locally would trigger a natural degradation. The lack of degradation products (i.e. low concentrations of cis-DCE and VC) proves that chlorinated compounds are moving with the groundwater flow, rather than being degraded.

Groundwater remediation technologies which could be implemented, may be differentiated into two main classes, depending on their "active", i.e. with energy application, or "passive" nature. For the first class, the most impacting inventory item category is normally identified in energy consumption, while for the second one, waste generated, for example, with the excavation of permeable reactive barriers (i.e. soil potentially contaminated and exhaust filling material to be properly disposed), can significantly increase the environmental impact of the clean-up intervention.

Heavy metals contamination is a typical drawback of mining activities, as well as agriculture, waste disposal, industrial emission and deposition. When released into soil matrix, heavy metals are likely becoming persistent into the environment and, therefore, accumulate into food chain. Serious health problems are associated to heavy metals uptake, generally accumulated in fatty tissue, with potential effects on nervous or circulatory system and consequences on internal organs functions. Phytoremediation is usually regarded as the best demonstrated available technologies (BDATs) for heavy metals remediation, due to excellent results obtained on the uptake of those substances from both soil and wastewater, but it appeared to be inappropriate for the specific application, due to contaminants distribution and planned use for the site.

THE USE OF AGRICULTURAL BY-PRODUCTS IN THE DEVELOPMENT OF AN AGRO-ENERGY CHAIN

Pezzolla Daniela[1], Venanzi Sonia[2], Sordi Alessio[1],
Cecchini Lucio[2], Ricci Anna[1], Torquati Bianca Maria[2],
Gigliotti Giovanni[1,*]

[1)] *Department of Civil and Environmental Engineering, University of Perugia, Via G. Duranti 93, 06125, Perugia, Italy*
[2)] *Department of Agricultural, Food and Environmental Sciences, University of Perugia, Italy*
[*] *: giovanni.gigliotti@unipg.it*

Introduction and study objectives

The anaerobic digestion (AD) is a process that is widely used in a large number of countries to produce renewable energy (biogas), but also for the waste stabilization and pathogen reduction. The residual organic matrix of the AD process (digestate) results in a more stabilized organic matter, which has become available for application to land as nutrient fertilizers or organic amendment.

Quality and quantity of biogas production is strictly affected by feedstock characteristics used for the AD as well as by the digester operating conditions. The silage maize is the energy crop mostly used in the AD plants for its high bio-methane production. However, the use of silage maize should be limited for its high costs and for its edibility.

The objectives of the present work are: i. to evaluate the anaerobic process using some agricultural and livestock by-products, in total or partial substitution of the silage maize, ii. to analyze the environmental and economical sustainability using these new mixtures, in order to define a possible agro-energy "virtuous" chain.

Methodology

In the agro-energy chain, the evaluation process of the use of by-products was divided from the methodological point of view into three interdependent and consequential stages. Firstly, alaboratory experiment was carried out to test the anaerobic bio-methane potential (ABP) of two homogenous mixtures prepared with by-products in total or partial substitution of silage maize: silage maize (24%), slurry (42%), manure (11%), poultry manure (8%), olive husk (15%) (MIX. A); slurry (32%), manure (21%), poultry manure (18%), olive husk (11%), grape pomace (9%), serum (9%) (MIX. B).Moreover, a mixture with 33% of silage maize was used as reference mixture (REFMIX.). All the initial mixtures and the digestates were analyzed for their main chemical characteristics. Secondly, to evaluate the environmental sustainability of the biogas production, in term of CO_2-eq per one kWh equivalent produced by the mixtures, a Life Cycle Assessment (LCA) analysis was developed. The system boundary included feedstock production and supply to both biogas energy production and utilization to digestate processing, composting and their use as fertilizer. Finally, the analysis of economic sustainability through the Life Cycle Costing (LCC) tool was carried outto evaluate the different scenarios of the agro-energy chain according to the tested mixtures. The LCC was simultaneously developedwith LCA, considering all fixed and variables costs associated to the processes included in the system boundaries.

Results and conclusions

The ABP results showed that the addition of by-products in the starting mixture, in total or by partial substitution of silage maize, did not lead to a negative effect on bio-methane productions. Indeed, boththe tested mixtures showed a higher ABP compared to the reference mixture; in particular, the MIX. B depleted its bio-methane production within 20 days. The correct behavior of the AD in the two tested mixtures, was supported by the chemical analysis carried out on the final digestates, as the decrease of volatile solids content and the decrease of C/N ratio.

The LCA results highlighted that the production of biogas and electricity registered a slight decrease comparing the three tested mixtures. On the contrary, the impacts of $kgCO_{2eq}$ showed a drastic reduction both for MIX. A and MIX. B, compared to the REFMIX. Mixture B seems to be more efficient both maintaining a satisfactory level of biogas production and determining a robust reduction of CO_2 emissions. The production of silage maize was the responsible for the most of the CO_2 emissions in the atmosphere, both in the REFMIX. and in the MIX.A. Regarding the MIX. B, the major impacts depended on the by-products supply and the cogeneration unit.

Concerning the production costs (euro/kWh), while transitioning from the reference diet to the MIX.A, no significant economic benefits were measured. In fact, despite a decrease in the costs due to the introduction of by-products, such effect is deleted by an equal reduction in the electrical energy production.The adoption of MIX. B, i.e. without silage maize, seemed significantly advantageous, resulting in a cost decreased per kWh and compared to REFMIX.

In conclusion, although MIX.A showed advantages regarding environmental impact compared to REFMIX. and MIX. B, from an economic point of view they were not significant. Whereas, the alternative use of by-products, as tested in the MIX. B, might allow achieving both environmental and economic sustainability targets.

EVALUATING THE EFFECTS OF CARBON COMPENSATION IN WATER FOOTPRINT

Laura Roibás[1,*], Antonio Cuevas[2], María Eugenia Vázquez[2], Marta Vilas[2], Almudena Hospido[1,*]

[1)] Group of Environmental Engineering and Bioprocesses, Department of Chemical Engineering, Institute of Technology, Universidade de Santiago de Compostela, Spain
[2)] Luis Calvo Sanz S.A., Carretera Coruña – Finisterre km. 34,5. 15106 Carballo, A Coruña, Spain
[*] :laura.roibas.cela@usc.es (Laura Roibás)

Introduction and study objectives

Global warming, a phenomena caused by greenhouse gas (GHG) emissions, is one of the most pressing environmental issues that humankind faces today. Numerous studies are thus aimed at the measurement, reduction and compensation of the GHG emissions of products and processes, often overlooking other environmental impacts. The carbon footprint (CF), an indicator which measures the amount of GHG emitted by a certain product throughout its life cycle expressed in CO_2equivalents, is frequently used for measuring this impact, and to help identifying possible reduction measures. Compensation actions can also be applied to neutralize GHG emissions, usually throughout (re)forestation projects, since trees absorb considerable amounts of CO_2.

This study starts from the determination of the CF of the flagship product of a Spanish company: a pack of 3 cans of tuna. This company is located in the Galician region, but some of its manufacturing processes take place in La Unión (El Salvador). Basically, tuna loins are pre-processed at La Unión and then taken to Galicia, where the final product is packed. This paper evaluates how compensating the GHG emissions of the company through forestation would affect a different environmental issue, water depletion, through the determination of the volumetric water footprint (WF). The WF of a product measures the use of freshwater associated with its production, and includes three components: blue water (taken from aquifers), green water (soil moisture taken by crops) and grey water (the amount of water needed to dilute pollutants discharged to water). The latter will be excluded of the assessment, as done by several authors, since it does not reflect actual water consumption and its definition is not consistent with the Life Cycle Assessment framework. The WF is used here to find the most suitable location for the compensation project, Galicia or El Salvador.

Methodology

The CF of a pack of tuna cans had been determined on a previous study: 1.32 $kgCO_2e$/pack. Given the yearly production of the company, its annual CF reaches 136 $MtCO_2e$/y. It should be noted that, unlike the usual compensation projects, this study would compensate the entire life cycle emissions of the final product, and not only the direct emissions from the company facilities.

The data contained in the Spanish regulation on CO_2 compensation (absorption rates of the different species, required forest lifetime) has been used to determine the required size of the forest. The species chosen for both locations is *eucalyptus globulus*, for several reasons: it has been widely used for reforestation in both countries, all required data are easily available, and it is the species with the highest CO_2 absorption. This choice, however, does not take into account other controversies linked to the use of eucalyptus for forestation (soil degradation, spread of forest fires).

The planting density chosen is 1,200 plants/ha, and the forest lifetime is set to 30 years. Under these conditions, 56 ha of forest are required to compensate the annual emissions of the company. The foreseen plantation is assumed to be rain fed, and its green WF (WF_{green}) is determined as follows:

$WF_{green}(m^3/ha/y)=ET_{green}(mm)\cdot 10$; where $ET_{green}(mm)= \min (ET_c, P_{eff})$

$ET_c=P(1+w\cdot E_0/P)/ (1+w\cdot E_0/P+ P/E_0)$; where $E_0=0.488T^2+27.5T+412$

P is the annual precipitation and Peff is the effective precipitation, both expressed in mm, T is the average temperature (°C) and w is an dimensionless constant (2 for forests). All values are calculated for both possible locations using climatic data from NewLocclim and the Cropwat software. The best location will be chosen based on the lower green water, in absolute terms but also considering the water stress both areas, using the Green Water Stress Index (GWSI).

$GWSI= WF_{green}/P_{eff}$; $0 \le GWSI \le 1$

Lower values of the GWSI indicate lower stress upon soil water.

Results and conclusions

In Galicia, the results of the yearly WFgreen would be 7,553 m3/ha/y, while in El Salvador this figure would raise up to 9,757 m3/ha/y. Moreover, the Galician GWSI is 0.8, while the Salvadorian one is 1, thus indicating that the establishment of the Salvadorian forest would cause significant water stress. The comparison clearly indicates that locating the forest in Galicia is the best option available.

The volumetric WF of producing one pack of tuna cans has also been calculated, and thus the next table compares the current situation and a prospective one where the CF of the pack has been compensated. While reducing its CF to 0, the WF of the product increases by 21%.

	Current scenario	Compensated scenario
CF (kg CO_2e/pack)	1.32	0
WF_{blue} (lH_2O/pack)	86	86
WF_{green} (lH_2O/pack)	657	815
WFt_{otal} (lH_2O/pack)	743	901

This study uses the WF to decide the optimal location for a CO2 sink, and evaluates the implications of the compensation of a certain amount of GHG emissions. The study could be improved by using more refined equations for the WFgreen calculation, although the authors believe that it would not affect the current recommendation. This study could be replicated to assess similar compensation projects for those companies having different location options.

LIFE CYCLE COST ANALYSIS OF ALTERNATIVES FOR CLOSING THE LOOP IN A MANUFACTURING SECTOR BASED ON ECO-INNOVATION AND ECODESIGN

Elena-Diana Comăniță[1, *], Isabela Maria Simion[1,2], Petronela Cozma[1], Camelia Smaranda[1], Raluca Maria Hlihor[1,2], Cristina Ghinea[1,3], Simona Cecilia Ghiga[1,4], Mihaela Roșca[1], Maria Gavrilescu[1,5]

1) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof.Dr.Docent D. Mangeron Street, 700050 Iasi, Romania
2) "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania
3) Stefan cel Mare University of Suceava, Faculty of Food Engineering, 13 Universitatii Street, 720229 Suceava, Romania
4) Romanian Association for Recycling, RoRec, 24 Sevastopol Street, 010 992, Bucharest, Romania
5) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
**: ed.comanita@tuiasi.ro*

An evidence-based and effective manufacturing strategy involves making investment decisions based on unbiased and supportable approaches. Life Cycle Cost Analysis (LCCA) has been developed to support managers in deciding on the most cost-effective manufacturing option among different competing alternatives. Similarly, Cost-Benefit Analysis (CBA) is applied as a proficient process for calculating and comparing the benefits and costs of a decision, to provide a basis for comparing manufacturing alternatives by attesting to what extent the benefits balance the costs.

Life cycle cost analysis (LCCA) was applied as a tool for the evaluation of the total cost performance of some alternatives possible to be implemented in corrugated board and packaging manufacturing, entailing the valorization of production waste so as to close the loop and extend the life cycle of cardboard. The analysis addresses a series of scenarios built to compare the advantages of extending the life cycle of waste production in the form of eco-innovated and eco-designed subassemblies made from corrugated cardboard versus waste recycling for paper manufacturing as recovered cardboard. Our study provides an economic appraisal of alternative sustainability options exhibiting different capital, operating costs or resource usage. It also offers information on the costs and benefits of incorporating sustainable options in the production process of a Romanian manufacturer and indicates the directions to follow so as to ensure viable management insight on the costs and resources, both near- and long-term, required to accomplish the objective of our project addressing the application of circular economy principles in resource usage. They provide a more comprehensive estimate of the true costs of a project or program than an estimate that only captures the project execution phases.

The following life cycle phases were analyzed in terms of LCCA (Fig. 1):

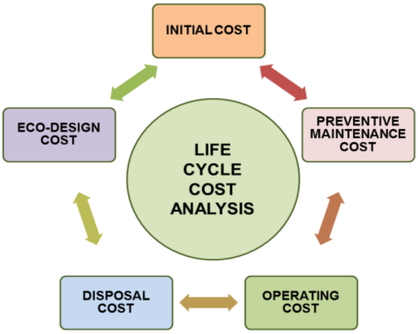

Figure 1: LCCA phases and cost appointment

(i) the need of the manufacturer to close the loop considering an extended life-cycle of corrugated board (in the form of production waste);
(ii) alternative basic scenarios: (a) manufacturing of some subassemblies in an eco-efficient manner, from production waste based on eco-innovation and eco-design concept vs. (b) recycling production waste to the paper mill as recovered paper;
(iii-a) selection of eco-innovation and eco-design alternative;
(iv-a) quantitative and dimensional analysis of production waste;
(v-a) development of eco-innovation and eco-design activities, based on existing equipment;
(vi-a) execution and packaging;
(vii-a) marketing;
(viii-a) surveillance and long-term maintenance;
(ix-a) recycling at subassemby end of life to the paper mill;
(iii-b) waste collection;
(iv-b) waste transport.

We selected the boundaries for the two series of alternatives. Some financial indicators were also estimated for the valuation of eco-innovation and eco-design such as: costs and benefits related to the implementation of eco-innovation and eco-design actions, net present value, payback time, internal rate of return and return on investment, used for the cost-benefit analysis.

Since there are only a limited number of studies on the economic return of an eco-innovation and eco-design integrated approach, our work will encourage the actions of the industry to implement a successful eco-innovation/eco-design approach that would enable them to make relevant incomes and eco-efficient decisions.

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CARBON FOOTPRINT EVALUATION OF NOVEL TECHNOLOGIES OF DETECTION OF WATERBORNE PATHOGENS – THE WIDER IMPACT OF THE AQUAVALENS PROJECT

Carmen M Torres-Costa[1,*], Francesc Castells[1],
Maria José Figueras[2]

[1)] Departament d'Enginyeria Química, Universitat Rovira i Virgili; Països Catalans 26, 43007, Tarragona, Spain
[2)] Departament de Ciencies Mèdiques Bàsiques, Universitat Rovira i Virgili
[*]: carmenmaria.torres@urv.cat

Introduction and study objectives

Life Cycle Assessment (LCA) can be applied to a wide range of case studies considering that it can be seen as a philosophy for undertaking the countable procedure of all pollutant and resources consumption exchanges between the system analyzed and the environment. This system can take the form of a variety of activities, services and products, from an entire industrial sector of a country to any particular action that a person can perform. The LCA practitioner must face the challenges posed by the peculiarities of each system, adapting the assessment to the demands on data availability, uncertainty of the input data, resolution of the model, necessary assumptions, sensitivity to unsettled parameters, etc.

In the presented study, we analyze the consequences of adopting decisions on the mentioned features in the design of the LCA models used. The systems to be evaluated are the novel platforms developed under the project AQUAVALENS for the detection of pathogens in drinking water. The aim of the project is to enable the water system managers, food growers and manufacturers to better control the safety of their water supplies by using newfangled technologies that integrate sample preparation and detection into a single platform. The Carbon Footprint calculation of these platforms will be used to determine their sustainability as part of final objectives of the project, which include the protection of human health, improving the effectiveness of Water Safety Plans, adaptation to climate change and control of outbreaks of infectious diseases.

Methodology

The Climate Change impact of these platforms is determined by means of the Carbon Footprint (CFP). Each of the novel platforms developed under the project, as well as the conventional protocols of field applications for their comparison, where modeled based on the information retrieved from the partners. As Functional Unit (FU) we have considered the processing (preparation and detection of specific microorganism i.e. virus, E. coli etc.) of one water sample. The selection of this FU allow us to compute both the platforms (i.e., analytical kit/tool) manufacturing and use, as well as the comparison between kits developed under the project and conventional techniques worldwide recognized.

The sources of primary data are the project partners that are at same time part of the LCA non-expert audience to whom the results are addressed. Therefore data collection and feedback strategies must be tailored to overcome the communication barriers and ensure the understanding of the findings. Three types of detection platforms designed and manufactured by the producer partners are tested experimentally in nine European locations by different partners. Two campaigns of data collection were conducted, first addressed to the platforms developer and/or manufacturer partners, and secondly, addressed to end users, i.e. partners in charge of field application of these new platforms. Specific questionnaires were designed to obtain flows of materials, energy and wastes, with special attention to packaging in platform production and transport and waste managing in platform use.

Results and conclusions

Regarding platform production, the impacts decrease with the number of allowed detection analyses per platform, and those platforms with higher level of dosage present higher impacts due to packaging. However, in the whole life cycle of the product, the use phase is by far the major contributor. Figure 1a) shows the contribution to the total CFP of the different stages considered in for the analysis of one sample of water, while the distribution by the nature of the inputs is shown in Figure 1b). As it can be seen in the figures, the filtration that includes the sampling stages, is the major contributor to the CFP. On the other hand, in Figure 1b) the negligible contribution of the detection kit manufacturing compared to the rest of inputs is displayed.

This fact demonstrates how LCA is an excellent tool to reduce the impact of the overall process, promoting in the preliminary design phase an impact reduction in the future use phase. Therefore, the interpretation phase is mostly focused on the platforms' use, or in other words, the behavior of the user during the lab work. The communication of the results aims to illustrate the consequences in the CFP results of the different decisions, analytical choices and laboratory management during the collection and analysis of the samples by different users represented by the testing partners. Besides, the conclusions are based on uncertainty analysis using Monte Carlo simulations, thus the variability of input data and the parametric uncertainty of the model are quantified and the results are expressed as expected values in confidence intervals.

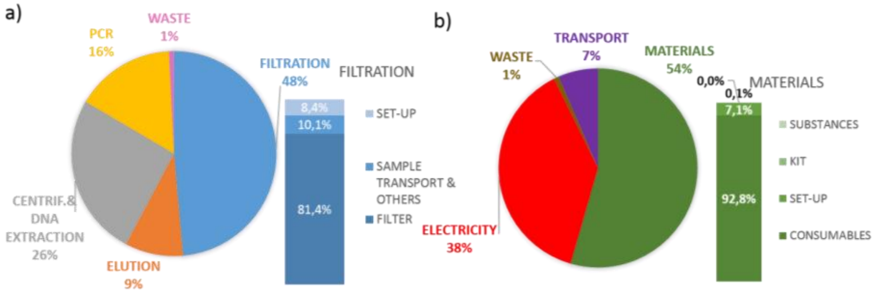


Figure 1:. Impact contribution to the total CFP of one water sample analysis: a) by stage of procedure, and b) by different types of inputs.

SUSTAINABLE DEVELOPMENT APPRAISAL FOR INDUSTRIAL SYSTEMS TOWARD CIRCULAR ECONOMY: CASE STUDY OF CORRUGATED BOARD AND PACKAGING MANUFACTURING

Camelia Smaranda[1,*], Teofil Câmpean[1,2], Cristina Ghinea[1,3], Petronela Cozma[1], Teodor Măluțan[4], Igor Crețescu[1], Adrian Cătălin Puițel[4], Elena-Diana Comăniță[1], Isabela Maria Simion[1], Raluca-Maria Hlihor[1,5], Dan-Alexandru Gavrilescu[4]

[1] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof.Dr.Docent D. Mangeron Street,700050 Iasi, Romania;
[2] Rondocarton SRL, Cluj-Napoca, 2 Aviatorilor Street, 407042 Apahida, Cluj-Napoca, Romania
[3] Stefan cel Mare University of Suceava, Faculty of Food Engineering, Suceava, Romania
[4] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Natural and Synthetic Polymers, Iasi, Romania
[5] "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, Iasi, Romania
*: *betianuc@tuiasi.ro*

Sustainable industrial production entails the accomplishment of multiple features which ensure that the production process as a whole and its components and phases work within economic, environmental and social boundaries according to the sustainable development concept. Usually, the progress in sustainable industrial production is associated with the circular economy, which stimulates superior resource usage by minimizing waste generation rates and avoiding environmental threats. There are various indicators which help in assessing sustainability in production systems, also enabling the comparison of industrial systems, subsystems or production alternatives.

According to the European Federation of Corrugated Board Manufacturers, the corrugated industry is perfectly positioned in the context of circular economy, assuming that it works towards minimising losses and reducing environmental impact. A Global Protocol on Packaging Sustainability established the framework to discuss and assess the sustainability of packaging as well as a measurement system for sustainability. Research and development based on eco-innovation, eco-design and increased eco-efficiency can offer solutions for increasing sustainability in these systems through knowledge transfer and other means. In this context, we performed an analysis in the frame of national projects addressing knowledge transfer from University to Industry. Our analysis entailed the sustainable development challenges in the corrugated board and packaging manufacturing so as to close the loop and extend the product life cycle according to the circular economy concept. Also, our approach on sustainability measurement has considered that the evaluations should include economic, environmental, and societal aspects. According to recommendations provided by specialists, we covered some steps in our analyses as shown in Fig. 1.

First we addressed the dual perspective of resource consumption and added-value by considering waste valorization in eco-innovated and eco-designed products, in an approach able to extend the life cycle. Our preliminary analysis revealed several relevant results: (i) the existing technologies for corrugated board manufacturing generates production waste of about 0.2-0.3%, although the manufacturer owns a modern technology; (ii) about 1.5-2% waste is generated during board packaging manufacturing. Waste valorization in the form of subassemblies currently manufactured from corrugated board sheets would determine the extension of corrugated board life cycle, instead of simple recycling to the paper mill as recovered cardboard. This would be possible by exploiting the existing experience and equipment, without significant investment, in a simple technological sequence developed as a result of eco-innovation and eco-design. This approach would save about 5100t wood / year, equivalent to almost 3200 spruce trees. A mature tree can absorb approx. 22kg CO_2 / year, acting as a natural filter; so it can be expected to save trees that can absorb approx. 70.5t CO_2 / year, decreasing environmental impacts associated with climate change, along with other positive environmental impacts.

Life Cycle Assessment (LCA) was applied as a tool able to make known, in a quantitative way, the environmental impacts considered as environmental indicators, over the corrugated board life cycle, so as to find the best alternatives to reduce the environmental impacts and resource consumption. Aside from this impact indicator, the LCA methodology represented the support for the minimization of other impact categories taken as indicators for environmental sustainability (abiotic depletion potential, acidification potential, eutrophication potential, global warming potential, human toxicity potential, photochemical ozone creation potential, acidification potential, eutrophication potential, global warming potential, nutrient enrichment potential, photochemical oxidant potential, terrestrial eutrophication, carcinogenic substances, heavy metals, winter smog, ecosystem quality, ecotoxicity, human health climate change).

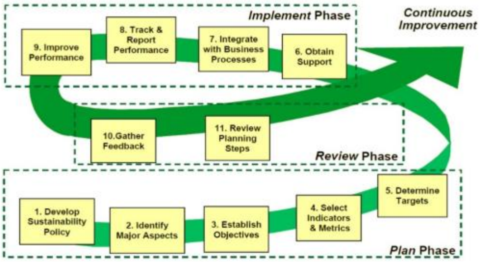


Figure 1: Steps in the assessment of sustainability performance

In another phase of the study we developed a Cost Benefit Analysis (CBI) since it is able to approach complex problems of comparison alternative scenarios, and provide a detailed and useful perspective to help the manufacturer in making choices over available production alternatives. The effects can be compared using a common monetary unit.

In this context we identified and assigned monetary values to all possible impacts of the selected alternatives proposed for evaluation. The results demonstrated that extending the life cycle based on eco-innovation and eco-design lead to sustainable production in economic terms, quantified by a benefit/cost ratio, which is considered as the main sustainability indicator.

Acknowledgement: This work was supported by two grants of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI: (i) project number PN-III-P2-2.1-BG-2016-0130, Contract 64BG/2016; (ii) project number PN-III-P2-2.1-BG-2016-0016, Contract 1BG/2016.

EVALUATING DIFFERENT RESPONSIBILITY SHARING APPROACHES FOR THE GALICIAN CARBON EMISSIONS

Laura Roibás[1,*], Eléonore Loiseau[2], Almudena Hospido[1]

[1)] Group of Environmental Engineering and Bioprocesses, Department of Chemical Engineering, Institute of Technology, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.
[2)] Irstea, UMR ITAP, ELSA Research Group for Environmental Lifecycle and Sustainability Assessment, 361 rue Jean-François Breton, BP5095, 34196 Montpellier cedex 5, France.
[*] :laura.roibas.cela@usc.es. (L. Roibás)

Introduction and study objectives

Global warming is one of the most pressing environmental issues that humankind must address nowadays, as demonstrated by the recent Paris Agreement, in which numerous countries committed to the temperature rise control. This phenomenon is mainly caused by the anthropogenic emissions of greenhouse gases (GHG), and thus the implemented measures should be aimed at their reduction.

However, prior to any reduction measures, it is required to compute robust national and regional GHG inventories. Due to globalization, GHG emissions are embodied in traded products, and their responsibility assignment is not straightforward. Usually, the producer principle is applied, where a certain country or region is responsible for the emissions that take directly place within its borders. The opposite approach is the consumer principle, where a certain region is only responsible for the emissions of the goods it consumes, regardless of their country of origin. Both approaches present disadvantages and thus a few authors have proposed intermediate principles. In this study, the GHG emissions of Galicia (a region located in northwest Spain) are determined and evaluated under the improved shared producer and consumer responsibility approach proposed by Lenzen et al (2006), which assigns emissions along supply chains between upstream and downstream activities.. In this study, only the emissions happening within the Galician borders have been quantified and assigned.

Methodology

This study starts from the direct emissions of the Galician economy, determined from the environmental input-output (EIO) model, and following the usual producer principle (1).

$$Cprod=B\cdot x+ Cd = B\cdot(Ax+y+e) + Cd \qquad (1)$$

Where Cprod represents the total GHG emissions of the Galician productive sectors, B is the matrix of environmental interventions (i.e. the amount of GHGs emitted to produce one unit monetary output of each industry), x is the vector of gross output for each productive sector, y is a vector of Galician final demand of domestic products, e is the vector of exports, and A is the intermediate demand matrix, defined such that each column of A shows the domestic intermediate industry input required to produce one unit of output. Last, Cd represents the direct emissions from households.

Lenzen's methodology has been used here to redistribute the emissions of the Galician economy among producers and consumers. It modifies equation (1) using sharing parameters based on the value added of the sectors, taken from the Galician IO matrix. This matrix (A) has been used combined with Spanish environmental data (B). All GHG emissions have been converted into CO2equivalents, through global warming potentials (GWP).

Results and conclusions

When evaluated with equation (1), the total GHG emissions of the Galician economy reach 22.10 MtCO$_2$e/y, divided into the total direct emissions of the Galician resident industries ($B \cdot x$=18.02 MtCO$_2$e/y, 82%) -whose major contributors are electricity production (4.80 MtCO$_2$e/y, 27%) and agriculture (3.22 MtCO$_2$e/y, 18%) - plus the direct emissions of the Galician households (C_d=4.08 MtCO$_2$e/y, 18%). These emissions have been redistributed here (Table 1), again split into sectors and into the six responsibility subgroups defined by Lenzen, which are further detailed below.

Table 1: Carbon emissions of the Galician economy, expressed in MtCO$_2$e/year.

		TOTAL	Agriculture livestock & related activities	Non metallic mineral products	Electricity & gas supply	Building	Terrestrial transport	Other activities
Consumer	Domestic final demand	2.68	0.27	0.02	0.44	0.25	0.26	1.44
	Foreign final demand	5.08	0.43	0.66	0.66	0.00	0.18	2.45
	Direct emissions	4.08						
	Subtotal	11.83	0.70	0.69	1.10	0.25	0.45	3.89
Producer	Internal demand	2.51	0.32	0.01	0.40	0.32	0.18	1.27
	Exports	2.58	0.50	0.29	0.61	0.00	0.13	0.92
	Intermediate demand	5.17	1.09	0.37	1.68	0.30	0.53	1.17
	Subtotal	10.26	1.91	0.67	2.70	0.62	0.84	3.36
TOTAL		22.10						

The total GHG emissions have been allocated to consumers (54%) and producers (46%) of the Galician goods. All the Galician consumers are responsible for 6.76 MtCO$_2$e/y, of which 60% are direct emissions from their households. The remaining 5.08 MtCO$_2$e/y correspond to foreign consumers (either households or industries) which buy imported Galician products.

Regarding the producer responsibility, the GHG emissions of the exports represent 25%, reflecting the share of the impacts of the exported products that corresponds to their Galician producing industries. The GHG emissions of the internal demand reach 24%, reflecting the share of the impacts of the final products produced and consumed in Galicia that corresponds to its producers. Last, the intermediate demand (50%) includes the impacts caused by the production in Galicia of the intermediate products required to fulfil the total demand of Galician products.

When focusing on the new distribution among sectors, the major contributors are still electricity production and agriculture. Both sectors, however, have now a lower share of the total emissions of the economy (21% and 14%, respectively), which is in turn split among Galician producers and consumers (either Galician or foreign). More significant variations between the producer and the shared approach appear when comparing other, less impacting sectors.

A more intuitive redistribution of the GHG emissions of the Galician economy has been presented, which can be a starting point for reduction measures: lowering the GHG emissions of electricity production and agriculture, either by lowering their domestic consumption or by using alternative production methods, would significantly reduce the Galician emissions. This case study proves the usefulness of Lenzen's method, applicable to any region where EIO data are available.

NEW CONCEPT OF URBAN AGRICULTURE BASED ON BIOTECHNOLOGY AND COMPLEMENTARY ECOINNOVATIONS

Jan W. Dobrowolski[1], Dong Renjie[2], Małgorzata Koncewicz-Baran[3], Tomasz Czech[3], Florian Gambuś[3], Jerzy Wieczorek[3], Justyna Kobylarczyk[4], Robert Mazur[5], Aleksandra Wagner[5]

1) Interuniversity Team of Sustainable Development and Ecoinnovation,
2) National University of Agriculture, Beijing, China,
3) Dept. of Agricultural and Environmental Chemistry, Faculty of Agriculture and Economics, UR-University of Agriculture in Krakow, Al. A. Mickiewicz 21, 31-120 Krakow, Poland,
4) PK-Cracow University of Technology, Faculty of Architecture, Dept. of Sustainable Design, Krakow, Warszawska 24,
5) AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland
**: dobrowol@agh.edu.pl; tomasz.czech@ur.krakow.pl , j.kobylarczyk@op.pl; mazur@agh.edu.pl, awagner@agh.edu.pl*

Introduction and study objectives

The concept of urban agriculture is becoming increasingly important in the context of rapidly increasing urbanization. Agriculture in urban areas is often a large part of the area of cities, for example agricultural grounds in London cover approximately 9% of the area, in Oslo it is 14% and in Krakow 44%. It is estimated that currently close to 1/5 of the world's food is produced in urban agriculture. Taking into account the systematic reduction of agricultural land, there are recommended study on innovation enhancing the crop yield, improve their quality and increase resistance to adverse environmental conditions. New concept of urban agriculture could be a big challenge for urban population in the 21st century. According to FAO there is a need to increase food production with 60% between 2005/2007 to 2050 to feed constantly increasing global population. Innovative trans-disciplinary concepts integrate application of environmental biotechnology for waste water treatment and organic wastes management with **renewable production of bioenergy and improvement of the conditions needed for sustainable development of food production for big cities**.

Methodology

The authors followed **system approach** to improve environmental quality. The methods applied were: case studies focussed on selected areas and research developing studies in the laboratory and in the field, with the application in model regions in Poland and China. A part of the study included creating innovative theoretical concepts for the improvement of environmental quality and production of **pollutant-free food**. We would like to recommend **underground localization of highly efficient waste water treatment plants and centres of utilization of municipal wastes for biogas and synthetic gas production for greenhouses, also located underground**. **Laser biotechnology** is recommended both for photostimulation of selected species of algae for bio-treatment of sewages, consortia of microorganisms for waste biodegradation as well as to enhance the growth of selected species of plants in underground greenhouses, supported by on-line low energy LED lighting network.

Results and conclusions

Expertise from complementary fields should make scientific-technological base for **sustainable design of new generation of eco-buildings** (e.g. eco-hotels with restaurants) and habitats, including underground gardens. Another concept of urban agriculture is based on big centres for cultivation of plants and breeding animals, surrounding new towns (especially in developing countries).

Municipal waste, wastes from restaurants in particular, food industry and biomass from hydro-botanic wastewater treatment plants will supplement rural wastes to enhance food production by the improvement of the quality of soil and as gas for vehicles, agriculture machines and for application in local buildings. Good practice connected with trans-disciplinary "case studies" and pilot research-developing projects in model areas should be accompanied with **problem-solving** graduate and postgraduate **training** of staff as well as life-long education of knowledge-based society for common action focused on **improvement of the human environment and health** including distance education and open for all University, cooperation with mass media etc. The authors intend to follow long-term good practice in integration of research-developing studies with **international education for the promotion of sustainable development, better quality of life** based on innovative biotechnology as contribution to the creation of **green jobs and bioeconomy** (both in developed and developing countries). Model Eco-houses with underground gardens may be especially useful for southern semi-desert countries (including adaptation to climate change) as well as to northern countries due to climatic conditions. Innovative projects on greening of selected habitats based on biotechnology in environmental engineering and sustainable design were subjects of international conferences for students (from developed and developing countries) followed by Project Workshops "Arch-Eco" for environmental NGOs of the Cracow University of Technology and AGH University of Science and Technology in Cracow city, as well as field case study in the region of the Pieniny Mts. border park and Szczawnica health resort. Review of different problems of sustainable development and new biotechnology for better cleaning sewage and wastes management from living houses was starting point for a new concept facing the expectations of the inhabitants of cities (according to socio-psychological study) in different places focused on modification of spatial planning for better quality of the outdoor and indoor environment, as well as to enlarge green areas in cities and suburbs, including allotments and agro-touristic centres (for the production of vegetables and fruits good for consumers' health). The output of the series of interdisciplinary Workshops at the Faculty of Architecture of CUT is a scientific book "Architecture of the place", including new projects of the most creative students. An important field of greening cities is eco-innovation of environmental engineering for the improvement of the quality of aquatic ecosystems in rivers and lakes connected with aquaculture, angling and **development of ecotourism** connected with **education** towards **common action** of experts and knowledge-based society for the **protection of the total environment and human health**.

CIRCULAR ECONOMY AND LCA TO PERFORM GREEN PUBLIC PROCUREMENT FOR ORGANIC WASTE

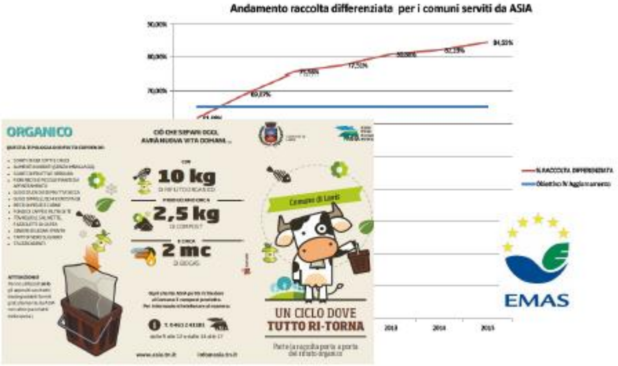
Francesco Baldoni*, **Valeria Bettini***, **Luca Pesaresi***,
Nicola Dalla Torre, **Gianpaolo Bonmassari**

Esalex srl and ASIA (special agency for the environmental hygiene)*
Esalex srl: via Cavour, n.24 – 61032 Fano (PU) Italy
**: baldoni@esalex.eu – www.esalex.eu*

Introduction and study objectives

ASIA is an Italian agency, whose owner are 26 local municipalities in the Province of Trento, and works their area for urban waste collection and trasport.

ASIA has a deep environmental committment and this is the reason why it has started a continuos improvement path to reach high percentage of recycled waste, to look for right strategies to eliminate impurities in collected wastes, to involve and raise public awareness in these activities and to reach the ambitious environmental UE certification EMAS (UE Rule n.1221/2009).



Anyway, it is always necessary to improve awareness in people and each stakeholder to public waste management, including purchasers, both for environment itself and economic/social aspects (i.e.: choosing best technology and plant management).

By this project, ASIA wants to integrate own procurement tender for the organic waste by inserting environmental purchasing criteria, inspired by circular economy, instead focus on the lowest price . The organic waste totally collected is more than 8.000 ton/year and cost is over 1 milion euro. Moreover, ASIA has to apply GPP (= Green Public Procurement), an instrument for EU policy that aims to encourage market for green products and services, starting from the public administration. It is important to note that the GPP is no longer a voluntary instrument in Italy and that the cost of procurement of goods and services in Italy, operated by different Public Authorities (PA), each year is around 50 billion euro (ISTAT data): PA can push towards a more green economy and a more sustainable market.

Methodology

To propose an invitation to tender for the first time characterized by green criteria for organic waste, we have performed an environmental assessment evaluating different time of waste's life: 1) storage after collection, 2) transport to plant, 3) treatment by aerobic/anaerobic plant, 4) use of end-product. Basically, we have performed a LCA study at screening level, because LCA has scientific and legal bases, focusing on different phase of waste treatment. The impact assessment is going to be performed by IPCC method to evaluate the carbon-footprint impact (CFP).

The aim is to determine a methodology and criteria, on the basis of carbon-footprint study, that may characterize the best approach to organic waste fate and reward purchasers that are closer to the principle of cyrcular economy.

We give great attention to UE raccomandation about use of waste to produce energy (Com.UE 26/01/2017: "The role of waste-to-energy in the circular economy").

Results and conclusions

The whole work is divided in a qualitative phase (described in this work) and a quantitative one (not yet done and it will involve economic decision directly by Asia Manager).

For the qualitative work, LCA study was useful to identify each phase of organic waste's life: 1) storage, 2) transport, 3) treatment plant and 4) use of end-product. Furthermore, the CFP assessment supported individuation of macro-criteria for LCA-phase n.2-3-4.

n.2) For transport, less distance and best car-efficiency guarantee less GWP and so better to environment

n.3) in an LCA perspective, it is better an anaerobic plant treatment technology than aerobic plant.

n.4) best high quality and quantity compost production are good to decrease GWP.

Anyway, this study has showed some problem in italian law: even if GPP is a need for italian law, we checked that public law prescriptions that force to burn biogas in torch and do not allow energy rescue from anaerobic production. So doing, it obliges higher GWP and increases environmental impact.

At the moment we cannot argue any quantitative evaluation (from technical and economic point of view), because time of study and tender is not yet public to suppliers: it will be written with new requirements, defined by this study, in the end of 2017 (total value: more or less 1.500.000 euro).

At present ASIA has not considered how much these new criteria will be important in the technical bid "means", but it might be 40-60% of the contract notice (in this case, ASIA will give to environmental criteria more importance than to economic criteria itself).

ON THE COSTS OF CIRCULARITY STRATEGIES: ENVIRONMENTAL LIFE CYCLE COSTING OF GLASS BOTTLE

Luca La Giglia[1,2], Monia Niero[1,*], Alessandra Bonoli[2], Stig I. Olsen[1]

[1)] Division for Quantitative Sustainability Assessment (QSA), Department of Management Engineering, Technical University of Denmark, Bygningstorvet 115, 2800 Kgs. Lyngby (DK),
[2)] Department of Civil, Chemical, Environmental and Materials Engineering (DICAM) University of Bologna
[*]: monni@dtu.dk

Introduction and study objectives

Ensuring sustainable consumption and production patterns is one of the 17 Global Goals set in the United Nations 2030 Agenda for Sustainable Development. The shift towards sustainable production and consumption patterns requires decoupling economic growth from resource constraints, i.e. a circular economy. The circular economy provides an alternative to the linear take-make-waste economic system, being an industrial system that is restorative or regenerative by intention and design. Packaging represents a large share of the material flows for many materials, therefore in a circular economy high priority is given to the packaging sector and to packaging waste management.

Glass is one of the most effectively recycled materials in Europe. In 2014 the average glass recycling rate in the EU28 zone was equal to 74%. The majority of such glass goes back into making new packaging: glass stands alone as the most closed loop recycled food and drink packaging in the EU and in the world. However, recycling is not the only circularity strategy that applies to beverage glass, since also reuse can be an option, depending on the packaging waste collection system.

Two different glass packaging systems are considered in the present study: the city of Bologna (IT) and the city of Copenhagen (DK). The main differences between the two systems are the options to recover glass bottle and the waste collection system. In Bologna, only one-way glass packaging is used and the glass packaging waste fraction is collected as part of the glass-metals fraction and sent to recycling. In Denmark, including Copenhagen, both refillable glass bottles and one-way bottles are sold. There is a deposit-return system (named DRS, Dansk Retursystem) that manages the collection of one-way and refillable packaging using a refundable deposit.

We performed an environmental Life Cycle Costing (eLCC) of the production, purchasing and waste management of glass beer bottles in the two cities. Three main perspectives were considered: producers, consumers and waste management operators, with the aim to compare the economic performances of the two systems and to identify potential cost reductions.

Methodology

The Code of Practice for Environmental Life Cycle Costing developed by the Society of Environmental Toxicology and Chemistry has been followed. The product considered is a 33 cl glass beer bottle, whose function is to contain and carry beer. Therefore, the functional unit (FU) has been defined as the delivery of 1 hl of beer in the two cities (Copenhagen and Bologna), corresponding to a reference flow of 303 units of glass beer bottle (33 cl).

The life cycle stages considered in the system boundaries definition are reported in Figure 1: manufacturing of glass beer bottle, beer filling, distribution, purchasing and consumption, and collection and disposal. The costs categories considered for the eLCC calculations are raw materials, logistic and transport costs, manufacturing costs, use costs and collection and disposal costs.

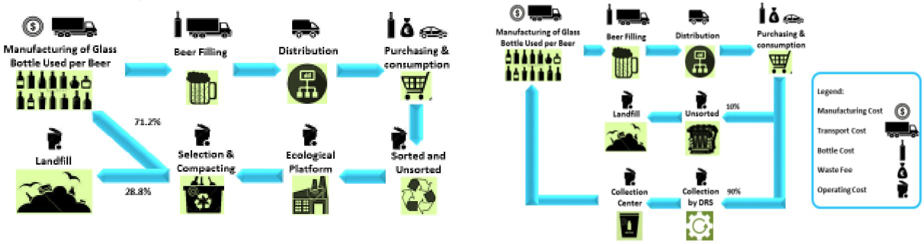


Figure 1: System boundaries for the city of Bologna (on the left) and Copenhagen (right)

Results and conclusions

The overall environmental LCC of the production, use and recovery of beer glass bottle is higher in the case of Copenhagen (167.02 €/FU) than in the case of Bologna (156.03 €/FU). The distribution between the three perspectives, i.e. producers, consumers and waste management operators, reported in Figure 2 shows that the main difference is in the waste management cost. This is mainly due to the high operating costs of the DRS.

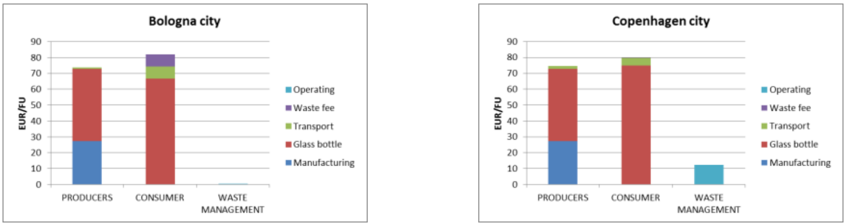


Figure 2: Environmental LCC for the city of Bologna (on the left) and Copenhagen (right)

The results show that a system that accommodates not only the recycling of glass bottle but also reuse, i.e. the case of Copenhagen, presents higher environmental costs in a life cycle perspective compared to a system that can only accommodate recycling (i.e. Bologna), thus suggesting that a higher degree of circularity can imply higher economic burdens.

Acknowledgements

M.N. would like to thank the Carlsberg Foundation for funding the project Absolute Circular Economy" (ACE) toolkit to support companies in the implementation of Circular Economy strategies from an Absolute environmental sustainability perspective.

A METHODOLOGY FOR THE ENVIRONMENTAL IMPACT ASSESSMENT OF THE SUBSTITUTION OF HAZARDOUS CHEMICALS

Semih Oguzcan[1,*], **Jolita Kruopiene**[2], **Jolanta Dvarioniene**[3]

[1,2,3)] *Institute of Environmental Engineering, Kaunas University of Technology (KTU), Environmental Engineering, Gedimino str. 50-311, Kaunas, Lithuania.*
**: semogu@ktu.lt*

Introduction and study objectives

The EU REACH regulation, which encourages the substitution of substances of very high concern, is in force since 2007 and obviously triggers the need to evaluate different aspects of the substitution. Although not legally required, foresighted company decision making would include consideration of the environmental impact of the substitution. To comprehensively assess the success of substitution, it is necessary to know the environmental impacts of both the baseline situation and the situation with the use of alternatives.

The environmental impacts of producing a product, or supplying a service is not solely local. Hence, life cycle assessment (LCA) methodology should be incorporated as a tool to the decision making, assuring that the total impacts have been reduced by the substitution. Hence, the shifting of burdens among impact categories and among life cycle stages of a product can be prevented. LCA studies are not designed to inform us if the risk to an entity in the areas of protection (AoP) is acceptable or not. For this, risk assessment (RA) is necessary to assess the absolute risk to the AoP (e.g. consumers, workers, freshwater organisms, etc.).

This study proposes a framework on how these assessments (LCA and RA) and other entities (emission estimates and substituted amounts) can be used in the environmental impact assessment with the derivation of appropriate environmental impact indicators.

Methodology

As a causal chain for the environmental impact indicator derivation, DPSIR (drivers, pressure, state, impact and response) framework has been adopted.

In the pressure category, the indicator suggested in the methodology is the yearly emission amounts of target substances (i.e. the substances to be substituted) from the company and from the use phase as well. Specific Environmental Release Categories (spERCs) will be used to estimate the emissions from the company.

In the state and impact category, the risk characterization ratio (RCR) and the environmental impact categories in the LCA methodology (ReCiPe methodology has been adopted) have been suggested as indicators.

For LCA, ISO 14044:2006 framework has been adopted, which is formed of 4 main sections; scope definition, inventory formation, life cycle impact assessment and interpretation. The scope will be defined case specific for each situation. Inventory is comprised of the input-output information gathered from the companies, and the life cycle inventory databases such as Ecoinvent database. Life cycle environmental impacts will be calculated by using the Recipe midpoint methodology for Europe. Midpoint methodology has been preferred due to its relatively low uncertainty in comparison to the endpoint methodology.

RCRs will be calculated by the guidance of established methodologies for risk assessment in Europe (i.e. under REACH regulation) with the help of established tools in this area. The scope of emissions for the formation of RCRs have been limited to the production in the company and the use phase. For RCRs of air emissions from industrial installations, the approach of the Estonian regulation has been adopted. Workers, users and the environment have been considered in the RCR derivation. For humans, long-term and short-term dermal, oral and inhalation routes are considered (for consumers, only long-term). For the environment, water, air and soil emissions are considered. In case of the missing data on emissions to air and water from the company, the use of spERCs have been employed. The toxicity data will be obtained mostly from the European Chemicals Agency (ECHA) database.

In the response category, the yearly amount of the substituted hazardous substances is suggested as an indicator.

Precautionary principle has been adopted as a policy in the formation of all the indicators.

The cooperation of the company's technical staff and their knowledge about their processes will be expected to be critical in the application of the methodology.

Results and conclusions

The methodology has been designed to cover, for all cases, many important grounds in the environmental impact assessment, such as climate change, eutrophication, biodiversity loss, worker and consumer exposure, etc. Missing data will be noted and conclusions will be drawn on the availability of such information. The methodology will be applied to various industries and is planned to target SMEs, and the results will be examined in terms of the potential importance of the incorporation of life cycle thinking into the environmental impact assessment studies.

Acknowledgements

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ROAD INSPECTION USING IMAGE PROCESSING AND ACQUISITION PROTOTYPE

Bogdan Cramariuc[1], Lucia Rusu[2, *], Dan Andrei Sitar-Tăut[2]

[1] IT Centre for Science and Technology 25 no., Av. Radu Beller str., 1 sector , Bucharest, 011702,
[2] Babes Bolyai University, Faculty of Economics and Business Administration, 1 no, M. Kogalniceanu str. 400591Cluj Napoca,
**: bogdan.cramariuc@ieee.org; lucia.rusu@econ.ubbcluj.ro*

This prototype has a central role in the proposed platform designed by PAV3M Intelligent management, monitoring and maintenance of pavements and roads. These techniques are used in modern imaging. Its aims are to create a system with minimal cost, non-specialized vehicle, enabling image acquisition of any kind of fields. We have developed a new image processing, analysis methods and enhance (more robust, efficient, dedicated) better than existing ones for solving the specific problems related to pavement analysis. System architecture for processing and acquisition of an image is represented in Figure 1., version consists of a system of digital camera, mobile workstation (laptop or robust embedded system) and GPS receiver mounted on the vehicle image processing and analysis modules (IPA) contains: image acquisition, image preprocessing, detection of pavement distress, and image post processing, together with image database in HPC (High Performance Computer). HPC provides high-performance computing facilities used for developing and running scalable methods of analysis (parallelized). In image processing algorithms, both in the pre-processing and post-processing, ensuring high speed image processing.

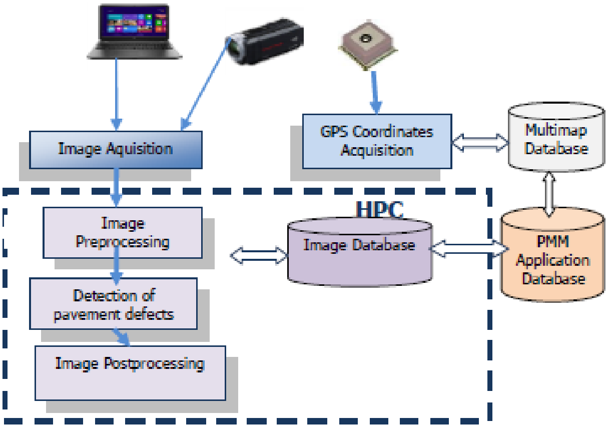

Figure 1. Image Processing and Analyzing Prototype –PAV3M

The main problems can be grouped according to the following categories:

- *Image preprocessing*: restoration (removal of artifacts introduced by the acquisition process), supper resolution, identification and removal of non-pavement details (shadows, stones, papers, oil spots, etc.), image correction due to variations in illumination.
- *Detection of pavement defects*: filtering (e.g. directional filters), texture analysis, image segmentation, post segmentation processing.
- *Image* post-processing: characterization of defects, clustering and classification, data fusion, defect statistics for whole road segments, etc.

GPS receiver offers road coordinates like GPS parameters (longitudes and latitudes) to provide accurate position of detected pavement defects. Differential GPS (DGPS) offers increasing resolution and this choice depends on additional information: ground-based reference stations or satellite based augmentation systems. The prototype offers an application integral for flagship in road maintenance and monitoring solution, using GPS and GPRS devices and geo-coding and reverse coding features of MultiMap Database. In the prototype performance specifications we are mentioning a few:

1. The speed of the vehicle is 120 km / h. This constraint leads to the necessity of using speed cameras, devices that raise the price of the equipment end, or the need to develop methods of analysis of images powerful enough so as to allow retrieval features in / defects, paving images even if these images have a lower quality possible.

2. Positioning inspection system is based on the GPS independent navigation information available internally of a carrier vehicle.

3. Data transmission protocols, including data compression in real time, were studied based on a collaboration with the University of Nantes / Ircynn.

4. Integrating images / video with positioning information (GIS) requires specialized expertise in the field of GIS (Geographical Information Systems). It studied this problem by working with GIS experts from Romania (Transelectrica SA). Image aquisition module offers image file as jpeg, gif or other image format.

For the risk identification and classification, based on the type of pavement distress, we followed *Pavement Condition Index (PCI)*, used by the American Society for Testing and Materials (ASTM) standards and the Long-Term Pavement Performance Program (LTPP). After we processed image in *Detection of pavement distress* we obtain a classification according to type of defects: cracking, potholes, raveling, patching, rutting, edge failure. Based on defects parameters (width, height, deep) we classified road conditions using risk analysis by type of distress (R_D) and give a PCI taking into account all kinds of images of any road.

Acknowledgements

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TWO-STAGE VS. SINGLE STAGE ACID GAS TREATMENT SYSTEMS: A PERFORMANCE ASSESSMENT BASED ON ECONOMIC AND ENVIRONMENTAL INDICES

Alessandro Dal Pozzo*, Daniele Guglielmi, Giacomo Antonioni, Alessandro Tugnoli

LISES – Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Alma Mater Studiorum – Università di Bologna, via Terracini n. 28, 40131 Bologna, Italy
**: alessandro.dalpozzo3@unibo.it*

Introduction and study objectives

Acid compounds like HCl and SO_2 are typical contaminants in flue gases generated in the incineration of waste and their abatement below the emission limit values set by the Industrial Emissions Directive in Europe (Directive 2010/75/EU) is a key step of flue gas cleaning in Waste-to-Energy plants. Acid gas removal is frequently performed by neutralisation with alkaline sorbents: a widespread configuration is the single stage (SS) system based on the injection of sodium bicarbonate, $NaHCO_3$, and the capture of reaction residues by fabric filter. Recently, a novel solution adopted in several Italian WtE plants is the introduction of an additional „Ca-based" stage of injection of calcium hydroxide, $Ca(OH)_2$, and capture of the related residues by fabric filter before the injection of bicarbonate, actually creating a two-stage (TS) acid gas treatment system.

While both systems safely allow emission limit compliance, in a holistic perspective of sustainability the identification of the best process alternative requires the evaluation of both the economic performance and the overall environmental footprint. The present study aimed at performing such comparative assessment between the SS and TS approaches, following a methodology which included the quantification of the indirect environmental burdens, related to the production of reactants and the generation of residues, and the evaluation of the economic performance in terms of operating and capital costs.

Methodology

The comparative assessment of the two process alternatives under given process constraints (composition of the incoming waste, concentration of acid gases at stack) was carried out on both the economic and the environmental viewpoints, by estimating a cost index I_{CST} and an environmental index I_{ENV}. The starting point of the methodology was the quantification of the reactant feed rate needed to obtain the required acid gas removal efficiency and the associated generation rate of solid residues, by means of an empirical conversion model calibrated on actual plant data. Subsequently, inventory data on energy consumption and emissions related to the supply chain of reactants and the disposal route of residues, along with estimates of the fixed and variable costs associated with the operation of the treatment systems, were used to calculate I_{ENV} and I_{CST}. In particular, I_{ENV} resulted from the weight summation of the environmental impacts on selected impact categories. A Monte Carlo sensitivity analysis was adopted to take into account the effect of the propagation of uncertainties in the data on the robustness of the results.

Results and conclusions

Different operating points of the two-stage acid gas removal system were simulated with the conversion model by varying the feed rate of $Ca(OH)_2$ in order to modify the degree of utilisation of the two stages. No utilisation of the Ca-based stage corresponded to the simulation of the single stage system. As shown in Figure 1a, I_{ENV} and I_{CST} varied as a function of Ca-based stage utilisation, given the different costs and environmental impacts associated with the use of $Ca(OH)_2$ and $NaHCO_3$. Two optimal operating configurations were found for the two-stage system: a point at which I_{ENV} is minimised (lower overall environmental impact) and a point at which I_{CST} is minimised (better economic performance), respectively at 33% and 60% HCl conversion in the Ca-based stage. A properly operated TS system appears to guarantee relevant savings compared to the SS, while retaining a similar environmental footprint. Focusing on the economic optimum of the TS system, a sensitivity analysis was performed to test the stability of the result. Whereas the I_{ENV} of TS and SS is confirmed to be comparable and the actual ranking is affected by variability in the input data (Figure 1b), on the economic point of view (Figure 1c) the TS invariably outperforms the SS alternative.

The analysis evidenced the overall higher performance of the TS approach, which is more cost-effective than the SS system without introducing additional environmental burdens.

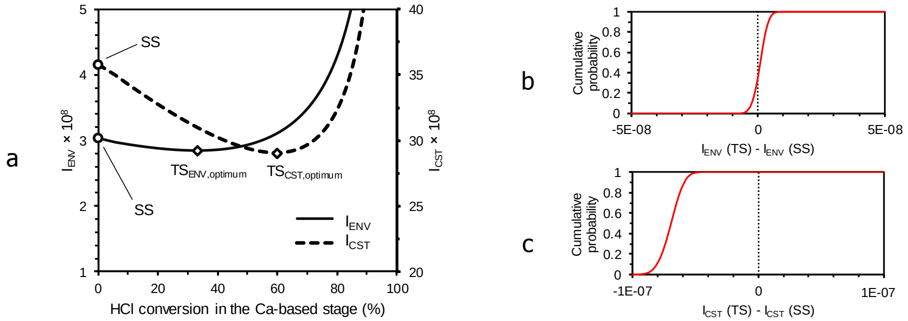

Figure 1: I_{ENV} and I_{CST} for the TS system as a function of Ca-based stage utilisation (panel a). HCl conversion in the Ca-based stage = 0 corresponds to the SS system. Cumulative probability of the difference in I_{ENV} (panel b) and I_{CST} (panel c) between the TS system at its economic optimum and the SS system when data uncertainties are taken into account.

SUSTAINABILITY AND CIRCULAR ECONOMY IN EDUCATION

Madlena Nen[1,*], Mihaela Hărmănescu[2], Ecaterina Stefan[3], Crina Rădulescu[4]

[1] Military Technical Academy of Bucharest, Bulevardul George Coşbuc nr. 39-49, Sector 5, BUCURESTI,
[2] "Ion Mincu" University of Architecture and Urbanism, str. Academiei nr. 18-20, 010014, Bucharest, Romania,
[3] University of Agronomic Sciences and Veterinary Medicine of Bucharest, 59, Mărăști Blvd., 011464, Bucharest, Romania
[4] National School of Political and Administrative Sciences, Expozitiei 30A,
*: *madlenanen@yahoo.com*

Introduction and study objectives

The Heritage Values Network is part of JPI-JHEP: JHEP is the Coordination action in support to the Joint Programming Initiative (JPI) on "Cultural Heritage and Global Change: a new challenge for Europe". JHEP intended to structure and support this JPI to implement the Action Programme for the area of research on cultural heritage in a changing world, through an improved coordination of the various stakeholders dealing with cultural heritage, including SMEs, heritage owners, public administrations, research partners, and local communities. One of the objectives of the projects was to design a network to start a European cross-disciplinary discussion highly topical issue that is mentioned in the recent EU 'Conclusions on cultural heritage as a strategic resource for a sustainable Europe' (20/05/2014). The actual study intended to examine how values are understood and used between disciplines and countries within Europe, between heritage practitioners, researchers and policy-makers on "heritage values", sustainability and circular economy in education. The term 'heritage values' refers to the meanings and values that individuals or groups of people assign to heritage and during the projects there were working groups on different topics to build a better understanding of the influence of cultural contexts on understanding heritage values.

The second workshop, where "Assessing, measuring and prioritizing heritage values", was designed to generate insightful critique of how heritage values are measured and assessed by heritage professionals, agencies and practicing academics across Europe.

Methodology

Case study. Romanian Facts

What are the study's key questions?

How are heritage values understood by policy makers, heritage professionals (e.g. conservators, archaeologists, architects, historians) and heritage theorists across Europe?

How can European Programmes as Life Programme, Erasmus+ Programme and SEE Programme can contribute to the sustainability assessments and eco-innovation process.

The study intend to present some research projects on the theme mentioned before and will try to try to analyse the impact and sustainability of them.

There will be exemples of mobilities and interinstitutional cooperation projects in the fieed of sustainability assessments and eco-innovation process

One of the problems in current public administration is lack of competence in electronic service delivery. Since this is a new field, and since public sector turnover is low, it is necessary to update employees on the new opportunities of digitalization.

This is why the cooperation project will consists in strengthening the institutional cooperation in higher education between partners and thus, establishing structured, intensive and long-term cooperation, especially regarding research projects in the fields of interest . The project's outcomes: a. for students: personal fulfillment, international competence, academic fulfillment in terms of progression, employment, international alumni, language competence; b. for staff: career advancement, language competence, collaborative research, curriculum development; c. for the universities involved: international profile, quality enhancement.

The cooperation will generate new and improved content of courses/case studies, and will facilitate the transfer of knowledge and expertise between partners.

In the same time, the role of the partner is to cooperate and support the beneficiaries and the activities agreed and to respect the principles and conditions of the EEA Grants guidelines.

Results and conclusions

We can consider that the collaboration between different practitioner from different countries and expertise, characterized existing approaches and tensions in assessing heritage values, as well as identify new issues and tensions, could find common and divergent issues in methods and identify new knowledge gaps, but also future direction in order to provide a sustainable approach and communication on the 'heritage value', sustainability and circular economy.

HARMONIZED INTERNET SYSTEM FOR LIFE CYCLE ASSESSMENT: EXPERT SYSTEMS APPROACH

Semih Oguzcan[1,*], Daina Kliaugaite[2], Alessandro Tugnoli[3], Jolanta Dvarioniene[4]

[1,2,4] Institute of Environmental Engineering, Kaunas University of Technology (KTU), Gedimino str. 50-311, Kaunas, Lithuania
[3] Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, Via Umberto Terracini, 28, 40131 Bologna, Italy
[*]: semogu@ktu.lt

Introduction and study objectives

Ignoring life cycle assessment (LCA) in decision making is a major factor in recent environmental degradation. The recent regulatory system lacks incentivizing the sharing of the information, among industries and to consumers, necessary for optimization of technosphere in terms of environmental impacts. As an example, the proximity principle for transport, although is defined in Europe for waste management (DIRECTIVE 2008/98/EC), it is not applied to other areas that are equally responsible for the environmental impact. While the application of LCA to such transport systems other than waste transport will further inform the decision makers about what is environmentally preferable, one might stress the consequences of such a wide application of LCA on free-trade. Another example is the application of ecolabels: although there are established ecolabels such as the EU Ecolabel, the application of it is frequently voluntary and insufficient (e.g. in Lithuania there are only 101 products/services that have the EU Ecolabel). Nevertheless, the necessity to incorporate life cycle environmental impacts in decision making is clearly identified. Well informed consumers and an adequate eco-labelling of life cycle impacts are necessary, especially while today we are at the historical peak of environmental degradation caused by humans. Recently, the application of LCA is done by LCA experts, and requires resources that not every company can pay, or is willing to pay. This is particularly true in case of SMEs. Also, those LCA studies use industry average data for a major part of their inventory, which adds up to the uncertainty in LCA results. By taking notice that each company already have their input-output and product information, this article proposes a harmonized alternative system for the application of LCA (shortly named as HIS-LCA) to the industry as a whole, by using 'expert systems' approach.

Methodology

In the study, current state in the application of LCA and related practical problems have been reviewed. An 'expert systems' approach was adopted in the application of the LCA to vastly eliminate the need for LCA experts by using automation and freely available user friendly internet based system. The application is devoted to companies, targeting consumers and companies themselves.

Results and conclusions

In the resulting methodology, the production chain is divided into and grouped as three stages (intermediate-producer, end-producer and distributor). Each group has different predefined scope and responsibilities under different conditions defined by this study. The information (e.g. inventory, location) flow from one company to another is established by the proposed internet based system. The system is designed to guide the user in scope and inventory definition. The proposed internet based system also incorporates a map similar to 'google maps', where users can indicate their location and transport routes and mode(s). Those local (company specific) inventories, for a specific product/service and distribution branch, are then used to evaluate the life cycle impacts for a given product. A simplified flowchart diagram for the proposed system can be seen in Fig. 1.

Expected advantages of the proposed methodology are (1) wider application of LCA for environmental impact optimization, (2) companies might be able to assess where their impacts come from (transport, energy, etc.) and focus on these areas, (3) each company will be given a code, and company specific data can be followed, (4) improvement in the use of case specific information instead of industry average, (5) end-product/service labelling by Life Cycle Impact Scores per functional unit, (6) LCA results, with uncertainty analysis incorporated, can be used in alternatives assessment, (7) does not need to define functional unit for every company (only the end-producers will be responsible for functional unit definition), (8) changes simultaneously affecting multiple end products/services can be evaluated based on the efficiency of the product/service system in fulfilling the total demand for those relevant functions, (9) localization can be improved by mapping the industry on real geographical map, (10) product composition do not need to be disclosed by the company to be used for LCA purposes, (11) opportunity to improve allocation, (12) encouraging companies by consumer pressure to decrease their emissions. Also, the expected challenges are: (1) all the other problems with LCA still present (e.g. single products with multiple functionality, allocation, recycling, worker exposure, metals, nanoparticles, missing data, weighting, etc.), (2) some training might be needed (on understanding the functional unit, allocation, HIS-LCA basics, etc.), (3) expert support might be needed (just once for each product/service type) for functional unit definition, (4) regulatory pressures need to be in place; regulation changes, (5) recycling should be encouraged by regulation, (6) at the present time, for alternatives assessment, infrastructure cannot be incorporated into the methodology due to the lack of databases for the baseline infrastructure (not a problem for future applications), (7) terminology harmonization needed when passing information (e.g. product names, process names, etc.).

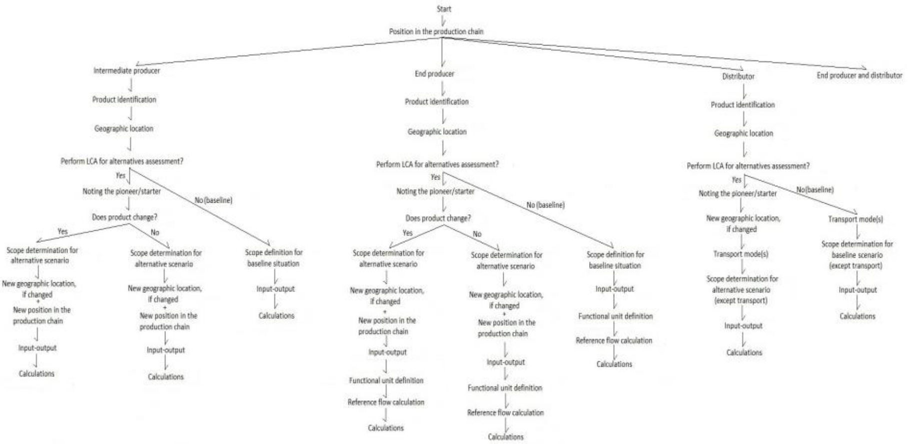

Figure 1: Simplified main flowchart of the internet based system

SECTION V

NOVEL MATERIALS FOR ENVIRONMENTAL AND ENERGY APPLICATIONS

ECO- MATERIALS AND ECO-PRODUCTS IN NOVEL SOLAR THERMAL FACADES

Ion Visa*, Anca Duta

R&D Centre: Renewable Energy Systems and Rcycling, Transilvania University of Brasov,
29, Eroilor Bvd. 500036 Brasov, Romania,
**: visaion@unitbv.ro*

Introduction

The EU strategy developed by the *European Renewable Heating and Cooling Technology Platform* outlines that by 2030 renewables could supply over half of the heat used in Europe (regardless the geographical location, thus meeting the demand for domestic hot water, heating and cooling in various ratios). The specific focus was set on the built environment, which accounts for about 40% of the thermal energy demand. Consequently, the EU Strategic Energy Technology (SET) Plan outlines the need to increase the solar fraction of systems per building, preferentially by installing solar-thermal systems. Thus, new, efficient, and affordable solutions are urgently needed, to extend the implementation of solar-thermal systems in the built environment.

One potential bottle neck is the limited available implementation area; suitably positioned solar-thermal arrays should be south-oriented, with an accepted abatement of $\pm 20^{o}$, not affected by shadowing; thus each south-facing part of any building should be used for mounting solar-thermal arrays (and associated technology), including the solar-thermal facades. By definition, these are highly visible places, therefore equally important prerequisites are related to functionality and aesthetics.

Obviously, the key issue is the market competitiveness of these solutions that is further mirrored by the need for: (1) high solar to thermal conversion efficiencies, obtained using (2) commercial materials and mature manufacturing technologies for the components and assembly. Built environment integration additionally requires (3) architectural and social acceptance, thus ST collectors with non-traditional colors and shapes, (4) easy mounting, easy maintenance and dismounting (plug and play).

The quest for feasible, affordable and efficient solutions for ST facades (STF) represents thus a current topic of worldwide research groups and significant results were recently reported.

The presentation will focus on the results obtained in developing sustainable solar-thermal facades, using as building blocks novel flat plate solar-thermal collectors with trapeze and/or triangle shape. The facades well match the eco-products typical features the development of low cost, environmentally friendly key components: the absorber plate and the glazing.

The Design Concept

The solar thermal facades should follow at least the following specifications:

(a) High coverage degree of the suitably positioned vertical areas of the building; considering the broad diversity of the facades aspect, this condition can only be met if lego-type arrays can be developed; a comprehensive study showed that the isosceles trapeze and the equilateral triangle shapes best support this aim.

(b) High conversion efficiency in the implementation conditions; the vertical mounting on facades reduces the maximum amount of input solar radiation, thus efficiency is an important feature that should not be compromised.

(c) Avoiding monotony by giving identity to the buildings/district that chooses the sustainability path and implements STF. This is insured by colored flat plate solar thermal collectors. Avoiding the traditional colors (dark blue or black) that, although efficient are rejected by the large majority of inhabitants.

(d) Using environmentally friendly materials: commercial materials are used for most of the components (e.g. replacing aluminum with plastics); however, the colored absorber plates should be developed following the green chemistry routes (e.g. sol-gel synthesis). Supporting functionality, self-cleaning glazing should be used as clogging poses a significant risk, particularly in the urban areas (where particulate and organics atmospheric pollution is a common fact).

Results and Discussions

Isosceles trapeze ($A=0.67m^2$) and equilateral triangle collectors ($A=0.22m^2$) were developed as demonstrators and considered building blocks for developing various solar-thermal arrays. The absorber plates could get various colors and were obtained by infiltrating an Al/Al_2O_3 matrix with sol-gel prepared red (Fe_2O_3), green (CuS) and orange (VO_x) pigments. The sol-gel synthesis used inorganic precursors, with significantly lower toxicity as compared to the organo-metallic ones. Sol-gel anti-reflective coatings with self-cleaning properties (SiO2/TiO2) can be deposited to match the design concept. Considering the spectral selectivity of the absorber plate and the overall conversion efficiency, STF with various geometrical surfaces are modelled and the thermal output is calculated. The results show that combinations of trapeze/triangle collectors can reach very high coverage degrees (80%), with a thermal output significantly higher as compared to the reference case, when traditional (rectangular) collector are used, even when these have a nominal efficiency higher than the new demonstrators.

These results outline that sustainability can be successfully implemented, based on a combination of eco-design and eco-materials and STF represent one eco-product that is likely to penetrate the market.

Acknowledgement:

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ALKALI PRE-TREATMENT AND ENZYMATIC HYDROLYSIS OF ARUNDO DONAX FOR SINGLE CELL OIL RODUCTION

Stefano Cianchetta*, **Stefania Galletti**

Council for Agricultural Research and Economics, Research Center for Agriculture and Environment; via di Corticella 133, 40128 Bologna, Italy,
**: stefano.cianchetta@crea.gov.it*

Introduction and study objectives

The exploitation of lignocellulosic substrates to produce single cell oil (SCO) to obtain second generation biodiesel is an interesting possibility, not yet deeply investigated. The fermentation of the enzymatic hydrolisate with oleaginous microrganisms (OM) must be preceded by a pre-treatment step to disrupt cell wall structures and to expose the holocellulose to hydrolytic enzymes. An optimized pre-treatment should minimize chemical inputs and generate few inhibitors. Moreover the hydrolysis step should be performed at the lowest enzymatic load, to reduce costs and final N content. In fact a high C/N ratio is desirable in order to favour lipid accumulation by OM. *Arundo donax* displays an impressive biomass production in warm-temperate environment. If harvested in winter, after N traslocation to rhyzome is completed, a high C/N ratio is easily obtainable. Alkali pre-treatments produce less furfural and hydroxymethyl-furfural as inhibitors than acid pre-treatments and it is less investigated. This work presents the preliminary results obtained with NaOH pre-treatment on winter harvested *A. donax*, followed by enzymatic hydrolysis with commercial enzymes in comparison with enzymes from a selected wild-type *Trichoderma* sp. strain.

Methodology

A sample of A. donax plants from a 2nd year harvest (January 2017) was oven dried at 50 °C, milled and sieved at < 0.25 mm. The C/N ratios of the milled biomass and of the dried cellulolytic enzyme C2730 (Sigma) were determined by an elemental analyzer (Leco, CHN Truspec). The fiber composition was determined according to Van Soest methodology.

One gram samples were treated with NaOH solutions to obtain NaOH/biomass ratios of 0, 2, 4, 6, 8, 10, 12, 14, 16, 18 % (w/w) in a final volume of 10 ml, at 120 °C, 20 min. Samples were centrifuged and opportunely diluted supernatants were spectrophotometrically analyzed in microplates (280-1000 nm). Pellets, three-fold washed in water, and the supernatants were dried at 70 °C to perform a mass balance, calculating the insoluble fraction and the water and alkali extractives.

A preliminary saccharification experiment was carried out on the samples treated at 0 and 10 % NaOH with a cellulase load of 6 FPU g-1 d.w of substrate, using commercial cellulase (C2730) or crude enzymes produced in laboratory from the xylanolitic Trichoderma sp. IK4. The experiment was performed in 96-deep-well microplates (in duplicate) containing citrate buffer 50 mM, pH 4.8 and the pre-treated slurries (0.5 % w/w), opportunely neutralized. Microplates were continuously mixed by rotary inversion (40 °C, 2 days). Samples of 20 µL were withdrawn at convenient time points after enzyme addition (0, 2, 4, 8, 24, 48 h), kept in ice during manipulation and stored at -20 °C before analysis in duplicate for reducing sugar equivalent concentration by a microplate-based DNS assay.

Total reducing sugar yields were calculated as % of the maximum theoretical yield on the basis of cellulose and holocellulose content of the feedstock.

Results and conclusions

The composition analysis by Van Soest methodology revealed that the untreated samples contained 41.4% cellulose, 28.6 % hemicellulose, 8.2 % acid detergent lignin, calculated on total solids. C/N ratio was 105 based on CHN elemental analysis (C = 46.1%, N = 0.44%). The high C/N ratio was due to the N translocation towards rhizomes which gradually occurs from the end of the vegetative cycle until the new growth. A high C/N is important since it is expected to promote SCO production by OM, according to the literature.

The supernatants of the alkali pre-treated samples, analyzed by spectrophotometer in the visible range, gave absorbance values increasing with the NaOH concentrations. A sigmoid increase in absorbance was observed up to a plateau corresponding to 14 % NaOH, while the half of the maximum was observed around 4-6 % NaOH. Near UV spectra showed two overlapped peaks at 300 and 330 nm, which can be related to the presence of aromatic compounds or compounds with double bonds, like alkali solubilized lignin. The absorbance increased along with the NaOH concentration. In particular a sigmoid increase in absorbance was observed up to a plateau corresponding to 16 % NaOH, with half of the maximum between 8 and 10 % NaOH. Thus the 10 % NaOH pre-treatment was chosen to carry on with the hydrolysis, considering its substantial delignifying efficacy.

The mass balance of the pre-treated samples (netted of added chemicals) showed 15 % of hot water extractives (120°C). The alkali extractives increased along with the NaOH concentration up to 29 %, leaving a solid insoluble fraction of 56 %. For 10 % NaOH pre-treated material, we calculated 15 % of hot water extractives, 17 % of alkali extractives and 68 % of insoluble fraction.

The pre-treatment with 10 % NaOH, followed by an enzymatic hydrolysis with 6 FPU g^{-1} on diluted slurry (0.5 % w/w) gave a final 2.5-fold increase of the saccharification of *A.donax* compared to 0 % NaOH pre-treatment, reaching a maximum of 75 % bioconversion of the holocellulose. The difference observed among the IK4 enzymes and the commercial mix was pronounced. In particular, IK4 enzymes at 8 h of bioconversion increased total sugar yields by 30 % with respect to the commercial mix. The greater effectiveness of IK4 enzymes could be due to the high xylanase content, able to remove hemicellulose and xylo-oligomers, acting synergistically with cellulase.

Further investigation are in progress in order to maximize sugar yields, assaying higher slurry and NaOH concentrations and optimizing the enzyme addition, in order to obtain an hydrolysate with the lowest N content, as required for SCO production.

Acknowledgement

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FLEXIBLE DESIGN OF CELLULAR Al_2TiO_5 AND Al_2TiO_5-Al_2O_3 COMPOSITE MONOLITHS BY REACTIVE FIRING

Eleonora Lalli[1,2,*], Nuno M. D. Vitorino[2], Carla A. M. Portugal[3], João G. Crespo[3], Cristiana Boi[1], Jorge R. Frade[2], Andrei V. Kovalevsky[2]

1) Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, DICAM, Università di Bologna, viaTerracini 28, 40131 Bologna, Italy
2) CICECO - Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193 Aveiro, Portugal
3) LAQV, REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal
**: eleonora.lalli2@unibo.it*

Introduction and study objectives

Aluminium titanate (Al_2TiO_5) ceramics, thanks to its particular properties, is an attractive material for different applications. It can be used as a thermal insulating material due to high melting point, excellent thermal shock resistance, low thermal conductivity, low thermal expansions and low Young's modulus. This ceramic material possesses poor wettability and good erosion resistance in contact with molten metals, making it appropriate for use in metallurgic melting. Finally, aluminium titanate, thanks to its high refractoriness, shock and corrosion resistance, finds important applications in the environmental field, such as filtration and separation applications including soot traps for diesel engines, filters for hot gas clean-up systems and water purification. These applications require flexible and rational design of highly porous materials: in order to give them the desired functionalities, the process conditions have to be optimized and the porous structure has to be tuned.

In this work we would like to present the results of a recently developed processing method for preparation of porous cellular ceramic monoliths through emulsification of ceramic suspensions. Taguchi experimental design was used to assess the effects of two-step firing procedure on phase composition and to obtain guidelines for the microstructural evolution in Al_2TiO_5 and Al_2TiO_5-Al_2O_3 composite ceramic monoliths.

Methodology

Cellular Al_2TiO_5 and Al_2TiO_5-Al_2O_3 composite monoliths were prepared through suspension emulsification and reactive ceramic consolidation. The precursor powders titanium oxide (TiO_2) and aluminium oxide (Al_2O_3), mixed in different titania:alumina molar ratios, were used to prepare aqueous suspensions. Liquid paraffin was then used as an organic phase for oil in water emulsification of the powder suspension: various paraffin:suspension volume ratios were considered. The consolidated and dried monoliths were subjected to the preliminary heat treatment to eliminate the organic phase under delicate conditions. After that, the ceramics were subjected to non-conventional two-step firing procedures: these were designed with relatively fast heating to a peak temperature, to trigger the reactivity, and then immediately dropping the temperature to a lower temperature plateau to attain ceramic bonding while retaining the cellular microstructures. In order to assess the impact of this thermal treatment on phase composition, porosity and other microstructural features, a Taguchi plan was implemented, involving three variable parameters (peak temperature, isothermal treatment temperature and time) with three levels for each variable.

Phase composition of fired monoliths was studied by X-ray diffraction (XRD) after crushing the samples to powder; porosity volume fraction was assessed by the Archimedes method, while fractured fired samples where characterized by scanning electron microscopy (SEM).

Results and conclusions

As observed from SEM images, stable cellular porous microstructures were obtained mainly in the case of Al_2TiO_5-Al_2O_3 composite materials. In fact, Al_2O_3 excess has the ability to: 1) retain highly porous cellular ceramic microstructures; 2) toughen Al_2TiO_5-Al_2O_3 ceramics; 3) complete the conversion of residual fraction of TiO_2, which may cause undue microstructural changes. This behavior was confirmed by XRD results and density measurements: porosity and residual fraction of titania in composite samples with lower titania:alumina ratio showed lower changes on varying the firing conditions. This resulted in the greater ability to process composite materials with porosity and phase compositions within narrow deviations from the designed characteristics.

Multivariate linear regression was also performed in order to evaluate relevant coefficients for the effects of firing parameters on residual fraction of titania and porosity: the results provided further evidence for combined effects of reactants ratio, paraffin contents and firing conditions. Using this approach it was still possible to demonstrate that the strongest effects of firing conditions were exerted on samples with titania:alumina ratio equal to 1:1, in line with the previous results. The effects of firing conditions depend also on the paraffin content, probably because it has a prevailing effect on porosity, with impact on rigidity of cellular materials.

It was possible to conclude that the flexible processing and design of Al_2TiO_5-Al_2O_3 rely on the ability to take advantage of the key role of titania, in order to minimize undue microstructural changes during reactive firing and to retain reproducible characteristics of the resulting cellular ceramics.

Acknowledgments

The author Eleonora Lalli is thankful to the University of Bologna (DICAM and the Marco Polo Scholarship) and to Professor João G. Crespo for financial support.

REMOVAL OF Cr(VI) FROM AQUEOUS SOLUTION BY LOW-COST KERATINOUS WASTE

Igor Cretescu[1,*], Ingrid-Ioana Buciscanu[2,*], Tudorel Balau-Mindru[2], Tudor Lupascu[3], Gheorghe Duca[3], Constantin Luca[1]

[1)] "Gheorghe Asachi" Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, 73 Prof. dr. Dimitrie Mangeron Blvd, Iaşi 700050, Romania,
[2)] "Gheorghe Asachi" Technical University of Iaşi, Faculty of Textile, Leather and Industrial Management, 71A Prof. dr. Dimitrie Mangeron Blvd, Iaşi 700050, Romania,
[3)] Institute of Chemistry, Academy of Science of Moldova, 3 Academiei Street, MD-2028, Chişinău, Moldova
*: *icre@tuiasi.ro, ibuciscanu@yahoo.com,*

Nowadays, chromium is a priority pollutant, generated in great amounts by different industries in both trivalent and hexavalent state. While Cr(III) is insoluble and considered an essential nutrient element, Cr(VI) is highly soluble and exhibits toxicity, carcinogenity and mutagenicity. It is compulsory for industries to treat their wastewater and reduce the Cr(VI) content below the enforced limit values. Amongst different methods currently used to treat Cr(VI)-contaminated water, adsorption has gained a particular attention, due to well-known advantages. Lately, research has been focused on low-cost adorbents with satisfactory sorption capacity, derived from locally available renewable resources like vegetable wastes, biomass, etc. The last decades, wool has lost ground in the favor of synthetic fibers and great quantities of raw wool are regarded as wastes that raise serious management problems. Keratin, the main protein constituent of wool, behaves like an amphoteric polyelectrolyte with considerable affinity for heavy metal cations and anions. Little research has been dedicated to investigating the potential utilization of wool for the removal of heavy metal anions from water.

It is the aim of this paper to study the adsorptive interaction between Cr(VI), and native and modified wool. Nature of wool treatment, solution pH, contact time, sorbent dosage were considered as influence factors upon the wool adsorptive capacity. A synthetic anion-exchange resin – Purolite A400- was used as reference sorbent.

Coarse fiber snippets were collected from a cross-breed sheep fleece and subjected to different treatments: (1) washing with water, (2) soda ash-detergent scouring and (3) scouring followed by non-solubilizing alkaline activation. The samples were dried at 40°C, cut into 5 mm pieces and used as sorbent material. A stock solution of 1000mg/L Cr(VI) was prepared from potassium dichromate in deionized water. The batch sorption studies were conducted on solutions with initial Cr(VI) concentration in the range of 10 to 160 mg/L, pH between 2 and 6, magnetic stirring at 200 rpm, adsorbent dosage 2 – 6 g/L, at room temperature. Under these conditions, equilibrium was reached in about 200 min contact time. The concentrations of Cr(VI) were determined by the 1,5-diphenylcarbazide complexation method, on a HACH DR/2010 spectrophotometer at λ_{max} = 542 nm. Reduction of Cr(VI) to Cr(III) on wool is a long-term process, so for the given equilibration times, Cr(VI) is considered the only species in solution.

Preliminary assessment of the sorbents efficacy (see Fig. 1) shows significant differences between the values of Cr(VI) percent removal, and maximum uptake at acidic pH. The scoured wool efficacy is about four times higher as compared with the washed wool; the activated wool almost doubled its Cr(VI) removal ability as compared with the scoured wool, and preserved some sorptive capacity at pH 6. The synthetic resin exhibited the highest efficacy and lower pH sensitivity.

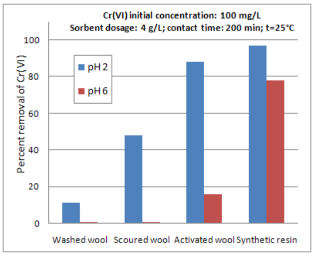


Figure 1: Percent removal of Cr(VI) on wool sorbents

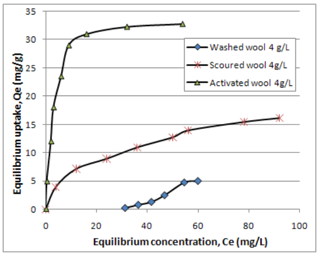


Figure 2: Sorption isotherms of wool sorbents at pH 2

The experimental adsorption isotherms (see Fig. 2), show an S-shape isotherm and very low Cr(VI) uptake for washed wool, which proves fiber inability to expose its active sites, due to its hydrophobicity. Scoured and activated wool exhibit Langmuir-type isotherms, which prove similar interaction with the adsorbate - strong binding at the active sites and saturation by monomolecular layer - but great difference between the Cr(VI) uptake. Scouring increases hydrophilicity and fiber porosity, which favors the acces of the HCrO4-, which is the predominat species at the working pH, to the active sites. The alkaline treatment enhances the density of the amino –NH2 groups, which are the active sites, on the fiber surface and improves the Cr(VI) uptake up to a maximum of 32,6 mg/g. The main factor affecting the sorption of Cr(VI) anion is the solution pH; pH decrease below the keratin isoelectric point increases the number of charged amino groups, –NH3+ able to establish electrostatic interactions with the metal anions . The ability of activated wool to adsorb Cr(VI) anions at pH 6 shows the shift of the isoelectric point due to the alkaline treatment.

This paper investigated the adsorption of hazardous Cr(VI) on raw wool waste and demonstrated a potential application of an inexpensive renewable resource of animal provenience for the treatment of heavy metal pollution. Straightforward chemical treatment raises the adsorption capacity up to effective values, as compared with other natural-derived adsorbents reported in literature. Further investigation can be extended to post-consumer waste, like wool clothing waste.

REMOVAL OF ORGANIC POLLUTANTS USING CYCLODEXTRIN-BASED ADSORBENTS

Irina Fierascu[1], Radu Claudiu Fierascu[1], Raluca Somoghi[1], Sorin Marius Avramescu[2,*], Alina Elena Olaru[2], Corina Bradu[2], Angel Nica[2]

[1)] The National Institute for Research & Development in Chemistry and Petrochemistry-ICECHIM, 202 Spl. Independentei, 060021 Bucharest, Romania
[2)] University of Bucharest-PROTMED Research center, 36-46 M. Kogalniceanu Blvd., 050107 Bucharest, Romania
[*]: sorin_avramescu@yahoo.com

Introduction and study objectives

Today, adsorption plays an important role in the industrial processes. Adsorption processes represents an important part of the water treatment technology since a large range of pollutants can be removed from water and is more versatile and inexpensive than other solutions. However the need for new adsorbent is stringent due some drawback associated with this approach like hindered access of pollutants to adsorption sites and difficult regeneration. Higher efficiency and insensitivity to toxic substances compared to the other conventional methods of water purification has made it much more popular. The current state of the art at international level refers to the use in water purification technologies of adsorbents starting from basic structures as activated carbon, silica gel, zeolites or clay minerals, to more complex and expensive structures, like carbon-based three-dimensional architectures or three-dimensional macrostructures. In this context, the use of cheap and relatively easy to obtain synthetic materials is a premise of using unconventional eco-technologies in environmental decontamination applications and particularly water treatment. The adsorbents based on nanoparticles with different type of adsorption sites grafted on them can solve the majority of problems encountered in case of use of classical adsorbents. The morphology for the new adsorbents was selected for this study with a view to exploit the benefits of slurry type adsorber and high specific surface of the nanoadsorbents. The main objective of this study consists in the development of a novel "environment-friendly" technology for water remediation and wastewater detoxification exploiting nanostructured adsorbents systems designed for advanced elimination of organic compounds from polluted effluents. The proposed adsorbents consist of a nanoparticle core (such as ferrite or silica) and a cyclodextrin shell.

Results and conclusions

Considering the cumbersome step of separation, the ferrite core allows a rapid removal of nanoparticles from the aqueous solution after applying a magnetic field. Another important aspect is that the modified cyclodextrin will permit to extend the range of pollutant classes which can be eliminated from contaminated effluents. Moreover, the materials selected for preparing the nanoadsorbents comply with sustainable development principles and ***green chemistry approaches.*** The spent adsorbent does not represent an environmental threat since cyclodextrin is biodegradable and the cores (ferrite, silica) are non-toxic materials.

The novel materials proposed in this project present a new morphology which allows an easier diffusion of pollutants to adsorption sites and high absorption capacity due to cyclodextrin moieties grafted on ferrite nanoparticles surface. Also the adsorbent are easily removed from aqueous effluents. The synthesized materials were characterized using several analytical techniques (using X-Ray Diffraction, X-Ray Fluorescence, (Scanning) Transmission Electron Microscopy, FTIR and RAMAN spectroscopy). The adsorbtion process was monitored using High Performance Liquid Chromatography. The dependency of the adsorption process to some parameters such as contact time, adsorbent dose, pH, and phenol concentration are also presented and discussed as well as the discussion of the kinetic data, equilibrium and thermodynamics aspects.

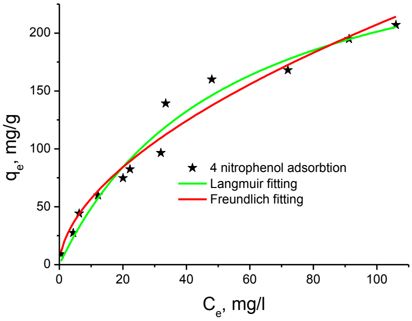


Figure 1: Typical adsorption of 4 nitrophenol on cyclodextrin based adsorbent (black stars) and Langmuir and Freundlich fitting

The results obtained demonstrate that the prepared materials have a significant potential for the removal of organic pollutants from wastewater.

Acknowledgement

This work was supported by grants of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PNIII-P2-2.1-PTE-2016-0063 and project number PN-III-P2-2.1-PED-2016-0251, within PNCDI III.

MAGNETIC ECO-SYSTEMS BASED ON CHITOSAN SUBSTRATE USED FOR Cr (VI) REMOVAL FROM WATERS

Ecaterina Matei[1], Andra Mihaela Predescu[1,*], Maria Râpă[2], Cristian Pantilimon[1], Claudia Drăgan[1], Cristian Predescu[1]

[1)] University POLITEHNICA of Bucharest – Faculty of Materials Sciences and Engineering,
Splaiul Independentei 313, 060042, Bucharest, Romania
[2)] ICPAO SA Medias, Romania
[*]: andrapredescu@yahoo.com

Introduction and study objectives

This study follows the development of a new class of nano-sized magnetic materials that display controlled selectivity, manufactured at low costs and that can be integrated to improve classical water treatment steps and protect natural waters, soil and subsoil. Thus, iron oxide nanostructures (ION) were synthesized through a green synthesis method and used to create magnetic eco-friendly systems by combining the nanoparticles with a natural polymeric substrate (chitosan), resulting in the ION-chitosan composite (ION-CS). The purpose of this study is to determine the suitability of these two magnetic eco-systems as ION and ION-CS in terms of Cr (VI) adsorption and efficiency. The main phenomena that magnetic eco-systems exhibit in comparison with classical pollutant removal systems are: (i) adsorption and/or ionic exchange and (ii) reduction processes.

Important features of eco-systems include high activity specific surface which can be obtained by controlling the particle size of the magnetic component and the dispersion of the powder inside polymer-type-stabilizers which are environmentally friendly. The polymers can be of different types. The focus is on the use of a natural polymer, such as polysaccharides or their derivatives (starch or chitosan) instead of the alternative synthetic polymers. The choose of polymers is sustained by the previous use in classical treatment processes as flocculating agents, for the destabilization process of double electric layers, resulting in the attachment of fine sediments on their surface which leads to an increase in sedimentation speed.

Methodology

The magnetite nanoparticles (ION) were synthesized through a chemical synthesis process that involved the use of a plant extract from spent rose leaves as the reducing agent. The nanostructured material that was obtained is then mixed with the chitosan while stirring continuously and then dried for 48h in order to develop a film of the composite ION-CS. Separately a chitosan film (CS) was also produced in which there are no magnetic nanoparticles for the purpose of comparing the morphology. All of the materials have been characterized by using AFM (atomic force microscopy), SEM (scanning electron microscopy) and XRD (X-ray diffraction) in order to observe details regarding morphology, crystallinity and particle sizes. The characterization of the materials follows strict protocols in order to avoid contamination and to obtain accurate results from analysis. The affinity of the hybrid nanocomposite for Cr(VI) adsorption was studied by using K2Cr2O7 (potassium dichromate) solution. The adsorption tests involved using chitosan and magnetic particles individually for obtaining a standard value and after that two different hybrid materials in terms of ION to CS proportions were analyzed. The adsorption time was also varied in order to observe the influence that contact time between the adsorbent and the solution has over the removal efficiency.

Results and conclusions

The amount of Cr (VI) adsorbed by the chitosan strip and the chitosan–magnetite nanocomposite strip from the synthesized aqueous solution was evaluated by using UV–visible and IR spectroscopy. The results confirm that the Cr (VI) removal efficiency of the chitosan–magnetite nanocomposite strip is 80 %, which is higher when compared to that of the chitosan strip, which is 72 %. The high performance of the magnetic eco-systems is the result of the controlled morphology in terms of size distribution and particle uniformity which results in high specific areas and increased adsorbent properties. These characteristics are observed by SEM and XRD analysis and they can be confirmed by AFM imaging. Through embedding in a polymer matrix it is possible to ensure a good dispersion and an increase in removal efficiency, good results being obtained in the removal of heavy metals, especially Cr (VI). In figure 1 are presented atomic force microscope images of the 3 materials (ION, ION-CS, CS) and it is observable that the particle size of the magnetic material is between 10 and 30 nm with spherical shape. We can also observe that the nano-hybrid displays a better dispersion of the magnetic material than the simple iron oxide powder.

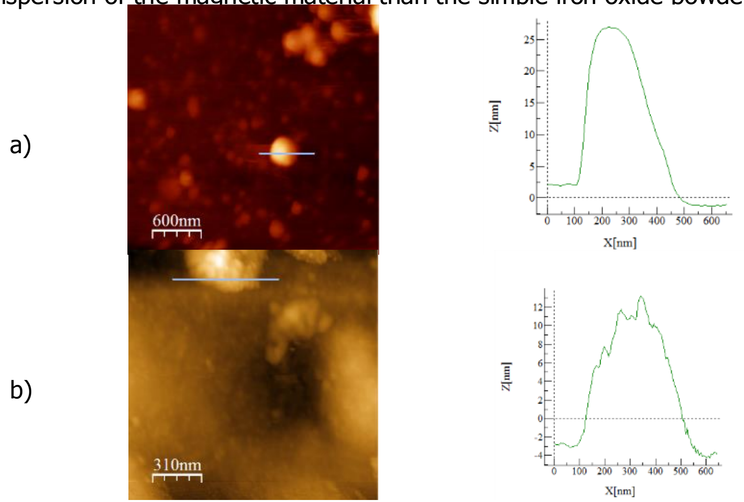


Figure 1: AFM images of materials synthesized through the chemical process: a) magnetite; b) magnetite and chitosan composite

TiO_2-SUPPORTED POWDER AND GRANULAR ACTIVATED CARBON FOR HUMIC ACID REMOVAL FROM WATER

Corina Orha[1,*], **Florica Manea**[2,*], **Carmen Lazau**[1], **Rodica Pode**[2]

[1)] *National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Condensed Matter Department, 1 P. Andronescu Street, 300254, Timisoara, Romania*
[2)] *"Politehnica" University of Timisoara, P-ta Victoriei no.2, 300006 Timisoara, Romania*
[*] *: haiduccorina@yahoo.com, carmen.lazau@gmail.com; florica.manea@upt.ro, rodica.pode@upt.ro*

Introduction and study objectives

The multiple environmental and human health problems caused by the presence of humic acid in water require its removal. Sorption and photocatalysis processes are very promising for advanced water treatment and the sorbent/photocatalyst represent the key of their performance. The aim of this study is to investigate the performances of granular and powder activated carbon functionalized with TiO_2 (G-TiO_2 and P-TiO_2) in comparison with granular and powder activated carbon (GAC and PAC) as reference, for humic acid removal from water by sorption and photocatalytic processes.

Methodology

The granular and powder activated carbon was functionalized with TiO2 using of titanium tetraisopropoxide (TTIP) as TiO2 precursors by sol-gel method.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the particle size and morphology.

Batch sorption and photocatalytic experiments were carried out under magnetic stirring at 20°C into a RS-1 photocatalytic reactor (Heraeus, Germany), under dark and UV irradiation.

Results and conclusions

XRD results presented in Fig 1 showed that the anatase form of TiO2 is predominant phase.

Both SEM images of G-TiO2 and P-TiO2 indicated the non-homogeneity immobilization of TiO2 agglomerates onto the surface of activated carbon. The TiO2 dispersion depended on the activated carbon morphology and size, the lower size of activated carbon the better dispersion of TiO2 (Fig. 2).

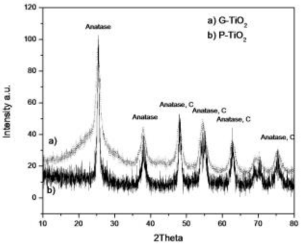


Figure 1: XRD pattern for a) G-TiO_2 and b) P-TiO_2

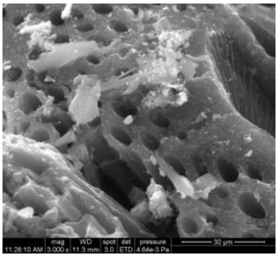


Figure 2a) SEM image for composite material G-TiO_2

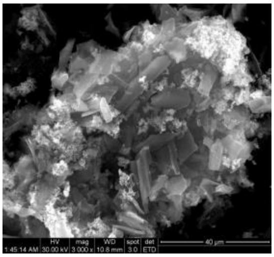


Figure 2b) SEM image for composite material P-TiO_2

Functionalization of activated carbon with TiO2 lowered sorption capacity for powder form that exhibited the best sorption capacity, while for granular form the sorption capacity is slight increased by TiO2 presence (Fig. 3). The photocatalytic activity of TiO2 is manifested by improving HA removal efficiency especial for granular form and also in longer lifetime of activated carbon until regeneration stage.

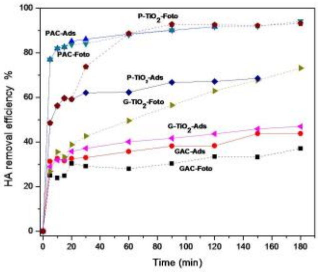


Figure 3: Evolution of process efficiency versus time for the removal of 25 mgL^{-1} HA from water using PAC, GAC, P-TiO_2 and G-TiO_2 catalysts by application of the sorption and photocatalysis processes

Acknowledgements: This work was supported by the Romanian National Research Programs PN 16 14 02 02 and PN-III-P2-2.1-PED-2016, PED 69/2017.

CATALYSTS FOR SELECTIVE CATALYTIC REDUCTION OF NO_X EMISSION

Tatjana Juzsakova[1,*], Zsofia Ifju[1], Noor Al-Jammal[1],
Igor Cretescu[2], Endre Domokos[1], Jozsef Nemeth[1],
Viktor Sebestyen[1], Akos Redey[1]

[1)] Institute of Environmental Engineering, University of Pannonia, 10 Egyetem St., Veszprem, 8200 Hungary
[2)] Gheorghe Asachi Technical University of Iaşi, No.73, Blvd. Mangeron, 700050, Iaşi, Romania,
[*]: *yuzhakova@almos.uni-pannon.hu*

Introduction and study objectives

Implementation of cleaner technologies is foreseen as one of the solutions for the existing environmental problems including the reduction of nitrogen oxides (NOx : NO and NO_2) and N_2O emissions. Improvements in reduction of the nitrogen oxides emissions can be accomplished by development of efficient catalysts for the decompotion of NOx in the technological processes. During recent years strict national and international regulations (e.g. Kyoto Protocol) had been introduced regarding the greenhouse gas emissions involving N_2O gas reduction as well. The primary sources of NOx (NO and NO_2) are fossil fuels, transportation and main source of N_2O are nitrogen industy and agriculature. High NOx concentration in ambient air results in serious problems such as photochemical smog or ground-level ozone formation, heatlh impacts and NOx made seroius impact on global warming and climate change as well.

In this work classical type of vanadium oxide-titania (V_2O_5/TiO_2) and new type iron-zeolite (Fe-ZSM-5) catalysts were studied and their acitivities were compared in the decomposiotion reaction of NOx during Selective Catalytic Reduction (SCR) where ammonia (NH_3) was used as reduction agent in the chemical process.

Methodology

The aim of the work was to study the physical-chemical, morphological properties of commercial available V_2O_5/TiO_2 and Fe-ZSM-5 catalysts by BET, XRD methods as well as SCR of NOx reaction conditions (such as reaction temperature range, NH_3/NOx feed, reactant amount) towards catalytic activity enhancement. The reaction temperature range was 200-450 °C, NH_3/NOx feed ratio was 0.9, 1.2, 1.6 and 2.2; the reactant concentrations were $C_{NOx\ avarage}$ = 4800 ppm, C_{NH3} = 4484 (5970, 7451 and 10400) ppm. SCR of NOx process was carried out in flow reactor with loading of 80 cm^3 catalyst. The main SCR reactions are the followings:

$$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O$$
$$6NO_2+8NH_3 \rightarrow 7N_2+12H_2O$$

Compressed air of constant amount of 1066 Ndm^3/h was used as source of oxygen for each catalytic run. The NO and NO_2 gases were bubbled through phosphoric acid scrubber and the concentrations were determined in the cooled outlet gas flow by non-dispersive infrared (NDIR) method using (Maihak UNOR 6N/convector HI 50 N) NO/NOx analyzer.

Results and conclusions

The V_2O_5/TiO_2 catalyst of spheric form having 3 mm diameter containes 10 wt % vanadia on titania (anatase) having surface area of 39 m^2/g and has avarage pore diameter of 21nm. The Fe- ZSM-5 zeolite catalyst with a rod shape of 3-10 mm containes 0.67 wt.% Fe and has Si/Al=31.3 ratio. Its surface area is 311m^2/g with average pore diameter of 2.5nm.

The studied SCR of NOx catalysts showed different and relatively broad optimum of operation temperature between 70 and 90°C. Note that both catalysts are not recommended to be used below 230°C. At low temperature the ammonia reacts with NO_2 gas producing explosive ammonium nitrate NH_4NO_3 and ammonia nitrite NH_4NO_2. Those components are deposited in inlet/outlet space of the reactor leading to clogging problems. V_2O_5/TiO_2 catalyst has high activity in temperature range of 250-320°C. The maximum 80-82 % NOx conversion was reached at NH_3/NOx 1.2 feed.

Fig.1. shows the effect of the temperature on NOx conversion and NH_3/ NOx feed for Fe-ZSM-5 SCR catalysts.

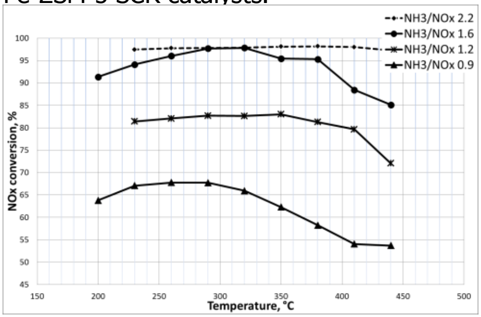


Figure 1: Effect of the temperature on NOx conversion and different NH_3/NOx feeds for Fe-ZSM-5 SCR catalysts

Zeolite based catalysts have been developed to function at higher temperature and it is supported by the outcome of our work as well. The Fe-ZSM-5 has higher NOx conversion of 97-98 % at 290-320°C at NH_3 /NOx 1.6 feed. At the highest NH_3 /NOx = 2.2 feed the conversion was constantly near to 98% in the studie temperature range. It is advisable to avoidfeed ratios much greater than 1 since it results in significant NH_3 slip (unconverted NH_3).

Fe-ZSM-5 is used also for the removal of N_2O gases e.g. during treatment tail gases from nitric acid plants.

Acknowledgement

This work was supported by GINOP-2.3.2-15-2016-00016 project: Excellence of strategic R+D workshops: Development of modular, mobile water treatment systems and waste water treatment technologies based on University of Pannonia to enhance growing dynamic export of Hungary.

NEW TiO_2-Ag NANOPARTICLES USED FOR ORGANIC COMPOUND DEGRADATION

Consuela Gómez de Castro[1], Catalina Nuțescu Duduman[2], Maria Harja[2,*], Doina Lutic[3], Tatjana Juzsakova[4], Igor Cretescu[2,*]

[1] Complutense University of Madrid, Faculty of Chemical, Department of Materials Science and Metallurgical Engineering, Av. Séneca, 2, 28040 Madrid, Spain
[2] Gheorghe Asachi Technical University of Iaşi, No.73, Blvd. Mangeron, 700050, Iaşi, Romania,
[3] University Alexandru Ioan Cuza Iasi, Blvd. Carol I No 11, 700506 Iaşi, Romania
[4] University of Pannonia, 10 Egyetem St. Veszprém, 8200 Hungary
: icre@tuiasi.ro; mharja@tuiasi.ro,

Introduction and objectives

In the latest years, nanomaterials were largely approached in research, due their specific, interesting properties. They are widely used as adsorbents, catalysts/photocatalysts, as magnetic materials, ceramic materials, semiconductors, biomaterials etc. These nanomaterials are intensively investigated due to their advanced photocatalytic performances, easy availability, stability in time, low toxicity etc. The TiO_2-assisted photocatalysis is used in a wide variety of applications and products from different fields. On another part, silver is a noble metal with exceptional antibacterial performance and its nanoparticles exhibit numerous applications as a disinfection agent in biomedicine, various therapies, as catalyst, photovoltaic applications and chemical sensing. Silver nanoparticles are usually prepared by the chemical reduction of a silver salt. TiO_2 nanoparticles with controlled properties are obtained by the simple and effective sol-gel method. The TiO_2-Ag nanocatalysts are cost-effective, efficient and environmentally friendly, being solids with highly efficient catalytic activity in the oxidation of organic compounds.

The main objective of this work was to prepare TiO_2-Ag nanocomposites and test their efficiency in the photocatalytic oxidation of stable organic compounds from wastewaters. The sol-gel method and chemical reduction were used as preparative methods.

Methodology

The TiO_2 nanoparticles were obtained using titanium isopropoxide ($C_{12}H_{28}O_4Ti$) as a precursor, while the Ag source was silver nitrate ($AgNO_3$). The activation of the sample was made by calcination at 650 ºC for 2 hours. The morphology and composition of the sample was performed by SEM, TEM, EDAX, XRD and DLS. The investigation of the porous structure was performed by BET nitrogen adsorption at 77K. The photocatalytic degradation was performed in a 500 mL glass reactor, equipped with a central quartz tube hosting an Osram UV-A lamp of 9W. The solutions were prepared using deionized water. The pH value was measured by a

Hanna HI 991003 pH-meter and settled to the desired value by adding sulfuric acid 0.1 M or sodium hydroxide 0.1 M. Prior to the photocatalytic run, the photocatalyst powder dispersed in the dye solution (Rhodamin 6G and Methylene Blue) was stirred for 30 minutes in dark, to reach the adsorption/desorption equilibrium, then the UV lamp was turned on. Samples of approximately 5mL were taken at defined time durations, filtered through 0.45 µm syringe filter and analyzed by spectrophotometry to measure dye concentration.

Results and conclusions

The structure type of TiO_2–Ag nanoparticles was investigated by powder XRD (Fig.1). The as-synthesized sample contains mostly anatase and quite an important amount of amorphous phase. The presence of Ag was confirmed by EDAX analysis and some small peaks in XRD pattern suggests the effective reduction of Ag metal at TiO_2 surfaces. After calcination at 650 °C, the solid contains both anatase and rutile phases and the metallic silver shows up as a distinctive phase, possible to identify in the XRD. The average particle size of calcined powder at 650°C was about 20 nm (calculated from Scherer equation). The TEM analysis allowed highlighting the presence of silver grains on the TiO_2 particles.

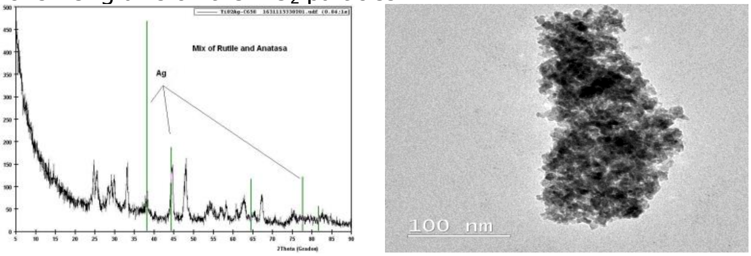


Figure 1. XRD and TEM analysis for TiO_2-Ag calcinated

The photocatalytic performances of the synthesized TiO_2-Ag nanocomposite were evaluated by photodegradation of two model organic dyes: rhodamine 6G (R6G) and methylene blue (MB) under UV irradiation (Fig. 2). MB was strongly adsorbed on the solid, then almost totally decoloriyed in less than an hour, while the R6G decomposition degree was of 42% in 120 minutes.

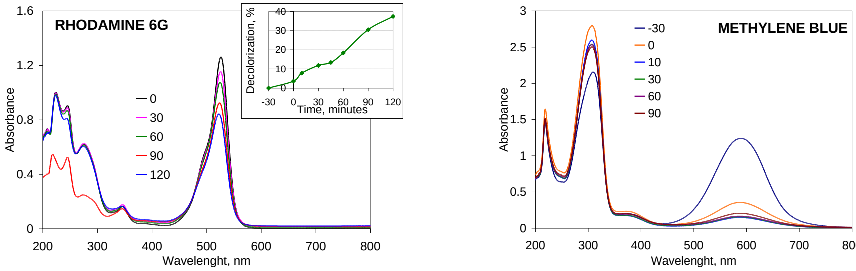


Figure 2: Evolution in time of UV-VIS spectra of Rhodamin 6G and Methylene Blue by adsorption and photocatalytic decomposition

DEVELOPMENT OF ADSORBENT FROM DEALUMINATED JORDANIAN ZEOLITIC TUFF IN OIL SPILLS CLEAN-UP (PRODUCTION, EFFICIENCY, UTILIZATION)

Noor Al-Jammal*, Tatjána Juzsakova, Ákos Rédey, Domokos Endre

Institute of Environmental Engineering, University of Pannonia, Veszprem, Hungary
*: *naljammal@almos.uni-pannon.hu*

Introduction and study objective

Spillage of crude oil in lands and in seas has triggered an interest in devising environment friendly and economic methods to clean up these pollutions and contaminations since the treatment of an oil spill remains a challenge to environmental scientists due to several hydrocarbon components which are toxic and exhibit a danger on the marine life, ecology and on the human beings. Adsorption is a popular technique, using sorbents such as activated carbon, polymeric resins and zeolites.

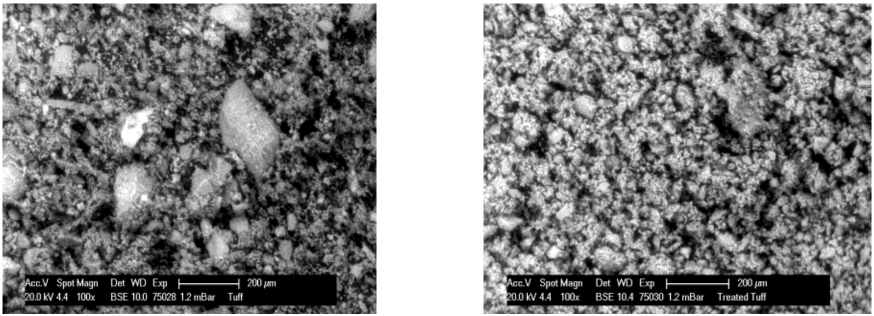
In this study, the possibility of using natural and modified Jordanian zeolitic tuff for removal of hydrocarbon as a model component of oil spills has been considered. A lot of attention is given to zeolite due to its exceptionally high adsorption capacity for oil–water separation and to their high hydrophobic properties as well as to the molecular sieve properties. Zeolitic tuff sieving properties, their ability to operate at the molecular level, and their excellent chemical, thermal and hydrothermal stability suggest that these materials may have technological potential as adsorbents in separation and purification processes in aqueous or wet media. The hydrophobic/organophilic character of high-silica zeolites has been long recognized by several researches. The hydrophobicity of Jordanian zeolitic tuff was enhanced by acidic treatment to dealumniate it, since the degree of hydrophobicity of zeolites is directly dependent on their aluminum content. This study aims at to examine the ability of natural and modified Jordanian zeolitic tuff to treat the oil-contaminated water by testing the adsorption capacity and removal efficiency. The effects of adsorbent dosage, adsorption time, initial oil concentration and kinetic modelling for the synthesized adsorbent were examined.

Methodology

Zeolitic tuff was obtained from the deposits of Tall Hassasn, Jabal-Arityan, south of Jordan and used as raw zeolitic tuff (RZT) with a SiO_2/Al_2O_3 ratio of 2.5. The method used in this work for treating RZT allows the separation of approximately 100 wt.% (mass fraction) 25 to 30 of other volcanic constituents (mainly iron, aluminum, magnesium, calcium and sodium oxides). Treated zeolitic tuff (TZT) has been used as adsorbent in this work and has been investigated by liquid N2 adsorption (BET method), X-ray diffraction (XRD), Energy dispersive X-ray (EDX) and scanning electron microscopy (SEM) to obtain information about the structural, chemical and physical characteristics of the synthesized adsorbent. Oil removal efficiency was investigated by TOC (TOC Vario elementar, detection range of 4 mg/l to 40,000 mg/l)

Results and conclusions

The purpose of acidic treatment is to increase the hydrophobicity of zeolite by removing aluminum and increasing the surface area of RZT by 71 % increment (from 77 to 270 m^2/g). As the degree of hydrophobicity of zeolites is directly dependent on their aluminum content. In simple terms, if the aluminum content decreased in zeolite the ionic charge of zeolite lattice will decrease. Less ionic charge means less polarity and so less hydrophilicity/more hydrophobicity. Structural changes and SiO_2/Al_2O_3 ratio were observed after HCl treatment of RZT and were proved by XRD and SEM analysis as illustrated in Fig. (1).



(A) (B)

Figure 1: Scanning electron micrographs of (A) RZT shows the associated materials covering RZT surface (B) SEM image for TZT

EDX was used in conjunction with scanning electron microscopy (SEM). EDX results give a further evidence for removal of aluminum and oxygen from the framework. Compared to raw zeolitic tuff (Z), the silicon to aluminum ratio increased to reach 15.1. Dealuminated modified Jordanian zeolitic tuff exhibits a strong hydrophobic/organophilic character (expected) since the adsorption data shows that the materials prepared were effective in sorbing petroleum compounds. The experimental data also revealed that the TZT achieved high oil removal efficiency to reach 98.98 % at room temperature.

Acknowledgement

This work was supported by GINOP-2.3.2-15-2016-00016 project: Excellence of strategic R+D workshops: Development of modular, mobile water treatment systems and waste water treatment technologies based on University of Pannonia to enhance growing dynamic export of Hungary

EFFICIENCY OF TWO PHOSPHOROUS SCALE INHIBITORS ON CALCIUM CARBONATE PRECIPITATION FROM RECLAIMED WASTEWATER USED FOR IRRIGATION IN A GOLF COURSE

H. Benlouali[1,*], **I. Karmal**[2], **M. Fallah**[3], **M.C. Harrouni**[4],
M. Hamdani[2], **R. Choukrallah**[1,5]

1) Salinity & Plant Nutrition Laboratory, Hassan II Institute of Agronomy and Veterinary Medicine, Agadir, Morocco
2) Laboratory of Electrochemistry, Catalysis and Environmental Science, Ibn Zohr University, Faculty of Science, Agadir, Morocco
3) Laboratory of Biotechnology and Valuation of Natural Resources, Ibn Zohr University, Faculty of Science, Agadir, Morocco
4) Department of Landscape Architecture and Environment, Hassan II Institute of Agronomy and Veterinary Medicine, Agadir, Morocco
5) International Centre for Biosaline Agriculture, Dubai, UAE, on leave from the Salinity and Plant Nutrition Laboratory, Hassan II Institute of Agronomy and Veterinary Medicine, Agadir, Morocco
**: h.benlouali@gmail.com*

Introduction and study objectives

The reuse of wastewater for irrigation has been widely considered as a major water resource within an integrated water management. In this framework, treated wastewater has been used for the irrigation of a golf course in Agadir, Morocco. However, because of its high content in soluble salts, the golf course is facing scale deposition ($CaCO_3$) that caused clogging of sprinklers and results in the non-uniformity of irrigation.

Continuous acid injection to prevent calcium carbonate precipitation is a classical approach but still complex and expensive. In the last decades, several new scale inhibitors have been reported to be efficient when injected continuously in quantities lower than 2 mg/L. As an example, phosphate based fertilizers are a good alternative, as they represent an additional source of fertilization while sequestering calcium and thus decreasing scaling tendency.

One of the methods to evaluate scaling tendency is the Fast-Controlled Precipitation (FCP). This method consists of CO_2 degassing from water using agitation and enabling to compare the scaling capacity using pH measurements in function of time. Thus, it shows the retarding effect of inhibitors on scale forming.

The objectives of this work were to: (1) study optimized experimental conditions for the FCP (temperature, agitation speed and water samples quantities); (b) compare scaling tendency and define the effect of different concentrations of two phosphate based fertilizers, namely MAP (Mono-Ammonium Phosphate) and DAP (Di-Ammonium Phosphate), on the reclaimed wastewater quality, using FCP method.

Methodology

A Fast-Controlled Precipitation experiment for a sample of reclaimed wastewater was set using different temperatures, agitation speeds and water samples quantities. The optimal values for each parameter was determined and used when studying the effect of MAP and DAP fertilizers on the reclaimed wastewater scaling tendency, using FCP method.

The fertilizers were tested at different concentrations based on their phosphate content. The MAP was tested at concentrations of 0 - 0.5 - 1 - 1.5 - 2 mg/L, while the DAP was tested at 0 - 2 - 5 - 8 - 10 mg/L.

The FCP method was performed as follows: on a heating plate, each fertilizer concentration was added separately, to the reference water that was put in a beaker and connected to a pH-meter, a thermometer and a magnetic stirrer. The pH was recorded in the course of time.

Results and conclusions

Application of phosphorus based fertilizers permitted to extend the time necessary for the precipitation of calcium carbonate (germination time) in the reclaimed wastewater. The germination time increased in correlation with the amount of MAP and DAP added to reclaimed water. The addition of 2 mg/L of MAP or 10 mg/L of DAP permitted the total inhibition of calcium carbonate precipitation for more than 2 hours under experimental conditions.

The inhibition of scale precipitation by phosphorous based fertilizers seems to be an interesting technique. It allows phosphorus supply to the crops and at the same time it avoids or at least retardates the clogging of the irrigation system. The estimated cost for phosphorus application is 0.0024 USD/m^3 when using MAP, and 0.003 USD/m^3 for the DAP.

Acknowledgements:

This study is supported by the AGROTECH Souss-Massa Association.

SYNTHESIS AND CHARACTERIZATION OF Zn_2TiO_4 USED IN DESULPHURISATION PROCESSES OF WASTE GASES WITH H_2S CONTENT

**Madelene Annette Dancila[1], Simona Caprarescu[1],
Violeta Purcaru [2], Eugeniu Vasile[3], Cristina Modrogan[1,*],
Alina Melinescu[1]**

[1)] „Politehnica" University of Bucharest, Faculty of Applied Chemistry and Materials Science, Ghe. Polizu Street # 1-7, 011061, Bucharest, Romania
[2)] National Research and Development Institute for Chemistry and Petrochemistry — ICECHIM, Splaiul Independentei, no. 202, 060021, Bucharest, Romania
[3)] Institute of Research and Development"METAV" SA, C.A.Rosetti Street # 31, 020011, Bucharest, Romania
[*] : cristinamodrogan@gmail.com

Introduction and study objectives

The work integrates with actual concerns regarding the prevention of the atmosphere pollution with sulphur compounds, as they are the most important atmosferic pollutants agents. A current concern regarding the atmosphere's pollution with sulfur compounds is the desulphurization of the raw materials or intermediate gasses when the predominant form of sulfur compounds is the hydrogen sulphide. An efficient desulphurisation system must achieve a high desulfurization yield, which implies, on the one hand, an advanced purification of industrial gases, and on the other hand, a high capacity for sulfur capture. Therefore, ZnO-based sorbents can be used.

The introduction of TiO_2 in the Zn mass has the advantage that ZnO is not reduced anymore by other gases. The main sources of sulfur compounds are coals or petroleum products used in order to obtain energy. The research aims to establish the optimum conditions for the calcination of zinc titanate sorbents getting Zn_2TiO_4 form, which is stable and has a very good reactivity in order to achieve the desulfurization process of waste gases.

Methodology

Depending on the mixing molar ratio of ZnO: TiO_2 and the preparation & calcinations conditions you can get different zinc titanates type $ZnTiO_3$, Zn_2TiO_4, $Zn_2Ti_3O_8$. Previous studies on the molar ratio ZnO:TiO_2 showed that for a ratio of 2:1 the predominant titanite form was Zn_2TiO_4. Therefore we chose the molar ratio between ZnO:TiO_2 to be 2:1 and we changed the calcination conditions.

The desulphurisation sorbent was prepared through a semi-wet mixing method between zinc oxide (type wurtzite) and titanium oxide (type anatase).

The paste obtained was dried at 105°C, precalcinated at 300°C and then calcined at different temperatures: 500, 600, 700, 800°C.

After preparation the samples were analyzed from a structural, morphological, and textural point of view through X-ray diffraction, scanning electron microscopy (SEM), FT-IR spectroscopy, adsorption isotherm.

Results and conclusions

The heat treatment undergone by the desulfurization sorbent of ZnO-TiO_2 induces compositional, structural and textural changes.

Increasing the calcination temperature was performed in order to obtain a certain type of zinc titanate with increased stability that can be used in the desulfurization processes of waste gases with containing H_2S. This zinc titanate is Zn_2TiO_4 type.

The structural sorbent characterization was made from X-ray diffraction and was evidential that at 300°C and 500°C temperatures only ZnO (würtzit form) and TiO_2 (majority anatase form) were identified.

Starting with 600°C calcination temperature, in the spectrum appear $ZnTiO_3$ and Zn_2TiO_4, and zinc titanate forms. The percentage of obtained titanates is small at this temperature, up to 8% with the specification that Zn_2TiO_4 forms is a priority.

At 700°C calcination temperature most zinc oxide and titane oxide quantities were transformed into zinc titanate but only Zn_2TiO_4 is identified, a fact which confirms that from the cristalization form of TiO_2- anatase Zn_2TiO_4 will be obtained.

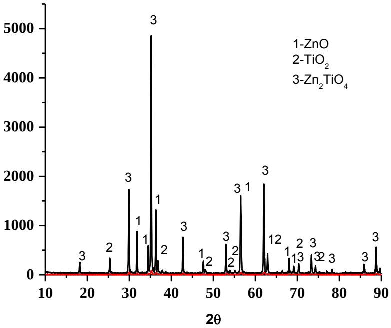


Figure 1: XRD spectrum of ZT-700

Subjecting the sample of sorbent at a temperature of 800°C calcination reinforces the idea that in order to obtain zinc titanate the calcination temperature should be above 700°C for Zn_2TiO_4 formation. All these analyses have revealed that the sample calcinated at 700°C leads to the synthesis of zinc titanate to Zn_2TiO_4 form.

This form has the qualities necessary to be used as sorbent in coal advanced desulphurisation processes.

NANOPARTICLES OF SILVER/LAYERED DOUBLE HYDROXIDES AS NANOARCHITECTONICS WITH SOLAR PHOTOCATALYTIC RESPONSE IN ENVIRONMENTAL CATALYSIS

Diana Gilea, Mihaela Vizitiu[1], Doina Lutic[2], Gabriela Carja[1,*]

[1)] Department of Chemical Engineering, Faculty of Chemical Engineering and Environmental Protection, Technical University "Gh. Asachi" of Iasi,
Bd. Mangeron no.71, Iasi 700554, Romania;
[2)] Faculty of Chemistry, Alexandru Ioan Cuza University of Iasi, Romania
[*]: gcarja@ch.tuiasi.ro

Introduction and study objectives

In recent years increasing attention is given on designing complex nanocomposites systems engineered to act as efficient photocatalysts for degrading dangerous pollutants. For nanostructured catalysts the unique nano-dependent transport properties related to photons are able to establish specific photoresponsive functions that cannot be achieved by their bulk counterparts. In this regard, manipulation of the photocatalytic properties by selective control of the catalyst nanoarchitectonics and by utilizing the collective properties of nanoassembly systems is a continuous challenge. Design of photocatalysts nanoarchitectonics refers not only to their simple construction as nanomaterials but also to ensemble different nanoscaled structural building units in designed and defined ways for creating complex formulations owning collective and synergic properties. Layered double hydroxides (LDHs) are a class of anionic clays. An important property of LDHs is their structural "memory effect"; it refers to the structural reconstruction of the layered clay matrix when the metal mixed oxides, evolved after the calcination around 550°C, are exposed to the aqueous solutions containing anions.

In this work we present the photocatalytic effiecency of AgNPS/MgLDH and AgNPs/ZnLDH self-assembled nanocomposites for degrading phenol pollutant from the aqueous solutions. Phenol is a dangerous pollutant known as human carcinogen and is of considerable health concern, even at low concentration, thus the efficient removal from aqueous solutions is of high interest.

Methodology

Using the manifestation of the LDHs structural "memory effect" we have recently reported a simple fabrication procedure of nanoparticles (NPs) of metal or metal oxides/LDHs as self-enssembled nanocomposites. According to this procedure the LDH matrix is able to rebuild its structure by using the anions of the solution as interlayer anions and also to adsorb the metal cations of the aqueous solution and organizing them as nanoparticles (NPs) of metals or metals oxides on its surface-denoted as MeNPs/LDHs. Nanocomposites with a large compositional diversity can be designed by modifying either the nature of the metal cations of the LDHs layers and/or the nature of the NPs from the surface. Nanoparticles of silver has attracted a great deal of attention in the last years. Hence, the joined functionalities of NPs of Ag and the specific ZnLDH and MgLDH composition might give rise to unique photoresponsive characteristics.

AgNPs/MgLDH and AgNPS/ZnLDH tested catalysts were thoroughly investigated by XRD, TG/DTG, XPS and UV-vis spectroscopic techniques in order to obtain information on their crystalline structure and identity, their Au content and photoresponsive properties. The morphology charcateristics of the samples were observed by TEM analysis.

Results and conclusions

Results show that AgNPs/MgLDH and AgNPS/ZnLDH nanoarchitecture consists of nanoparticles of Ag, with an average diameter of 7 nm, deposited on the larger nanoparticles (~100 nm) of the LDHs. The size of AgNPs increased for the catalysts calcined at 550°C. UV-Vis analysis and the calculated optical direct band gap (Eg) values indicate the high absorbance capability of the samples under UV and solar light and the formation of Ag-LDHs heterojunctions.

After 7 hours, over the entire range of wavelength, AgNPs/ZnLDH, obtained by photoirradiation, shows the highest degradation efficiency of phenol with almost 90% degradation under solar irradiation while AgNPS/ZnLDH calcined at 550°C shows the maximum activity, degrading almost 57% of phenol. This reveals that the uncalcined samples are the most effective catalysts , under the UV irradiation, pointing out that the surface OH groups are an advantage for the photocatalytic process. Comparing the photocatalytic systems described in this study, the best efficiency for the phenol photodegradation from the aqueous solutins was observed for the AgNPs/ZnLDH and AgNPs/MgLDH where the resulting degradation slurry contains no traces of p-benzoquinone, the mineralization products being CO_2 and water. Moreover, it is noteworthy that the presence of highly hydroxylated brucite-type sheets in the LDHs structure is an advantage for the photodegradation process of phenol.

The catalysts architecture clarified here for AgNPs/MgLDH and AgNPs/ZnLDHand the derived mixed oxides obtained by LDHs calcination may contribute to open new perspectives in designing complex nanoarchitectonics based on LDHs for obtaining efficient solar responsive photocatalysts.

CATALYTIC OZONATION OF ORGANIC POLLUTANTS USING APATITIC MATERIALS

Radu Claudiu Fierascu[1], Irina Fierascu[1], Bogdan Trica[1], Sorin Marius Avramescu[2,*], Corina Bradu[2], Alina Elena Olaru[2], Angel Nica[2]

[1] The National Institute for Research & Development in Chemistry and Petrochemistry-ICECHIM, 202 Spl. Independentei, 060021 Bucharest, Romania
[2] University of Bucharest-PROTMED Research center, 36-46 M. Kogalniceanu Blvd., 050107 Bucharest, Romania
[*] : sorin_avramescu@yahoo.com

Introduction and study objectives

In the hydrologic cycle, water is the basis for food production, trade, human needs and a healthy aquatic ecosystem. According to the Water Framework Directive (WFD) 2000/60/EC of the European Council and Parliament, which sets the framework for Community policy on field of water, "*Water is not a commercial product like any but a heritage which must be protected, defended and treated as such*". Due to the diversity of industrial and agricultural activities anything can come across in the polluted aqueous effluents like: heavy metals, dyes (since the invention of synthetic dyes 8000 of these compounds have been discovered and used in the industry), endocrine disruptor compounds, phenols, detergents, pesticides, etc.

The largest user of freshwater resources is agriculture, and also, agriculture is both cause and victim of water pollution. Oxidation processes cannot be effective in the purification of a large part of industrial effluents and, even were applicable; the energy consumption could be prohibitive from the economic point of view. A significant part of pollutants escape to the current treatment methods and reach surface and ground waters. Therefore, in spite of great success in treatment of water and wastewater the existing bottlenecks (high costs to obtain adsorbents, diffusion limitation which hinder the process, large amount of solid waste after use) limits the application of adsorption processes. In order to improve the process performance a new approach is required. In this context many researchers shows that nanotechnologies can be harnessed to solve critical development problems, including wastewater pollution.

The objective of the study is to demonstrate the effect of ozonation and decorated hydroxyapatite (at nanoscale) on loaded water with organic pollutants (endocrine disruptor compounds – EDC).

Results and conclusions

The use of hydroxyapatite and substituted hydroxyapatite as potential adsorbents for the removal of organic pollutants was already presented by our research group. However, the use of hydroxyapatite and metal-decorated hydroxyapatite for the catalytic ozonation of organic pollutants represents an approach far less studied.

In the present study, hydroxyapatite was synthesized and metal-decorated, using two different approaches: a *salt-approach* (decoration with metallic ions from their respective salts solution) and a *nano-approach* (*in-situ* decoration of metallic nanoparticles). The obtained materials were analytical characterized (using X-Ray Diffraction, X-Ray Fluorescence, (Scanning) Transmission Electron Microscopy, BET), confirming the synthesis and metal-decoration.

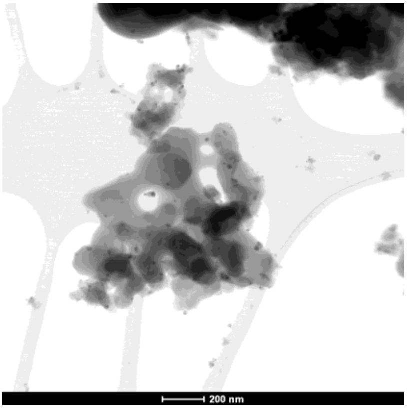


Figure 1: Representative STEM image of metal-decorated hydroxyapatite

The effect of the catalytic ozonation was determined using High Performance Liquid Chromatography, focusing on endocrine disruptors (especially Ibuprofen). Some of the main operating parameters like temperature, catalyst and ozone doses exerted a positive influence in the ozonation rate. Also, leaching tests were performed, in other to study the stability of the proposed materials.

The results obtained demonstrate that the prepared apatitic materials have a significant potential for the catalytic ozonation of organic pollutants.

Acknowledgement

This work was supported by grants of the Romanian National Authority for Scientific Research and Innovation, CNCS/CCCDI – UEFISCDI, project number PNIII-P2-2.1-PTE-2016-0063 and project number PN-III-P2-2.1-PED-2016-0198, within PNCDI III.

CLEAN TECHNOLOGY DEVELOPMENTS IN THE CHEMICAL INDUSTRY

Noor Al-Jammal*, Tatjana Juzsakova, Endre Domokos,
Jozsef Nemeth, Viktor Sebestyen, Akos Redey*

Institute of Environmental Engineering, University of Pannonia, 10 Egyetem St., Veszprem, 8200 Hungary
*: *naljammal@almos.uni-pannon.hu; redey.akos@gmail.com*

Introduction and study objective

Cleaner production is an efficient way to prevent and avoid the industrial pollution caused by the chemical and other industrial activities. The basic objective of all technology developments is to reduce, mitigate the pollution emissions into air, water or soil. The most important goal is to contribute to the improvement of the quality of life and to provide healthy environment for the people. The clean or cleaner technology means any process, procedure, product or public service, which supports the realization of the sustainable development by eliminating the emissions into the environmental elements and systems.

The scope of the cleaner technologies is very wide. Some available tools can be mentioned, e.g.: LCA, eco-balancing, environmental impact assessment, environmental performance evaluation, environmental management systems, etc.

Methodology

The paper deals with two major topics in the field of chemical industrial technologies. The first discusses the developments in ammonia synthesis, the second topic deals with the production of biodiesel fuel with using agricultural wastes to produce potential high quality of diesel fuel component.

Results and conclusions

The steam reforming is the first step in the ammonia synthesis since it is indispensable to procedure hydrogen for the ammonia synthesis which is a vital step to produce fertilizers. The heterogeneous catalytic process is complex chemical conversion including several chemical reactions which are to be taken into consideration. The mathematical modelling of the chemical reaction and the optimization of the reaction parameters are necessary to increase the capacity of the ammonia plant. The conversion of the synthesis gases to ammonia, the recycling of the unconverted hydrogen and nitrogen after the cooling and separation are important to provide high yields and capacity for the next reaction steps to produce fertilizers for the agriculture.

The agricultural wastes exhibit significant environmental problems all over the world and the utilization of the agricultural waste into potential raw materials is an important target.

In this study biodiesel production using waste vegetable oil (WVO) over naturalmzeolitic tuff from Jordan as heterogenous catalyst was studied. The results showed that Jordanian zeolitic tuff is an attractive and promising solid catalyst for the preparation of biodiesel from WVO. Moreover, the physical and chemical properties of the produced biodiesel were determined. The results showed that most of the produced biodiesel properties meet the specifications of the EN and ASTM standards for biodiesel.

The highest yield of biodiesel was achieved with a MeOH/ waste vegetable oil ratio of 0.5 v/v (11.5 M ratio), catalyst concentration was 6.4 wt./wt. and 50°C reaction temperature was used. A yield of approximately 96.7% was achieved at reaction time of 2 hours. The cetane number of the bodiesel produced was 70.30. This value is higher than that of diesel fuel with CN of 52, thus the fuel cut with good ignition characteristic had been produced. It is to be mentioned that the catalyst used is a promising catalysts due to its reasonably high activity, ease of preparation, simple separation and low cost. This way the biodiesel production from waste vegetable oil is economically feasible.

Acknowledgement

This work was supported by **GINOP-2.3.2-15-2016-00016** project: Excellence of strategic R+D workshops: Development of modular, mobile water treatment systems and waste water treatment technologies based on University of Pannonia to enhance growing dynamic export of Hungary

REMOVAL OF BISPHENOL A IN AQUEOUS SOLUTIONS USING DIFFERENT CARBON NANOMATERIALS (CNM). SIMPLE MODELS OF ADSORPTION

I.Ion[1], R. M. Senin[1,2], R. Stoica[2], S. Doncea[2], A. C. Ion[1*]

[1)] University Politehnica of Bucharest, 313 SplaiulIndependentei, 060042, Romania
[2)] National Research & Development Institute for Chemistry and Petrochemistry ICECHIM,
202 SplaiulIndependentei Str., 060021, Bucharest, Romania
[*]: ac_ion@yahoo.com

Introduction and study objectives

Carbon nanomaterials (CNM) present interesting properties which offer them potential for environmental applications. Carbon nanomaterials, especially nanotubes and fullerene can be detected in environmental matrices as a result of several production processes. Taking into account their hydrophobic surface, there appears strong interactions between organic pollutants and carbon nanomaterials. The adsorption of organic compounds by CNM sorbents depends on conditions such as: contact time, amount of adsorbent, initial concentration of adsorbate, temperature and pH.

In the literature there are presented examples of nanotubes (CNTs) and fullerenes used for the removal of one of the several environmental organic pollutants from water by adsorption. Bisphenol A (BPA) is an endocrine disruptor which was intensively studied in the last years.

This paper describes preparation procedures for stable dispersions of fullerene C60 and MWCNTs further used as sorbents for bisphenol A, an important endocrine disruptor. Several influences over the sorption process are studied and sorption models are discussed. Future applications of the studied CNM as environmental sorbents for certain organic pollutants are envisaged.

Methodology

Pristine fullerene C60 and MWCNTs were purchased from Aldrich (USA). Bisphenol A (> 99 %) and all the organic solvents used in these experiments were of chromatographic grade and there were purchased from Sigma Aldrich (USA). The C60 samples were dispersed before sorption studies by using a solvent exchange method and a physical mixing method. The suspensions obtained by all the methods mentioned above were then filtered with 0.45 µm cellulose acetate membrane filters to remove large C60 aggregates. The samples were kept in the dark at 4 ^{o}C and were stable for more than six months. In the sorption studies 50 mL of C60 suspensions were prepared with different concentrations of BPA and several influences such as: the initial concentration of BPA, the amount of CNM used as sorbent, the influence of the contact time, the temperature, the pH, the sample matrix were studied.

Results and conclusions

Physicochemical properties of the C60 adsorbents were studied, the results indicating that BPA is distributed on the surface of C60 as a monolayer. Fourier

Transformed Infrared optical spectra and thermogravimetric analysis are presented in Fig. 1 and Fig. 2.

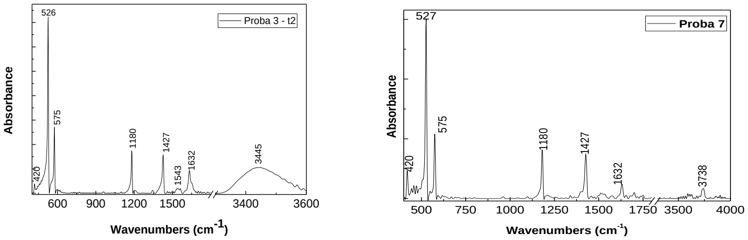


Figure 1: FTIR spectra of C60 before and after BPA adsorption

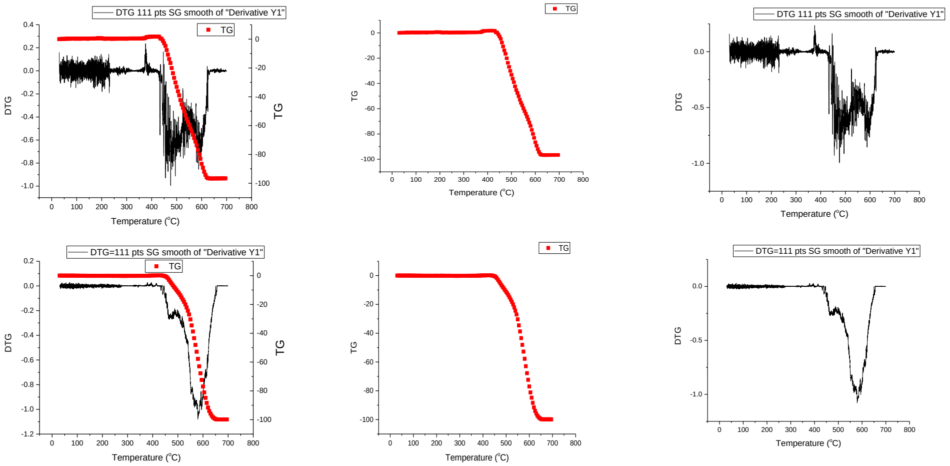


Figure 2: TGA curves of C60 before and after BPA adsorption

The adsorption isotherms of BPA to the studied CNM, kinetics and thermodynamics of the sorption process will be presented in the manuscript. Adsorption data were fitted with the Freundlich model q=KFxCn, where q (mmol/kg) and C (mmol/L) are the equilibrium concentrations of BPA on C60 and MWCNTs and in solution, respectively; KF (mmolL-1/kg) is the Freundlich affinity coefficient and n is the Freundlich linearity index. The Freundlich model fits the adsorption data reasonably well, the fitting parameters being presented in the manuscript. These results further demonstrate the complex mechanism controlling the interactions between the studied CNM and the organic contaminant BPA, having significant effects for the environmental assessment of the risk analysis.

Acknowledgments: This research was performed in the frame of ERA-NET SIINN, funded by the European Commission within the 7th Framework Programme and supported by the Romanian Executive Agency for Higher Education and RDI Funding (Unitatea Executiva pentru Finantarea Invatamantului Superior, Cercetarii, DezvoltariisiInovarii: UEFISCDI).

THE POTENTIAL APPLICATION OF MINERAL SORBENTS FOR THE SIMULTANEOUS REMOVAL OF DISPARATE ORIGINATING POLLUTANTS

Maja Đolić[1,*], Vladana Rajaković-Ognjanović[2], Milica Karanac[3], Ljiljana Janković-Mandić[1], Antonije Onjia[1], Ljubinka Rajaković[4]

1) Vinča Institute of Nuclear Sciences, University of Belgrade, Serbia
2) Faculty of Civil Engineering, University of Belgrade, Serbia
3) Innovation Center of the Faculty of Technology and Metallurgy ltd. In Belgrade, University of Belgrade, Serbia
4) Faculty of Technology and Metallurgy, University of Belgrade, Serbia
** : mirkovic.maja@gmail.com; mdjolic@vinca.rs*

Introduction and study objectives

Minerals are widely spread substances in the environment and their physical and chemical properties strongly depend on geological formations. The prevalence of minerals has a significant impact on ion exchange and adsorption capacity when present in soil and/or sediment, as well as on the acidity and porosity of the matrix. The large internal and external surface area of such covalent bound materials enables various pollutants to be adsorbed, whether originating from a solid or aquatic medium. Therein, the abundance of mineral materials improves the quality of water and soil which may indirectly impact human health. A variety of heavy metals may be present in natural form of a number of minerals; therefore, prior to their use as a sorbent, they must be purified. The aim of this study has been to investigate the ability of natural minerals previously purified by different extraction solutions to inactive microbial cells and remove silicon ions when combined in a mixture. The material's purification allows for the mineral sample to be utilized for the simultaneous removal of disparate originating pollutants. Therefore, the potential of minerals may prove to be promising in biochemical applications in environmental remediation technologies when used as sorbents and antimicrobial carriers.

Methodology

A natural mineral sample, a mixture of quartz, clinoptilolite and calcite, was the subject of purification in order to decrease the content of heavy metals in the tested material. The sequential extraction procedure (SEP) in 5 consecutive iterations was performed by different 0.1 M solutions: HOAc, EDTA, and EDTA/NaOAc-HOAc. The sorption and desorption experiment were carried out in singular batch mode, under slightly acidic conditions, as well as stimulated by ultrasonic and magnetic stirring, respectively. Mineralogical and radiochemical performances of the native and purified samples were determined by the X-ray diffraction (XRD) and gamma spectrometry techniques. A concentration of adsorbed and realized ions was detected by inductively coupled plasma optical emission spectroscopy (ICP-OES). Antimicrobial tests of HOAc, EDTA and EDTA/NaOAc-HOAc purified samples were performed by using the standard dilution method against Gram- negative bacteria *Escherichia coli*, Gram-positive bacteria *Staphylococcus aureus,* and fungi *Candida albicans*.

Results and Conclusions

The purification process of the natural mineral manifested in different aspects: i) decreased heavy metals content of the native sample; ii) improved sorption capacity; iii) adsorption of silicon ions; and iv) microbial cell removal from the aquatic medium. The highest decrease of heavy metal content was obtained using 0.1 M HOAc. The average decrease of the initial content of heavy metals (K, Ca, Sr, Cr, Mn, Fe, Ni, Cu, Zn, and As) in the raw sample was: 31.92 % using HOAc, 26.88 % using EDTA, and 25.95 % using EDTA/ NaOAc-HOAc. Conversely, the sorption capacity for the selected ions (Cr, Ni, Cu, Zn, Cd and Pb) had the following rate: EDTA/NaOAc-HOAc>EDTA> HOAc. The silicon-ions removal was the most effective using EDTA/NaOAc-HOAc treated sample. The results of the antimicrobial activity are presented in Table 1. The best antimicrobial activity was found in the EDTA/ NaOAc-HOAc purified sample against *E. coli* for a 24h exposure period.

Table 1. The Antimicrobial Activity of the Sample Purified by HOAc, EDTA, and EDTA/NaOAc-HOAc

Sample	***E. coli***		***S. aureus***		***C. albicans***	
	CFU/mL	**R (%)**	**CFU/mL**	**R (%)**	**CFU/mL**	**R (%)**
Control sample	$4{,}10 \times 10^5$		$5{,}50 \times 10^5$		$1{,}40 \times 10^5$	
Purified						
HOAc	$4{,}60 \times 10^4$	88,78 ± 0,1	$3{,}00 \times 10^5$	45,45 ± 0,2	$7{,}20 \times 10^4$	48,57 ± 0,2
EDTA	$7{,}70 \times 10^3$	98,12 ± 0,1	$2{,}70 \times 10^5$	50,91 ± 0,1	$6{,}00 \times 10^4$	57,14 ± 0,2
EDTA/NaoAC-HOAc	$4{,}20 \times 10^3$	98,98 ± 0,1	$2{,}40 \times 10^5$	56,36 ± 0,2	$1{,}00 \times 10^4$	92,86 ± 0,3

The biochemical application of the natural minerals in this study depends on the surface properties of the tested materials. The modification of the selected sample treated by different chemical agents and the appearance of new functional groups improved its sorption and antimicrobial characteristics.

A NEW APPROACH TO OBTAIN AEROGELS FOR GAS SAFETY APPLICATIONS

Corneliu S. Stan, Marcel Popa, Petronela Horlescu,
Gabriela Soreanu*, Igor Cretescu*

Technical University "Gheorghe Asachi" of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management,
73 D. Mangeron Blvd, Iasi 700050, Romania
**: icre@tuiasi.ro; gsor@tuiasi.ro*

Introduction and study objectives

Aerogels are versatile materials that can be tailored for various applications, such as thermal insulation, energy storage, flame retardancy, adsorption of undesirable compounds from different environmental compartments etc. On the other hands, one of the common barriers in aerogels application refers to the high manufacturing costs, which in turn can explain, for example, the lack in studies concerning the application of aerogels in environmental protection. These aspects suggest the research need for developing new preparation methods for obtaining cost-effective aerogels with assessed potential in practice.

This work presents a new approach for developing a cost-effective polymer aerogel dedicated to high-performance environmental application such as required in gas safety context. A model organic gaseous pollutant will be used to simulate a contamined environment for which a gas mask equipped with a specific material such as the actual developped aerogel would be required. Pointing out the particularities of the synthesis method and the influence of the material characteristics (e.g. pore-size) on the gas retention performance will be presented.

Methodology

The polymer aerogels were prepared using 2-Hydroxyethyl methacrylate and N,N′-methylene bisacrylamide as crosslinker. In the first step, the monomer and the crosslinker are dissolved in water followed by the addition of the photoinitiator (2-Hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone). The preparation path requires an intermediary stage for obtaining a polymer cryogel which undergoes at 250K in the presence of 320 nm UV radiation as excitation source for the photoinitiated polymerization. The final aerogel is obtained by freeze drying the resulted cryogel.

The resulted polymer aerogel (Figure 1) is highly porous with an interconnected pore structure with pore size in the hundreds nanometer – micrometer range. As could be noted from Figure 2 a,b as the amount of solvent used for cryogel preparation is raised, the pores dimensional characteristics are subsequently higher.

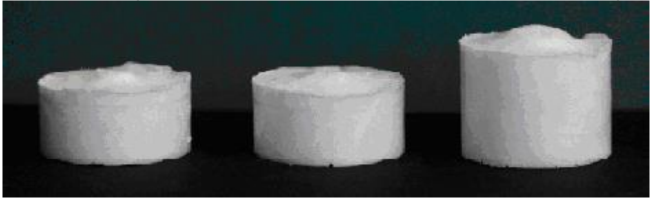


Figure 1: Prepared cylindrical shaped polymer aerogels with different porosities

The described method allows the tuning of the porosity degree of the aerogel by changing the amount of the solvent (water). The described method allows the preparation of aerogels with a density as low as 0,005 g/cm^3 which are among the lightest and porous materials prepared so far. Also, the prepared aerogels could be shaped according to the application requirements, by simply using a mould with the desired geometry in the intermediary stage of cryogel formation.

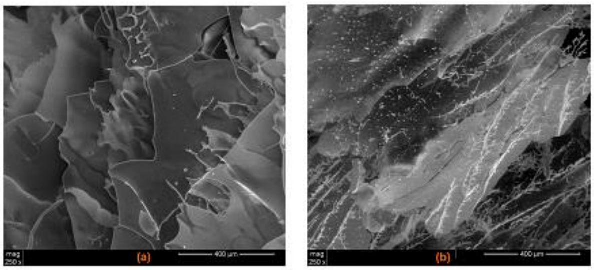


Figure 2: SEM micrographs of the prepared aerogels
(a) density 0,09 g/cm^3, (b) density 0,03 g/cm^3

Structural investigation of the prepared aerogels was performed using FTIR while the morphology of the resulted polymer aerogels was investigated using SEM and BET analysis. Thermal behavior was evaluated through thermal analysis.

Results and conclusions

The performance of the obtained aerogel (e.g. Figure 1) in the retention of a specific gaseous pollutant is depicted, along with the characteristics of the obtained material by the new approached method. Results of isobutylene retention from air on aerogels are comparable with those obtained on activated carbon (purification degree is > 95%) at small gas flowrates (e.g. 0.25 L/min), but are more sensitive to the gas flowrate increase. However, the results are promising and suggest the aerogel potential for a new interesting application. Recommandations for future application in the frame of gas safety context are provided.

SELF-ASSEMBLIES OF NANOPARTICLES OF GOLD/LAYERED DOUBLE HYDROXIDES AS EFFICIENT PHOTOCATALYSTS FOR THE SELECTIVE PHOTOREDUCTION OF CO_2

Diana Gilea[1], Elena Seftel[2], Gabriela Carja[1,*]

Department of Chemical Engineering, Faculty of Chemical Engineering and Environmental Protection, Technical University "Gh. Asachi" of Iasi, Bd. Mangeron no.71, Iasi 700554, Romania;
[*] :gcarja@ch.tuiasi.ro

Introduction and study objectives

The increase in CO_2 pollution and the deficiency in sustainable energy sources have driven the need for research aimed at obtaining energy-rich chemicals using light energy, H_2O and CO_2. A key technological target to reach efficient photo-conversion of CO_2 to fuels (i.e. artificial photosynthesis) is to develop a performant and robust photocatalyst. Extensive research has been devoted on obtaining cost-effective materials able to efficiently and selectively drive the photoreduction of CO_2 by H_2O, under mild conditions. Among the various semiconductor photocatalysts tailored compositions of layered double hydroxides are promising photo-responsive catalytic formulations. Layered double hydroxides ($Me^{2+}Me^{3+}$LDHs) are layered porous matrices belonging to the class of anionic clays with many actual and potential applications in catalysis. Defined by a versatile chemical composition $Me^{2+}Me^{3+}$LDHs have basic properties while their thermal treatment around 600°C gives rise to porous mixtures of mixed oxides. An important factor limiting the conversion efficiency of almost every active photocatalyst is the high rate of charge-carrier recombination. Recently, it was demonstrated that the recombination problem is significantly alleviated by combining nanoparticles (NPs) of plasmonic metals (Au, Ag) and semiconductor supports. In NPs/support co-catalytic systems the manipulation of MexOy photo-responsive effects gives rise to specific electron transfers at the interface that reduce the charge-carrier recombination rate and facilitate the overall photocatalytic activities in which electrons are involved.

With an aim at exploring how the efficiency of CO_2 photoreduction might be enhanced by combining metal oxides nanoparticles (MexOy) and semiconductor supports we successfully prepared the self-assemblies of nanoparticles of Au/layered double hydroxides (denoted as AuNPs/LDHs) as novel photocatalysts for CO_2 reduction by H_2O, at room temperature. In this work we report, for the first time, the photocatalytic effiecency for CO_2 reduction to CO of AuNPs/ZnAlLDH and AuNPs/MgCeAlLDH.

Experimental details

ZnAlLDH and MgAlLDH (molar ratio 2/1) was obtained by coprecipitation method. Calcination at 600°C gives rise to secific mixtures of mixed oxides. AuNPs/ZnAlLDHs and AuNPs/MgCeAlLDH. as photocatalytic systems, were obtain by exploiting the structural „memory effect" of ZnAlLDH and MgCeAlLDH in specific Au salts (e.g. AuCl3) aqueous solutions of defined concentrotions and specific pH values within the range [4-5]. The morphology and structural characteistics of the obtained photocatalytic systems were studied using a Perkin Elmer diffractometer with filtered CuKα radiation (XRD), a field-emission scanning microscope (Jasco FESEM) and a transmission electron microscope (HRTEM Hitachi H900 operating at an accelerating voltage of 200 kV). UV-Vis absorption spectra were recorded on a Jasco V550 UV-Vis spectrophotometer equipped with an integration sphere for solids. For photocatalytic tests a closed circulating system equipped with a photoreaction quartz cell that had a flat bottom (32.1 cm^2) was employed. 170 mg of the LDH catalyst was uniformly spread in the photoreaction cell and was evacuated b at 294 K for 2 h until the desorbed gas was detected by an online gas chromatograph (GC).

Results and Conclusion

Results point that under irradiation with visible light of AuNPs/LDHS precursors conversion of CO_2 was lower than 21% though for the derived mixed oxides obtained after calcination at 550°C were enough active under UV irradiation. Furthermore, when solar light was irradiated onto AuNPs/ZnAlLDH and AuNPs/MgCeAlLDH the conversion of CO_2 to CO was 11 % and 17 %, respectively. Consequently, when UV light irradiated onto AuNPs/LDHs electron-hole pairs are generated, hence, CO_2 is reduced to CO by two photogenerated electrons. Considering that the process of CO_2 photoreduction to CO is induced by two photogenerated electrons in concluded that the assemblies of AuNPs with the anionic matrices of ZnAlLDHs and MgCeAlLDHs, respectively, might initiate a reduction in electron-hole recombination thus can contribute to the reduction of CO_2 to CO.

This work demonstrates, for the first time, how the joining contribution of nanoparticles of AuNPs and the specific compositions of ZnAlLDH and MgCeAlLDH might contribute to establish the conversion efficiency of CO_2 photoreduction to CO, by water, at room temperature.

DRONES IN ENVIRONMENTAL MONITORING

Tatjana Juzsakova[1], **Tamas Frater**[2], **Igor Cretescu**[3],
Endre Domokos[1], **Akos Redey**[1,*]

[1)] *Institute of Environmental Engineering, University of Pannonia, 10 Egyetem St. Veszprém, 8200 Hungary*
[2)] *PureAqua Kft.,6 Lőszergyári St., Veszprém, Hungary*
[3)] *"Gheorghe Asachi" Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, Iaşi, Romania,*
[*] *: redey.akos@gmail.com*

Introduction and study objectives

The Unmanned Aerial Vehicles (UAVs) or drones provide a new, highly efficient, economic alternative to the aerial environmental monitoring, e.g. photogrammetry, sensor based surveying or sampling. In photogrammetry, aerial photos taken from vertical axis are useful in geoinformation systems by transforming them into orthographic projection and use as map layers. These airborne photographs could be high-resolution conventional photos or lower-resolution photos but from a special, well-defined spectral range (multi/hyperspectal imaging, IR/UV imaging). Both of them can be used in environmental protection: the first one e.g. in natural disasters, forest fires or in the monitoring of natural reserve areas etc., the latter one is in the measurement and mapping of pollutants such as an oil spill on a lake or sea.

Methodology

In our survey, three UAVs were used, a so-called multicopter (a helicopter with several rotors), and two fixed wing aircrafts (Figure 1.) The aircraft types were the following: a MULTIPLEX Easy Star (a), a STYROMAN Smile (b) and a TAROT 690S hexacopter (c). The most important technology data of these UAVs could be found in Table 1.

Figure 1: The three UAVs used in the experiments

These UAVs were equipped with electric motors (TURNIGY and BLUE RAY types) and were controlled by a 2.4 GHz RC remote control system (FUTABA). A lightweight full-HD (1280×720) camera was used for imaging.

Table 1. The most important data of the UAVs used in the experiments

	MULTIPLEX Easy Star	STYROMAN Smile	TAROT 690S Hexacopter
Wingspan (m)	1,4	2,7	1,3 (total width)
Payload (g)	200	2500	3500
Flying weight (g)	800	4000…4500	>5000
Material	Plastic foam (Elapor)	Plastic foam (EPP)	Carbon composite
Price (EUR, 2016)	300	650	2 000

Results and conclusions

The flights were carried out in the area of Bakony Mountains, in Hungary. Several aerial photographs were taken on forests, agricultural fields and on ecological important territories, like wetlands. One of the investigated wetlands (a lake near to Csehbánya village) was found rather interesting, since a significant part of the lake exhibited the signs of eutrophication. The growth of algae is hardly detectable from the shore of the lake (ground view), however, it is clearly visible from the air (Figure 2). Since this algae growth has only been detected very recently, further investigations are necessary in different seasons to study the ecology of the lakes and to devise a solution for this problem, if necessary.

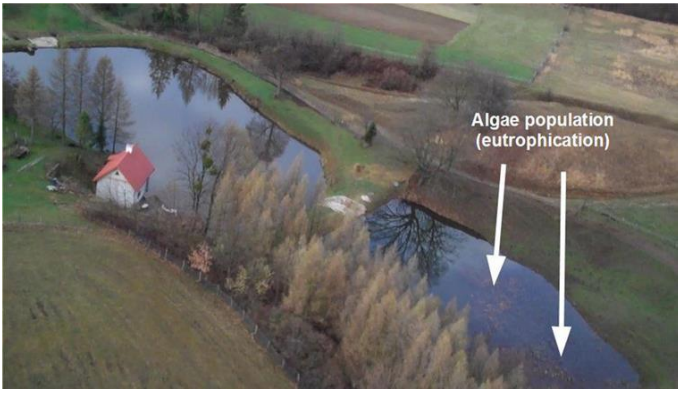


Figure 2: Image made by the authors on a lake in Bakony Mountains

It was found that UAVs are feasible for monitoring of natural reserve areas such as small lakes since they are very silent and - contrary to big aircrafts and helicopters - do not disturb the ecology even in natural reserve areas. Comparing the fixed wing aircrafts to multicopters it was concluded that multicopters possess the ability of hoovering providing more opportunities in aerial photographing (better accuracy), and need less clear area (e.g. a glade) for take off and landing.

Acknowledgement

This work was supported by **GINOP-2.3.2-15-2016-00016** project: Excellence of strategic R+D workshops: Development of modular, mobile water treatment systems and waste water treatment technologies based on University of Pannonia to enhance growing dynamic export of Hungary.

SECTION VI

MONITORING AND MODELLING OF ENVIRONMENTAL POLLUTION

MONITORING THE FATE OF A GENETICALLY MODIFIED MICROORGANISM IN A WASTEWATER TREATMENT PLANT

**Salvatore Puccio*, Andrea Nuzzo, Claudio Martina,
Gonzalo Martinez, Fabio Fava, Lorenzo Bertin, Giulio Zanaroli**

*Department of Civil, Chemical, Environmental and Materials Engineering (DICAM),
University of Bologna, via Terracini 28, I-40131 Bologna, Italy
: salvatore.puccio2 @unibo.it

Introduction and study objectives

Polyhydroxyalkanoates (PHAs) represent one of the most interesting biopolymers for replacing the petrochemicals-based plastics in various applications since it can be obtained from renewable resources by fermentation. Large-scale production-fermentations frequently use genetically modified microorganisms (GMMO) and generates big amounts of liquid waste, which must be treated to limit environmental (COD) and biological risks associated with the release of GMMO or their genetic material. Therefore, the aim of this study was to verify the fate of the genetic trait associated to a target mutant strain in terms of persistence and thus its possible release into the environment in case of delivery of mutant culture waste effluent to a conventional wastewater treatment plant.

Methodology

The GMMO used in this work (*Pseudomonas putida* KTOY06) was kindly provided by Prof. George Chen; obtained from the wild-type *P. putida* KT2440 after deletion of the genes *fadB* and *fadA* involved in the β-oxidation pathway. The growth of the GMMO was carried out in a 3 L bench-scale bioreactor (Sartorius Biostat B) using a mineral medium. Two different carbon sources were used: glucose during balanced growth of cells and octanoic acid for the accumulation of PHAs.

A scale-down of a typical plant was set up to simulate the wastewater treatment. The process consisted of 3 units, namely: the anoxic and aerobic reactors, and the settler. The system worked in continuous mode, with two recycle lines (Fig 1). The plant was fed with a synthetic solution that simulated the inlet of a municipal plant. After reaching the stationary state, the GMMO biomass obtained by fermentation was inoculated in the anoxic reactor. The mass ratio between the sludge and the GMMO was 2.5 grams of sludge per gram of GMMO biomass; potentially to occur at full scales.

All compartments of the simulating plant and the effluent were sampled at various time intervals to monitor the main chemical parameters and the GMMO persistence. An optimized protocol for the detection and quantification of *ΔfadBfadA* gene trait of the selected GMMO was developed based on selective amplification by qPCR (with SYBR green chemistry).

Results and conclusions

The simulating wastewater treatment plant achieved the stationary state after 26 h and showed good performances in terms of total nitrogen, total P and COD abatement. The addition of the fermentation broth containing the GMMO did not affect the waste treatment process. Only a slight alteration of the chemical parameters was detected after the inoculation, and the system was reestablished in the following 7 hours.

The molecular analysis allowed to detect the GMMO genetic trait at the inoculation time only in the anoxic reactor. The target genetic trait was detected in the other units after 20 minutes from inoculation. The total number of copies detected in the system was approximately constant for the first 7 hours (Fig. 2, orange line). During this time, the cumulative number of copies (Fig. 2, gray line) in the effluent achieved 5x10^{10}, corresponding to 7% of the inoculated amount. This implies a limited but significant release of the genetic material of the GMMO. Then, the total number of copies present in the plant (Fig. 2, blue line) decreased by several orders of magnitude, while the cumulative number in the effluent did not increase. The possible causes were: i) about 93% of the GMMO material was degraded during the treatment, or ii) the cumulative amount exiting in the effluent after 7 hours was diluted as a consequence of the sampling procedure and thus below the detection limit of the molecular assay. This last hypothesis is being studied by repeating the experiment with slightly modification on the effluent sampling. Finally, in order to better assess the risk of GMMO release, further studies are requested to associate the presence of detected gene copies with the occurrence of living GMMO cells which could be released through the effluent.

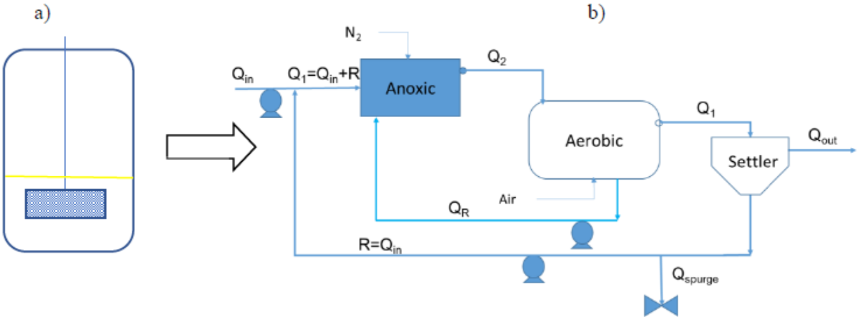


Figure 1: Experimental approach a) PHAs production and b) wastewater treatment plant at laboratory scale

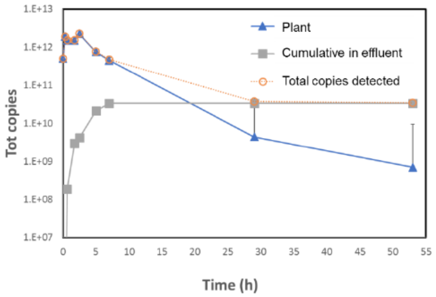


Figure 2: Trend of the total number of copies of the target gene

IDENTIFYING THE WEAKNESS OF LARGE CENTRALIZED WASTEWATER TREATMENT PLANTS OPERATING IN A CRITICAL AREA: THE CASE STUDY OF REGI LAGNI (SOUTHERN ITALY)

Raffaele Pica[1], Sabino De Gisi[2,*], Gianpaolo Sabia[1],
Michele Notarnicola[2]

[1)] ENEA, Department for Sustainability of Production and Territorial Systems, "Water, waste and raw materials integrated management technologies" Lab., Via Martiri di Monte Sole n. 4, 40129 Bologna (BO), ITALY
[2)] Department of Civil, Environmental, Land, Building Engineering and Chemistry (DICATECh), Technical University of Bari, Via E. Orabona n. 4, 70125 Bari (ITALY),
[*]: sabino.degisi@poliba.it

Introduction and study objectives

Centralized wastewater treatment systems provide for the collection of wastewater into the sewer and transportation in a wastewater treatment plant (WWTP), usually located on the urban area boundary. In line with the activities of the IWA Specialist Group on Large WWTP, the study of proper functioning as well as failures can provide useful information especially in the planning stage of such wastewater systems. With reference to the context of the Regi Lagni in Campania District (Southern Italy), the paper aims to identify the main weaknesses of five LWWTPs capable of treating a total of 2.2 million population equivalents (PE). The basin of Regi Lagni covers an area of approximately 1000 km^2 and includes a total of 99 municipalities (See Fig. 1). Still, it is considered a critical area from the environmental point of view because of the many critical environmental issues present in the area (i.e., waste management).

Methodology

The experimental plan has provided the following phases: (i) Characterization of the socio-economic activities that fall in the basin; (ii) Characterization of the quality of water bodies; (iii) Assessment of performance of the LWWTPs investigated; (iv) Identification of weaknesses as well as proposal of appropriate upgrading measures. The assessment phase involved the use of several performance indicators as reported in Table 1. Finally, the five LWWTPs investigated are as follows: Acerra; Foce Regi Lagni; Napoli Nord; Area Nolana; Area Casertana.

Results and conclusions

Table 1 shows the main results of the assessment phase. Overall, on 30 points highlighted by ENEA in 2001 for the investigated LWWTPs, there were 16 missed interventions, 10 worsening and 4 improvements. The improvements relate to the Area Nolana WWTP that has undergone a series of upgrading actions such as the realization of new oxidation basins, the implementation of the Ludzack-Ettinger process configuration, sand filtration and disinfection with peracetic acid (See Fig. 2).

The obtained results show the key role of the size: the smaller the size and greater the capacity to intervene effectively. Finally, the following weaknesses were identified: (i) Generalized inadequacy of the treatment scheme to comply with the new discharge limit values set by the Italian and European Law; (ii) Absence of efficient control systems both on the sewage system both inside the WWTPs.

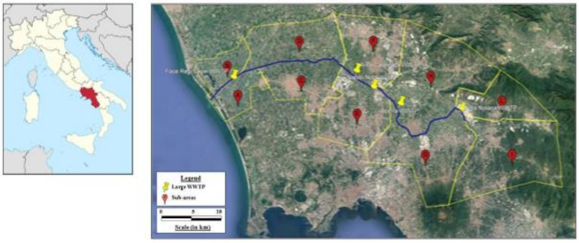


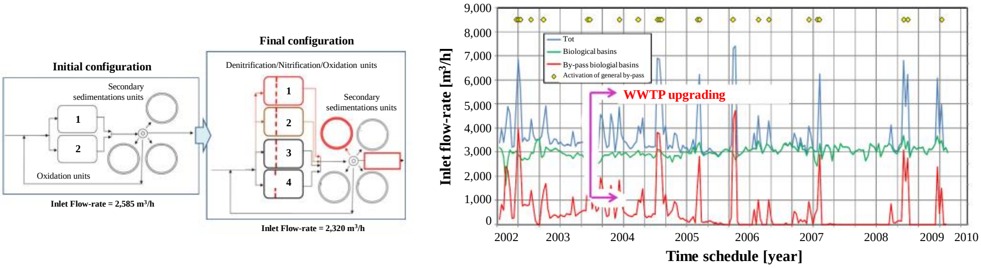
Figure 1: The study area: The Regi Lagni catchment area in the Campania District (Southern Italy).

Table 1. Synthesis of the treatment capacity of the WWTPs under investigation (initial phase).

WWTP	Indicator												
	Size				Water line efficiency			Waste to disposal		Electricity consumption [kWh/m^3]	Biogas production [m^3/month]	Personnel	
	Flow-rate [Mm^3/month]	PE_{des}	PE_{eff}	PE_{eff}/PE_{ds} [%]$^{(a)}$	%BOD$_5$	%TSS	%N-NH_4^+	Sludge [kg/m^3]	Sand [kg/m^3]			No.	10^3 m^3 pers day
Acerra	1.49	828,000	252,000	30.4	89.0	88.0	81.0	0.32	~0	n.a.	~0	47	1.05
	★★★☆☆	-	-	★☆☆☆☆	★★★☆☆	★★★☆☆	★★★☆☆	-	-	-	-	-	-
Foce Regi Lagni	3.21	632,000	500,000	80.0	84.0	72.0	20.0	0.00	0.04	0.16	~0	69	1.54
	★★★☆☆	-	-	★★★☆☆	★★★☆☆	★★☆☆☆	★☆☆☆☆	-	-	-	-	-	-
Napoli Nord	1.97	886,000	227,400	26.0	84.0	81.0	16.0	0.56	~0	0.56	~0	68	0.96
	★★☆☆☆	-	-	★☆☆☆☆	★★★☆☆	★★★☆☆	★☆☆☆☆	-	-	-	-	-	-
Area Nolana	2.56	311,000	406,000	130.0	93.0	88.0	80.0	0.16	0.125	0.48	~0	48	1.03
	★★☆☆☆	-	-	★★★☆☆	★★★☆☆	★★★☆☆	★★★☆☆	-	-	-	-	-	-
Area Casertana	4.58	800,000	850,000	106.0	85.0	78.0	47.9	0.30	0.015	0.22	26,000	84	1.08
	★★★★☆	-	-	★★★★★	★★★☆☆	★★★☆☆	★★☆☆☆	-	-	-	-	-	-
Total	-	3.5·10^6	2.2·10^6	65.0	86.0	80.0	48.0	0.20	0.03	0.29	26,000	316	1.19

(a): PE = Population equivalent; PE_{des} = design data; PE_{eff} = effective data;

(b): WWTPs quality status, legend: Insufficient = ★☆☆☆☆; Just sufficient = ★★☆☆☆; Sufficient = ★★★☆☆; Good = ★★★★☆; Excellent = ★★★★★.



a b

Figure 2: Example of upgrading actions realized in the study area. Considering the Area Nolana WWTP, the Figure shows: (a) New biological basins with denitrification/nitrifications tanks, secondary sedimentation and sand filtration before the difinfection; (b) Trend of the inlet flow-rate with particular attention to the by-pass flow-rate related to the biological section (in red).

REPRESENTATION OF DYNAMIC PARAMETERS FROM MULTIVARIATE CLIMATE DATA AND POTENTIAL APPLICATIONS IN POLLUTANT TRANSPORT AND DISPERSION

Marius Gavrilescu[*]

"Gheorghe Asachi" Technical University of Iași, Faculty of Computer Engineering and Automatic Control, Department of Computer Engineering, 27 Mangeron Blvd., 700050 Iasi, Romania,
[*]: mariusgav@tuiasi.ro

The prevalence and frequency of extreme climate phenomena has increased substantially in recent decades, which warrants the need for modern tools and methods for the prediction and analysis of unexpected and abnormal weather and climate-related events. Specifically, the frequency of hurricanes has increased substantially and correlates with an increase in the effects of global warming. Certain regions with particular weather and oceanic current flow patterns have seen a steady increase in the frequency and destructive effects of hurricane winds – for example, the American lower-east coast and multiple regions of Central America. As a consequence, there are on-going efforts to develop tools for the analysis of data acquired via meteorological radar in regions affected by on-going hurricanes, extreme phenomena associated with pollutant transport and dispersion. In this regard, we propose a visualization tool to represent complex hurricane scans in a comprehensive and intuitive manner. This approach also has significant potential in the evaluation of persistent pollutant dynamics in the atmosphere, especially where long distance transport is concerned. The input data consists of a discretized region of space where the data points are arranged in a regular grid of 500x500x100 resolution, spanning a volume of approximately 85.73 million km^3. Each data point is assigned multiple values representing parameters such as the concentration of water vapor, local temperature, pressure, wind speed and direction etc., which constitute factors with significant influence on the fate, transport and dispersion of persistent pollutants. The data is also available over multiple phases, each phase representing an instant of the scanned phenomenon at a point in time. Traditional means of analysing such data involve an inspection on a „slice-by-slice" basis, where a slice is a collection of data points from the same altitude and time phase. The visual or automated inspection of multiple such slices, over multiple time phases and incorporating multiple parameters values, can be a daunting and time consuming task. We therefore propose an approach where most of the information required for a thorough analysis is incorporated into the same image, thereby facilitating a rapid visual analysis of the data. We represent the data using a volume raycaster, a method which has seen common usage for medical imaging, but which can be easily adapted to meteorological scans.

Volume raycasting is a strongly-parallelizable image-ordered rendering method which allows leveraging the computational power of the Graphics Processing Unit (GPU) in order to achieve real-time rendering performance. We first reconstruct a continuous volume from the discrete data using linear interpolation via hardware-supported texture filtering. Then, the resulting volume is sampled along rays emitted from each pixel, and the corresponding data values are retrieved from the sampled position. Depending on the nature and purpose of the retrieved parameter values, a manually-adjusted transfer function maps the data values to visual properties (color and opacity). Subsequently, the color and opacity values of the sampled points are composited along each ray, resulting in a color value for the corresponding pixel. This approach allows for the representation of a large amount of data for different parameters and along multiple time phases in the same image without generating visual overload. The displayed information depends to a large extent on the type of analysis being carried out. For instance, the vector field depicting wind speed and direction is used to determine the center of rotation (the "eye" of the hurricane). Given this data, the local rotational force of the hurricane can be determined. A correlation between angular speed, temperature and pressure is useful in assessing the destructive potential of the hurricane for all data points and across all phases (Fig. 1). Furthermore, similar correlations are used to deduce the local dispersion potential of each interpolated spatial position, which is an indicator of the localized pollutant transport capacity of the hurricane. The result is represented via color coding, where brighter, warmer colors are used to indicate greater levels of danger, while cooler colors point out regions of reduced risk. A 3D-based approach can make effective use of varying opacity levels to display this information at multiple altitudes simultaneously.

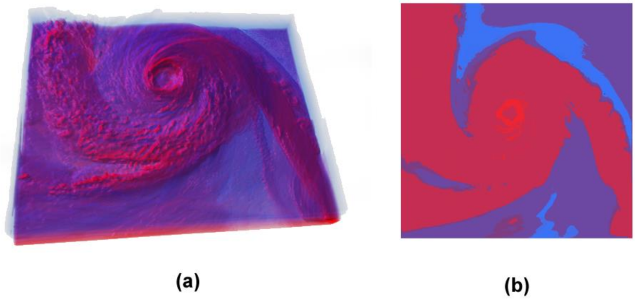


Figure 1: Rendered images of the hurricane dataset. (a) shows the color-coded result of correlating temperature, pressure and local rotational velocity for all slices, averaged across the available time phases. (b) shows a discretized version of the same information for one slice only.

Our software prototype allows for the intuitive tuning of the various parameters involved, using commonly-encountered interface elements, as well as the interactive specification of color and opacity via transfer function editors. The presented techniques are meant to assist in the analysis and assessment of the risk factors associated with such weather phenomena, in an effort to reduce the related negative health, economic and environmental impacts.

Acknowledgements

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AQUEOUS PHYTOREMEDIATION MODELING OF RED MUD POLLUTION BASED ON ARTIFICIAL NEURAL NETWORKS

Vasile-Mircea Cristea[1], Alexandra Csavdari[1,*], Horia Hangan[1], Norbert-Botond Mihály[1], Paul Şerban Agachi[1,2]

[1)] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, CAPE Research Center, 11 Arany Janos Street, 400028, Cluj-Napoca, Romania*
[2)] *Botswana International University of Science and Technology, Palapye, Botswana*
[*] *: acsavdari@chem.ubbcluj.ro (A. Csavdari)*

Introduction and study objectives

Red mud, the main waste product of the Bayer process in alumina industry, can be a major environmental threat due to its high alkalinity: the pH of untreated aqueous slurry lies between 9.2 and 12.8. Moreover it also raises economic concerns since 77 million tones, which have to safely stock-pilled, are produced yearly. Cassettes often fail and undesired leakage causes radical pH increase in aqueous eco-systems.

Aqueous phytoremediation by pond-weeds, such as *Salvinia natans* and *Eichhornia crassipes,* is an environmentally-friendly and potentially efficient approach to lower the pH of contaminated sites to values compatible with various life forms.

Artificial Neural Networks (ANNs) are inspired by the w human brain processes information. They rely on simple computing elements called neurons which are organized in input, hidden and output layers. The ANN versatile structure of weights and biases may be calibrated (trained) such as to respond to the input signals with the desired outputs, and be further used for predicting the outputs corresponding to new inputs. They represent much appreciated model alternatives for systems that have complex input-output relationships. This is also the case of the aqueous phytoremediation of red mud pollution where the effect of different factors on efficiency of the remediation process is difficult to formalize under the form of explicit mathematical expressions.

The objective of the present work was to design and train ANN based models using the data obtained by experiments performed during 3 weeks for the phytoremediation of a laboratory scale red mud contaminated aqueous solution. The ANNs are further employed in modeling and simulation of the pH evolution of an aqueous ecosystem during phytoremediation caused by accidental red mud pollution. They can be used for prognosis purposes as well as to find the optimal conditions for the remediation of a contaminated site. The novelty consists in describing the dynamics of phytoremediation as well as in the use of employing ANNs to do so.

Methodology

The ANNs were designed to predict the pH change of red mud contaminated aqueous solutions, as response to the changing input factors consisting in the mass of red mud, plant biomass, air humidity, temperature of air and water, light intensity and time. The feedforward type of ANN associated to the backpropagation Levenberg-Marquardt algorithm was considered for training the weights and biases. One hidden layer was found to provide good training results.

Available experimental data were divided in training and testing sets. The latter was used to check the quality of the training procedure. Furthermore, the training set was split into the validation and actual-training sets. The former of these sets was used for preventing the ANN overfitting during the training process. Training was performed with scaled data in order to avoid improper calculations due to different order of magnitudes of the input factors and the output. Applications for training and testing the ANNs have been developed using Neural Network Toolbox of *Matlab* software environment.

Results and conclusions

The trained ANNs showed good fit between simulated and experimental pH values, as their correlation coefficients exceed R=0.99. The same is true for the testing data sets. The reduced relative errors have values less than 2.5% and therefore prove the appropriate ANN architecture as well as the quality of both training procedure and predicting capability.

Simulation results with data unknown for the ANNs but verified experimentally revealed very good prognosis aptitudes and the capability of describing complex intrinsic input - output relationships (e.g. for quantitative assessment of the mass of red mud and biomass influence on pH change).

Designed ANNs were employed to calculate the sensitivity of the pH change to different input factors. A phytoremediation performance index was defined by the authors as the maximum achieved pH difference by a given amount of biomass. Plotted against the red mud quantity, it can be used to find the best conditions of effective phytoremediation in case of an accidental pollution. An example is illustrated in Figure 1 for *Eichhornia crassipes*. Good agreement between computed and experimental results is to be observed.

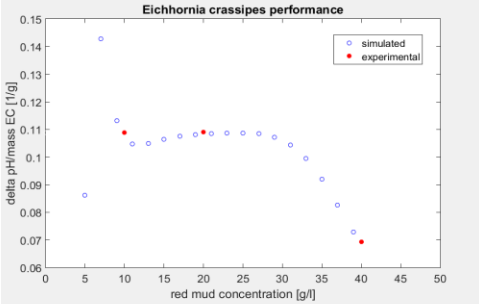

Figure 1: ANN computed (blue dots) against exerimentally obtianed (red dots) phytoremediation performance index for *Eichhornia crassipes*.

Acknowledgments:

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APPLYING OF A NEW METHOD BASED ON THE ICF ALGORITHM TO THE WATER QUALITY EVALUATION OF THE HUNGARIAN-ROMANIAN CROSS-BORDER RIVERS

Zsófia Kovács[1,*], Éena Jakó[2], Igor Cretescu[3,*], Endre Domokos[1]

[1) University of Pannonia, Institute of Environmental Engineering, 10 Egyetem St., Veszprém, 8200 Hungary
[2) Eötvös University, Budapest, Dept. of Plant Systematics, Ecology and Theoretical Biology
[3) "Gheorghe Asachi" Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, 73 Prof. dr. Dimitrie Mangeron Blvd, Iaşi 700050, Romania,
[*]: zsofiakovacs@almos.uni-pannon.hu, icre@ch.tuiasi.ro,

Introduction and study objectives

The aim of the Water Framework Directive (WFD) [2000/60/EC], as long-term water policy of the European Union (EU), is to assure the good quality of surface waters. In light of the objectives of the integrated water management it was aimed at to devise water quality assessment methods on the basis of the data bases established.

There is growing demand for the use of modern discrete mathematical tools for various chemical and biological applications. Boolean algebras can play a very important role in mathematical modelling. The BOOL-AN program package was based on a novel discrete mathematical approach: the Iterative Canonical Form (ICF). ICF is suitable for the minimization and the classification of binary strings as well as sequences. Graph-theoretical representations of the ICF promote understanding the new method and visualizing its structure.

The surface water analysis (physical-chemical parameters), data visualization and evaluation method based on the ICF algorithm are the main issues of the research. For the evaluation of the surface water quality a new Water Quality Module (WQM) have been developed for the BOOL-AN software and it was applied onto the Hungarian-Romanian cross-border rivers.

Methodology

After grouping we have coded and arranged the main 13 physical-chemical parameters (to the ICF 4-cube graph system, where the number of vertices in each rank represent rows in Pascal's triangles, being 1:4:6:4:1. Then we have calculated the distances (etc: Euclidean, Hamming, ICF rank and code) between data on the basis of well-known metrics. Dendrograms and point maps show the classifications of the water bodies. According to the obtained results, the trees generated by the WQM distinguished the water bodies associated with critical water quality parameters reliably.

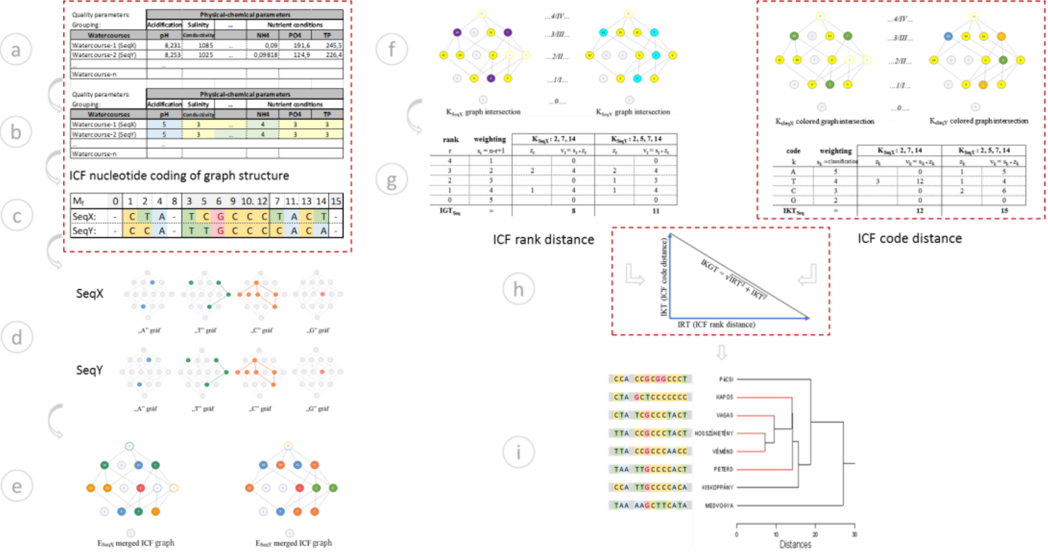

Figure 1: Main elements of the new Water Quality ICF method

Results and conclusions

The ICF graph is a unique fingerprint of watercourses which helps to assess the quality of water bodies. The ICF underlines problematic cases, so these can operatively be checked based on raw data. Our goal in the future is to expand the ICF method elements which are necessary for the evaluation of ecological status (i.e. biological elements, other specific pollutants, hydro- morphological elements).

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NATURAL REMEDIATION OF THE MAIN AFFLUENTS OF TROTUȘ RIVER AFFECTED BY HEAVY METALS POLLUTION

Gabriel-Alin Iosob[1], Maria Prisecaru[2], Florin Prisecaru[3], Iuliana-Mihaela Lazăr[4]

[1) ”Vasile Alecsandri” University of Bacau, Doctoral School, Calea Marasesti 157, 600115, Bacau, Romania,
[2) "Vasile Alecsandri” University of Bacău, Faculty of Science, Department of Biology, Ecology and Environmental Protection, Bacau, Romania,
[3) National Administration "Romanian Waters" Water Basin Administration SIRET, str. Cuza Voda Nr. 1, 600 274, Bacău, România
[4) "Vasile Alecsandri” University of Bacău, Faculty of Engineering, Calea Marasesti 157, 600115, Bacau, Romania,
*: *iosob.gabriel@gmail.com, prisecaru_maria@yahoo.com, ilazar@ub.ro*

The hydrographic basin of Trotuș River is a region of scientific importance because of the geographic variety and important construction on watercourses with important ecological impact. The uncontrolled anthropic intervention is present and continues to affect the natural water ecosystem. Each action involved in changing the environment have many consequences. Therefore, is required to realize detailed studies looking for the impact of toxic pollutants, like heavy metals on river basins by monitoring the quality of the hydrographic network. Studies published so far have not focused on monitoring the water quality in terms of heavy metal pollution on Trotuș River effluents.

The purpose of this paper is to highlight the natural remediation related to heavy metals (Cd, Pb, Hg and Ni) pollution of the main tributaries of the Trotuș River from Bacău County in 2010-2015. The variation of the annual average value of heavy metals from water is represented in Figure 1.

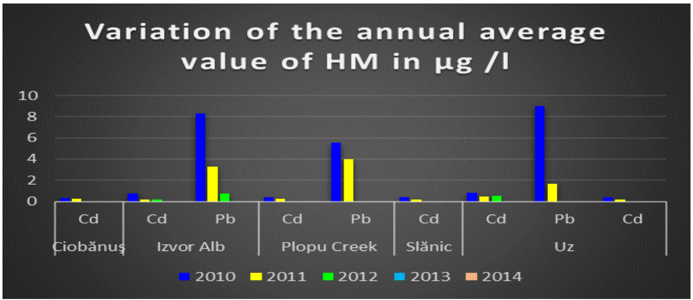

Figure 1:. Natural remediation on main tributaries of the Trotuș River from Bacău County

From year 2010 to 2015 the presence of heavy metals: cadmium (Cd) and its compounds, lead (Pb) and its compounds, mercury (Hg) and its compounds, nickel (Ni) and its compounds was monitored from Trotuş River and its main tributaries: Ciobănuş River, Asău River, Izvorul Alb River, Plopu creek, Slănic River, Tazlău River, Tazlăul Sărat River and Uz River. For monitoring purposes, the hydrologic basin was divided into nine sections: sTrotuş River; Asău River; Ciobănuş River; Izvorul Alb River; Plopu creek; Slănic River; Tazlău River; Tazlăul Sărat River; Uz River.

The data from each year was collected and following an internal procedure, an annual average for Cd, Ni, Pb, and Hg was calculated. To establish the working parameters, the analysis of samples was performed for Cd, Ni, Pb and Hg with an atomic absorption spectrophotometer (AAS) Zenit 700, with flame and automatic graphite oven, computerized with transversal heating, deuterium lamp for background correction and hollow cathode lamps. For fixing the samples at $pH < 2$ super-pure HNO_3 was used to keep the low pH and for preventing the precipitation of metal ions at high pH value. The readings were made directly on the machine to a calibration curve. For determination of Cd, Pb and Ni the SR EN ISO 15586:2004 method was used and for Hg determination, SR EN ISO 17852:2008, with modifications for suitability to the matrix type analyzed. Each determination was performed in three repetitions. The detection limits for Cd was 0.05 µg/l, for Pb was 0.3 µg /l, for Hg was 0,005 µg /l and for Ni was 0,6 µg/l.

Table 1: Heavy metal concentration is the studied section for 2010-2012 period exceeding the annual average of 0.08 µg/l for Cd and 7.2 µg/l for Pb

River / Year	Ciobănuş River	Izvorul Alb River		Plopu creek		Slănic River	Uz River		Poiana Uzului Lake
	Cd (µg/l)	Cd (µg/l)	Pb (µg/l)	Cd (µg/l)	Pb (µg/l)	Cd (µg/l)	Cd (µg/l)	Pb (µg/l)	Cd (µg/l)
2010	0.378	0.85	15.5	0.496	12.75	0.455	0.922	16.21	0.45
2011	0.36	0.262	10.5	0.32	11.21	0.28	0.558	8.88	0.23
2012		0.251	7.95					7.75	

In the coming years, 2013, 2014 and 2015, in all sections of the river were not exceeded the yearly average values of heavy metals, all concentrations detected being within the permissible limits according to the Water Framework Directive 2000/60/CEE or under detection limits.

In conclusion, there were some exceedances of acceptable concentrations of Cd and Pb during the monitoring period 2010-2012, as a result of the existence of pollution sources upstream sections of study, it appears that the trend is decreasing in 2012. In the next years, 2013 to 2015, in all monitoring sections, the concentrations of these metals were within the permissible limits or below the detection limit of the analysis device. Throughout the study period were not exceeding of the concentration of Hg and Ni in any monitoring section. This decrease of heavy metal pollution is primarily due to basic management measures applied on these watercourses.

RECLAMATION OF CHROMIUM POLLUTED SALINE SOILS USING QUINOA.

Cicatelli Angela[1,*], Guarino Francesco[1], Karina B. Ruiz[2], Biondi Stefania[2], Castiglione Stefano[1]

[1)] Università degli Studi diSalerno, Dipartimento di Chimica e Biologia
"A. Zambelli", Via Giovanni Paolo II, 132- 84084 Fisciano (SA), Italy;
[2)] Università di Bologna
acicatelli@unisa.it

Introduction and study objectives

Soil metal pollution and salinity represent a constant and heavy legacy of modern human activities. An intensive use of non-renewable mineral resources, industrial and agricultural activities, as well as an irrigation with saline water, seawater intrusion in coastal areas, are some of the specific causes of metal contamination and salinization of natural and agricultural soils. Despite a considerable improvement in knowledge, progress in management and control of soil metal pollution and salinization, they persist and represent threats to the environment and sustainable agriculture, jeopardizing the well-being of many people over a wide geographic areas. Among soil remediation approaches, phytoremediation of metal- or salt-affected soils using halophyte plants has been studied and can be recommended as an efficient and inexpensive strategy, protective of environment and human health. The purpose of this research was to assess whether quinoa plants are useful to reclaim soils affected by chromium (Cr) and/or salt (NaCl) using a phytoremediation approach. Chromium enviroment contamination, though partly natural (volcanic eruptions, bedrock erosion, etc.), is mainly due to industrial processes, such as textile and leather tanning processes; it is classified among the 'Priority hazardous substances' and its use is severely restricted under the European legislation. At the same time, quinoa (*Chenopodium quinoa* Willd.), an ancient Andean crop largely cultivated for its edible and highly nutritious seeds, is a facultative halophyte plant species, able to cope with many types of abiotic stresses, including high salinity levels and metals. Although many mechanisms involved in soil salinity tolerance have been investigated, only few information are available regarding growth, uptake and translocation capacity of quinoa, whenever it is exposed to high Cr and/or salt concentrations. Therefore, the aims of the present study are to: i) evaluate the effects of high doses of Cr(III) and/or NaCl on growth and biomass production of quinoa; ii) investigate the potential of Cr and/or Na phytoremediation capacity of seedlings; iii) assess Cr and Na plant uptake and organ distribution, as well as the effect of both elements on P and Fe metabolism (both potentially alterated by Cr and/or NaCl soil content).

Methodology

Quinoa seeds were sown in plastic pots and, when the plants reached a height of 15 cm, Cr and/or Na were added to pots in three consecutive weekly doses, up to the final concentrations of 500 mg kg^{-1} soil dry weight of Cr (as

Chromium nitrate nonahydrate) and of 150 mM NaCl. The experimental design included 4 experimental theses, with three pots for each treatment. At the end of the experiment (approximately 3 months after seed sowing), plants were harvested, separated into roots, stems and leaves, and then weighted. Metal (Cr, Na, Fe) and nutrient content (P) were evaluated using an emission spectrophotometer techniques, after digestion with acid mixture. Pot filling soils were characterized for total or available metal content, at three different time points during the trial. The Translocation (TF) and Bioaccumulation (BAF) factors were calculated to estimate the ability of plant to transfer elements from root to shoot (TF), or from soil to plant biomass (BAF).

Results and conclusions

At the end of the experiment, quinoa plants did not show any symptoms of toxicity or stress on spiked soils. In fact, the Cr and/or Na addition had no impact on plant biomass, furthermore an increased leaf biomass was detected in plants grown on Cr-spiked soil, probably due to the addition of metal as nitrate salt. In order to evaluate the effects of Cr and/or Na addition on quinoa phytoremediation capacity, the amounts of Cr, Na, P and Fe were determined in roots, stems and leaves at the end of the experimentation. Roots of quinoa, grown on Cr-spiked soils, accumulated higher amounts of Cr than the aerial organs; furthermore, when both Cr and Na were added together to the soils, Cr root concentration significantly increased. On Na-spiked soils, the quinoa plants accumulated Na in all organs, even if it was mainly translocated in leaves. Sodium was highly accumulated when the salt was singularly added to the soils. Quinoa plants accumulated Fe in roots; in particular Fe content was significantly improved when the salt was singularly added to soils. On the contrary, P was mainly translocated in the leaves, but a significant decrease was observed in the leaves caused by Cr and/or Na additions. The response of quinoa to Cr and/or Na treatments was also evaluated in terms of TF and BAF. The TF values for Cr were extremely low (close to 0) showing that quinoa did not translocate this metal from root to shoot. On the contrary, the TF values for Na were high (>1) in all treated plants, mainly when Cr or Na were singularly added to the soils. The BAF values for Cr and Na were high (>1) for quinoa plants grown on Cr or Na- spiked soils. The soil background concentrations of total Cr and Na, at the beginning of experimentation, were those of a common agricultural soil. At the second sampling, the concentrations of the two elements increased as a consequence of the artificial soil pollution, while, at the plant harvesting, Cr and Na soil contents was decreased in all analysed pots, revealing the capacity of quinoa plants to absorb and accumulate Cr and Na. The available Cr and Na contents were always low in all soils during the experimental trial.

In conclusion, our study revealed that quinoa plants were able to tolerate high Cr or Na amounts, even when they were added together to soil. In particular, quinoa plants could be efficiently used for Cr phytostabilization and Na phytoextraction. In fact, plants were able to accumulate Cr in the roots and Na the leaves, to a greater extent when Cr and Na were singularly added to the soils respect when they were added together. The combined soil addition of Cr and Na negatively influenced nutrient (P) absorption and accumulation in quinoa; while Fe uptake increased only in the presence of high salt concentrations.

MANAGING PESTICIDE RESIDUES IN SOUR CHERRIES: A HUMAN HEALTH RISK ASSESSMENT APPROACH

Raluca Maria Hlihor[1,2,*], **Manuela Olga Pogăcean**[1,3],
Petronela Cozma[1], **Isabela Maria Simion**[1,2], **Vasile Stoleru**[2],
Maria Gavrilescu[1,4,*]

(1) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str.,
700050 Iasi, Romania
(2) "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine of Iasi, Faculty of Horticulture, Department of Horticultural Technologies, 3 Aleea Mihail Sadoveanu, 700490 Iasi, Romania
(3) Phytosanitary Office Mureş, Regional Laboratory for Quality Control of Pesticides, Târgu Mureş, Romania
(4) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
[*]: raluca.hlihor@ch.tuiasi.ro, mgav@ch.tuiasi.ro

Pests and diseases are considered among the restrictive factors for farmers in their efforts to obtain good crops, with higher yields. The largest part of pest management strategies are still dependent on the usage of synthetic pesticides, which can unfortunately bioaccumulate in plants, vegetables, fruits and enter the food chain. An important side effect of pesticides use is the potential threat they can pose to human health and environmental quality. World Health Organization (WHO) established that over 30% of consumers' diet in Europe consist of fruit and vegetables since they provide vitamins, fibers, minerals, antioxidants. However, they can be a source of pesticide residues as well, with toxic effects for human health, particularly when children are fruits consumers, since they are mostly vulnerable to pesticides exposures and risks. In the last years, the concern for diminishing the risk of pesticide residues found in fruit and vegetables grew continuously due to a stricter policy of the European Union, while the interest of scientists in human health monitoring and risk analysis for children, adults and the general population continues to be highly topical.

Human exposure to pesticides can result from dietary intake of plant products containing pesticide residues accumulated during crop treatment or by inhalation, dermal contact and ingestion of direct emissions from the fraction that is "lost" in the environment during pesticides application. This work is focused on the assessment of human health risk induced by the presence of pesticide residues in sour cherries. The experimental procedure considers the application of four treatments with eight fungicides (chlorothalonil, myclobutanil, folpet, captan, boscalid, pyraclostrobin, cyprodinil, tebuconazole) and five insecticides (chlorpyrifos ethyl, deltamethrin, alpha-cypermethrin, lambda-cyhalothrin and acetamiprid) on field, in single and double doses on sour cherries, according to their phenological growth stages.

The pesticide residues in samples of sour cherries were analyzed at certain time intervals and at harvesting time by gas chromatography coupled with mass spectrometry with flight time (GC-TOF-MS). The results allowed the assessment of future potential risks to human health associated with the consumption of sour cherries containing pesticide residues at harvest, based on fruits consumption estimates released in 2015 for 2013, of 188.60 g/capita/day in EU-28.

The risk assessment of pesticides residues showed that the hazard indices values for adults, adolescents and children do not exceed the safety limit values for human health. These results recommend the need of continuous programs of study and monitoring of pesticide in all food products, in order to protect the end user - the consumer - to pesticide exposure.

Acknowledgements

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PLANT BIOCONCENTRATION AND TRANSLOCATION FACTORS OF HEAVY METALS IN AN AREA UNDER THE INFLUENCE OF A THERMAL POWER STATION

Gorkem Akinci[1], Gulden Gok[2], Melayib Bilgin[2]

1) Dokuz Eylul University, Faculty of Engineering, Environmental Engineering Department, Tinaztepe Campus, 35160 Buca, Izmir, Turkey
2) Aksaray University, Faculty of Engineering, Environmental Engineering Department
**: gorkem.akinci@deu.edu.tr*

Introduction and study objectives

Heavy metals (HMs) are one of the most important environmental concerns (Alloway, 1994). HM uptakes from soils and their translocation from plant roots to aerial parts have an important impact on HM bioaccumulation in food chain. However, in many parts of the world agricultural activities are realized in areas close to HM emitting sources such as fossil fuel power plants, mining sites, and industries. The influence of HM emitting sources on bioaccumulation and translocation of HMs in plants are poorly reported in the literature. Here, bioconcentration and translocation of HMs in plants growing in an agricultural area surrounded by a coal mine, a thermal power plant with an annual capacity of 8.1 billion kWh and a coal ash landfill site are studied for well understanding of bioaccumulation and translocation of HMs in plants under extensive emissions.

Methodology

The soils and plants (sunflower, sugar beet, eggplant and apricot) were sampled from nine different fields in the area. The sampling point distances from the HM emitting sources were between 200 m and 10150 m. Soils were collected from the surface (core sampler: 5 cm in diameter, 15 cm in length), the plants were uprooted from the soil and the fruits were picked by hand. The samples were stored in plastic bags at 4°C until the analysis. Soil samples were dried at 60°C, sieved from 2 mm screen and homogenized. Plants were divided as root, leaves, seeds and/or fruits, the parts were washed with running tap water and rinsed with distilled water before they were dried at 60°C. Dried samples were powdered, multi acid digestion procedures applied, the extracts were analyzed by ICP-OES for As, Cd, Co Cr, Cu, Mn, Mo, Ni, Pb, V and Zn levels. All tests were triplicated. Bioconcentration factors were determined by dividing the plant parts' HM concentration to soil, while translocation factors were calculated by taking HM concentration ratio of plant aerial parts to roots.

Results and conclusions

It's found that only Mn and V levels in soils are decreasing with increasing distance from the sources. High correlations between the soil concentrations of As-Ni (r:0.92, $p<0.01$), As-Pb (r:0.872, $p<0.01$), Cd-Zn (r:0.892, $p<0.01$), Co-Mn (r:0.927, $p<0.01$) and Ni-Pb (r:0.941, $p<0.01$) were found. Statistically significant relations between As-Co (r:0.755, $p<0.05$), Co-Ni (r:0.845, $p<0.05$), Co-Pb (r:0.846, $p<0.05$), Cr-V (r:0.775, $p<0.05$), and Mo-V (r:0.828, $p<0.05$) in soil were also detected.

Table 1. Soil and plant concentrations and plant bioconcentration factors (BCF) of studied heavy metals with reference values (*Pais and Jones, 1997)

	Soil Concentrations	*Total Concentration	Plant Concentrations	*Normal Range	BC Factors	*Soil- Plant Transfer
	(this study) Min.-Max.	in Soils, Min.-Max.	(this study) Min.-Max.	in Plants Min.- Max.	(this study) Min.- Max.	Coeff. Min.- Max.
As	4.0-13.8	0.1-48	0.1– 5.1	0.009-1.7	0.02-0.75	0.01-0.1
Cd	0.3-0.5	0.01-3	0.08-0.4	0.1-1.0	0.03-0.99	1-10
Co	13.0-22.8	1-40	0.06-12.15	0.03-0.57	0.00-0.63	0.01-0.1
Cr	55.8-122.4	5-1000	1.9-81.2	0.02-0.2	0.03-1.16	0.01-0.1
Cu	23.6-37.2	2-100	2.76-34.49	1-10	0.12-1.10	0.1-10
Mn	494-765	200-3000	8.0-538	10-500	0.02-0.66	n.a.
Mo	0.4-2.5	0.5-40	0.08-8.64	0.1-3.0	0.17-5.25	n.a.
Ni	79.4-205.4	1-200	1.6-73.8	0.3-3.5	0.01-0.73	0.1-1.0
Pb	9.4-19.2	3-189	0.17-7.79	1.0	0.01-0.61	0.01-0.1
V	47-104.5	3-230	2.0-52	0.27-4.2	0.03-0.75	n.a.
Zn	53.3-95.3	10-300	5.0-59.4	10-100	0.08-1.11	1-10

Table 2. Average translocation factors (TF) of studied heavy metals in plants (SF: Sunflower, SB: Sugar Beet, EP: Eggplant, L: Leaves, S: Seeds, F:Fruits, R: Roots)

	TF	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	V	Zn
SF (n=4)	L/R	1.61	1.31	1.02	1.12	2.06	1.58	2.66	1.18	1.34	1.40	1.34
	S/R	0.95	1.13	0.65	0.65	1.92	0.72	0.80	0.87	0.76	0.78	1.40
SB (n=3)	L/R	2.00	3.26	2.50	2.50	2.48	3.25	7.27	2.74	3.21	2.70	1.69
EP (n=1)	L/R	2.75	1.33	1.61	1.46	1.46	2.54	4.36	1.88	2.54	1.45	0.95
	F/R	0.38	0.78	0.14	0.68	0.93	0.51	2.52	0.16	0.25	0.18	0.69

Plant HM levels above the normal range (except Cd and Zn) were detected. BCFs of HMs, except Cd, Cu, Pb and Zn, were generally higher than reference upper value. The lowest BCFs were found for apricot and eggplant fruits, and sugarbeet roots, where the highest BCFs were calculated for sunflower roots and leaves and eggplant leaves. TF>1 were found for all plants and HMs, mostly for the leaves; the highest TFs were calculated for sugar beet and eggplant leaves having large surface areas, where the lowests were determined for eggplant fruits and sunflower seeds. TFs are generally higher than previously reported.

The HMs sources in plants may be originated from soil, irrigation water, fertilizers and fumigation agents, and from industrial and traffic emissions. Here, although the soil HM concentrations are in the world range (except Ni and Zn), unusually high BCFs and TFs found for the studied plants. Sugar beet is known as a high accumulator of Cu, Ni and Zn (Pais and Jones, 1997), however the concentrations and BCFs of these metals in sugarbeet are found lower than sunflower, whose BCFs are much lower than the reported values in the literature (Niu et al., 2007).

As a result, it is understood that emissions from surrounding mining site, thermal power plant and ash landfilling activities and the agricultural chemicals used in the area significantly contribute to the aerial plant parts HM levels.

MONITORING OF MERCURY CONTENT IN THE MAIN ENVIRONMENTAL COMPONENTS CAUSED BY LIGNITE COMBUSTION IN TURCENI POWER PLANT (ROMANIA)

Delia Nica-Badea[1], Iuliana Gabriela Breaban[2,*],
Igor Cretescu[3,*], Catalina Daniela Stan[4]

1) Faculty of Medicinal and Behavioural Sciences, Department of Sport and Health, "Constantin Brancusi" University, Eroilor Street No.30, Târgu-Jiu, Romania
2) Faculty of Geography and Geology, Department of Geography, "Alexandru Ioan Cuza" University of Iasi 20A Carol I 20A Blvd., 700505, Iasi, Romania
3) Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, "Gheorghe Asachi" Technical University of Iasi, Blvd. D. Mangeron No.73, 700050 Iasi, Romania,
4) Faculty of Pharmacy, Department of Pharmaceutical Science II, "Grigore T. Popa" University of Medicine and Pharmacy, 16 Universităţii Street, 700115, Iasi, România
*: icre@ch.tuiasi.ro

Coal is still an important source of energy in Europe, covering about a quarter of electricity production. Burning coal is one of the main source of mercury emitted into the environment, burning fossil fuels produces 45% of the total mercury emitted from human activity worldwide. Among the 20 largest coal-fired facilities located in Europe two power plants are from Romania (Turceni and Rovinari). The mercury content of coal, reported worldwide ranging between 0.01 to 1.0 $mg\cdot Kg^{-1}$, being present in the form of sulfide and organic matter associated with pyrite in some cases. The incomplete combustion of coal in the thermal power plants generates fly ash (instead of carbon dioxide and mercury which is associated with it). The thermal power plants, based on coal burning, dominate non-uniform spatial mercury distribution. A number of studies have reported that presence and accumulation of mercury in both soils and vegetation around power plants: local (2 to10 km) to regional scale (20 to 50 km). Mercury is one of the most hazardous contaminants emitted to the atmosphere due to its toxic effects on the environment and human health including damage to the central nervous system (neurotoxicity), kidney, developing fetus(organic mercury, methylmercury), can cause birth defects and attention deficit hyperactivity disorder. Due to these considerations the admisible limits have been established for food and medicines by health authorities (Commission Regulation No 1881/2006).

Based on literature data, to predict the local impact of mercury accumulations, the present study deals with the analysis of local mercury discharge from coal power plants, by examining samples of ash, slag, soil, spontaneous vegetation and crop plants, using as analytical techniques the cold vapor atomic absorption spectroscopy (CVAAS).

The environmental monitoring is aimed to determine different harmful pollutants from environmental components such as: air, water, soil, vegetation in urban and in rural areas. The methodology of sampling, preparation and extraction of heavy metals (Hg) from soil and plants are in accordance with the requirements of instrumental analysis of multicomponent environmental samples. Soil and plant sampling was conducted on the Jiu river corridor, in the NW-SE direction, considering the relief of the area and the predominant directions of the atmospheric circulation adjacent to the pollution sources (the power station and cinder deposit). The determination of total mercury concentration was carried out by CVAAS according to international standards with using a Thermo Electron Model S Series AA SOLAAR spectrometer equipped with software platform.

The performance of analytical method applied in this study, permit the mercury detection in all the analyzed samples from local environmental components with values ranging between 0.004 to 0.12 mg·Kg^{-1}. Analyzing mercury content as total forms, it is confirmed the presence of both mercury and its compounds in the distribution chain and accumulation: lignite, ash and slag, soil and spontaneous or cultivated vegetation in the power plantarea of influence, slag and ash deposit on the flanks of Jiiu river corridor, between Brănești – Ceplea and Turceni- Ilieşti, located in NW-SE direction (Figure 1). Mercury determined in samples of lignite (0.020 mg·Kg^{-1}) was found in fly ash samples retained by filters (0.037 mg·Kg^{-1}), bottom ash transported in deposit (0.022 mg·Kg^{-1}), adjacent soils landfill and the power plant (0.12 mg·Kg^{-1} and 0.049 mg·Kg^{-1}, respectively). The mercury content in vegetation presents different values depending on the bioavailability of plants, location of the monitoring area in respect of the emission source, etc. The mercury content presented values ranging between 0.014 and 0.005 mg·Kg^{-1} in the wild flora and respectively 0.022 mg·Kg^{-1} to 0.006 mg·Kg^{-1} in the plants crop.

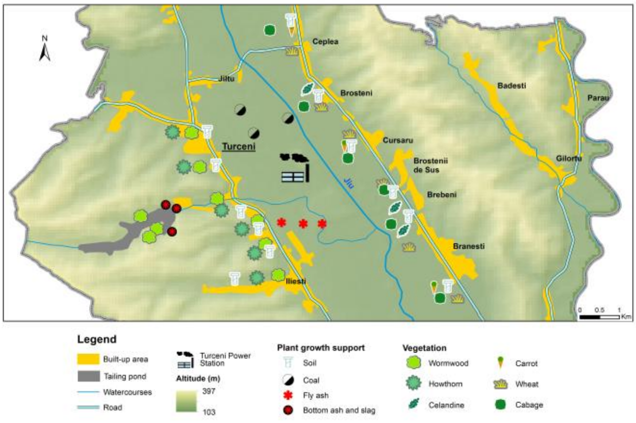


Figure 1: Distribution of the samling points in the Turceni power plant region

The production of electricity in coal-fired power plants is an additional source of mercury released from the coal matrix in space, with the tendency to accumulate and concentrate in soil, plants and animals, resulting in harmful effects on the human health.

ASSESSMENT OF SOCIAL VULNERABILITY IN A RURAL AREA WITH FLOOD HAZARD

Roxana Tincu[1,*], **Maria-Ema Faciu**[2], **Iuliana Lazar**[1]

[1)] *"Vasile Alecsandri" University of Bacau, 157Marasesti Str, Bacau 600115 Romania,*
[2)] *"Al. Vlahuta" Technological School Podu Turcului, 95 Tudor Vladimirescu Street 607450-Bacau, Romania*
[*]*: roxanatincu@gmail.com*

Introduction and study objectives

Assessment of the flood risk represents one of the themes which are focusing the attention of many researchers, not only because of the frequency of occurrence but also because of the multilevel impact of floods. Vulnerability assessment, often neglected in traditional approaches, can be considered one of the most important characteristics of risk assessment. It defines the ability of an element (be it here represented by people) or activity to resist when it is exposed to hazard. The vulnerability helps us to explain why the same hazardous event has different effects on exposed elements of hazard, i.e. the people and infrastructure.

This research is focused on social vulnerability nested in the environmental sphere and deeply intertwined with the economic sphere.

The main objective was to assess the vulnerability of the elements exposed to floods hazard from two villages, Ghimes and Faget, in order to quantify the risks. It can be mentioned that the current study represents a new stage after achieving the hazard map and identification of the elements exposed to flood hazard of a more comprehensive study which aimed flood risk assessment in a rural area.

Methodology

This research represents a new stage of a more comprehensive study regarding flood risk assessment in this area. Firstly we realized the hazard map according with the Swiss method of hazard assessment, based on a matrix diagram which defines three levels of risk (i.e., low, medium and high). Secondly, using this hazard map we identified the elements exposed to flood hazard. A new stage in the risk assessment takes place by calculating the vulnerability of exposed elements on hazard maps.

The hazard maps completed with correspondent recommendations according to classification may be used in the process of urban planning, during the preliminary proposals for flood protection measures, but more data is necessary in order to assess the risk of the flood on population and local economy and to design an efficient flood risk management plan.

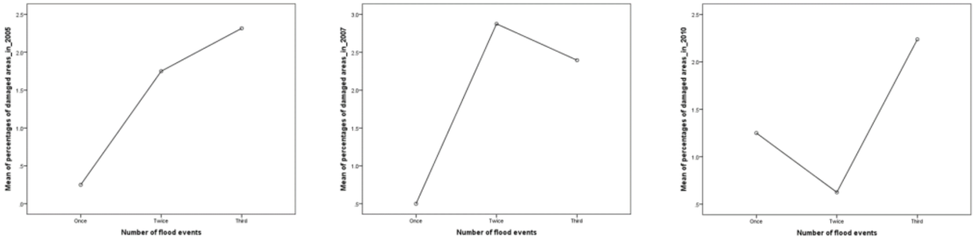
Thus, an application form was designed structured into five sections: building characteristics, social and economic characteristics, the experience of flooding and support; totalizing 36 items addressing the three components of vulnerability: exposure, sensitivity, and ability to cope. The form was used to achieve a micro-census, people from 80 households, living in Ghimes – Faget area and exposed to flood hazard, being interviewed. In order to assess the vulnerability and to calculate the vulnerability index, data analysis was run using SPSS statistical software, while mapping of indexes and spatial correlation analysis were conducted using ArcGIS10.

Results and conclusions

Hazard maps were designed considering categories like demographic classifications, social and economic situation, health, transport; in order to assess individual and collective propensity for risk exposure and reaction capability to a dangerous event.

Land use maps were transformed into "acceptable risk maps" according to acceptable risk classification: Low – for residential, agricultural, transport, and industrial areas; Medium – for sport and recreation areas; and High – for water areas and pasture. Hazard maps were overlaid with transformed land use maps and processed by GIS analytical tools. The existing and anticipated areas with exceeded acceptable risk were highlighted.

From the analysis of vulnerability highlighted areas, it was observed that the older buildings are more exposed than the newer ones (from the last 20 years). Considering the correlation with the age of the inhabitants, with the state of health and with the number of family members, it can be concluded that the Flood risk management plan needs to include an intervention procedure addressed especially to the elderly, which have also a low ability to cope.



a b c

Figure 1: Percentages of damaged areas function of number of flood events at 2005 (a), 2007 (b) and 2010 (c)

From the correlation analysis applied on data regarding flooding events from 2005 and 2007, it was observed a strong correlation (p=0.695, Sig. 0.000) between percentages of damaged areas, which raises possible faults in the urban plans. Also, percentages of damaged areas were significantly influenced by a number of flood events mainly at 2005 and 2007 and less in 2010 (Figure 1). So, the Flood risk management plan proposed by this study may be used to improve the current urban plans.

BIOLUMINESCENCE APPLICATION TO CONTROL MICROBIAL CONTAMINATION

Maria A. Kirillova[1,*], Elena N. Esimbekova[1,2],
Valentina A. Kratasyuk[1,2]

[1] Laboratory of Bioluminescent Biotechnologies, Department of Biophysics, Institute of Fundamental Biology and Biotechnology, Siberian Federal University, Krasnoyarsk, Russia
[2] Institute of Biophysics SB RAS, Federal Research Center "Krasnoyarsk Science Center SB RAS", Krasnoyarsk, Russia
[*]: kirillva@mail.ru

Introduction and study objectives

Nowadays biosensors based on enzymes of bioluminescent organisms are widely used to analyze biological contaminations as well as chemical pollution in food industry, clinics and environmental monitoring. For example, biosensor contained enzymatic system of luminous bacteria NADH:FMN-oxidoreductase (Red) and luciferase (Luc) is used to determine toxic properties of testing probe (1, 2). The main principle of the bioluminescent toxicity enzymatic assays is inhibition of Red and/or Luc activities by the toxic compounds. The coupled enzyme system Red and Luc is successfully used for toxicity analysis of wastewater, air, soil etc. The use of enzymes as a test-object allows to increase the sensitivity and to simplify the assay comparing with those involving living organisms.

$$FMN + NADH + H^+ \xrightarrow{\text{NADH:FMN-oxidoreductase}} FMNH_2 + NAD^+ \quad (1)$$

$$FMNH_2 + RCHO + O_2 \xrightarrow{\text{Luciferase}} FMN + RCOOH + H_2O + Light \quad (2)$$

Firefly luciferase is commonly used for detection of bacterial contamination and the analysis is based on detection of adenosine-5'-triphosphate (ATP) that is linearly correlated with amount of cells. There is a possibility to employ the coupled enzyme system Red and Luc for quantitative analysis of bacteria in the sample instead of firefly bioluminescent system. In the case of Red and Luc system quantitative control of microorganisms is based on determination of flavin mononucleotide (FMN) or nicotinamide adenine dinucleotide (NADH) content in analyzed sample. Indeed, FMN and NADH are coenzymes of many metabolic pathways of bacterial cells, and simultaneously they are substrates of coupled enzyme system of luminous bacteria Red and Luc.

In the present research we try to design a new technique for quantification of bacterial cells in a sample based on the bioluminescent enzyme system of luminous bacteria Red and Luc.

Methodology

The optimal assay conditions were chosen to achieve the highest sensitivity of the coupled enzyme system Red and Luc to key substrates FMN and NADH. The concentrations of enzymes (NADH:FMN-oxidoreductase and luciferase) and substrates (tetradecanal, FMN, NADH) that allow to achieve the lowest limit of detection were found. The assay was performed as follow: compounds of reaction mixture contained 300 μl 0.05 M phosphate buffer pH 6.8, 10 μl solutions of luciferase and NADH:FMN-oxidoreductase, 50 μl 0.0025% tetradecanal, 10 μl FMN and 50 μl NADH, were placed into the tube and mixed quickly. The tube was placed into luminometer Lumat LB 9507 («Berthold Technologies», Germany) and the maximum of luminescence was detected. Before the addition of the last component of the reaction (FMN or NADH) the background light emission was measured. The limit of detection was found when the luminescence signal was three times higher than background light emission.

We used *Escherichia coli* cells as a model of bacterial contamination. Cells were destroyed by sonication, diluted and added into reaction mixture instead of FMN or NADH.

Results and discussions

The correlation between light intensity of bioluminescent enzyme reaction and concentration of substrates FMN and NADH was observed. The coupled enzyme system Red and Luc was more sensitive to NADH than that for FMN. The lowest limits of detection were 1.2 nM FMN and 0.1 pM NADH. The ranges in linearity were from 0.1 pM to 1 nM and from 1.2 nM to 10 μM with added NADH and FMN correspondingly.

The light intensity was proportional to amount of bacterial cells in the reaction mixture. The sensitivity of bioluminescent system Red and Luc was 3.9 million cells/ml and 800 thousand cells/ml in cases of detection based on FMN and NADH respectively. According to literature the sensitivity of mutated firefly luciferase to bacterial cells can come up to 1 cell/ml, that is about 6 times higher than sensitivity of bioluminescent system Red and Luc demonstrated in the study.

In conclusion, the coupled enzyme system of luminous bacteria Red and Luc can be used for quantification of bacterial cells in highly contaminated environmental samples, such as water etc., where amount of cells is more than 800 thousand cells/ml; otherwise the use of firefly luciferase is more preferable.

Acknowledgements

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ADAPTIVE RESPONSE OF SIX MARINE BACTERIAL STRAINS TO DIATOM POLYUNSATURATED ALDEHYDES TOXICITY

Milva Pepi[1], **Hermann J. Heipieper**[2], **Cecilia Balestra**[1],
Marco Borra[1], **Elio Biffali**[1], **Raffaella Casotti**[1,*]

[1] Integrative Marine Ecology , Stazione Zoologica Anton Dohrn, Napoli, Italy;
[2] Helmholtz Centre for Environmental Research – UFZ, Permoserstr. 15, 04318 Leipzig, Germany
[*] : raffaella.casotti@szn.it (R. Casotti)

Introduction and study objectives

In the marine world, as in any ecosystem, bacteria contribute to key ecological processes and elemental cycles. In the plankton, they permeate the water medium and strictly interact with nearby microbes by using the organic compounds excreted by them or decomposing their dead matter. Diatoms are ubiquitous photosynthetic eukaryotic microbes, able to carry out about 20% of primary production on Earth, and are at the base of the marine food web. Diatoms and bacteria strictly interact and this interaction is mediated by specific metabolites acting as infochemicals, allelochemicals or pheromones.

Under senescence or nutrient limitation, diatoms produce and release significant amounts of bioactive metabolites involved in activated chemical defense in response to grazing by copepods. Among these, PolyUnsaturated Aldehydes (PUAs) are produced from fatty acids degradation, strongly impacting copepod reproduction as teratogens. PUAs are also toxic to surrounding phytoplankton and bacteria, reducing their metabolism and growth at low concentration and determining their community composition and structure. Resistance to PUAs may therefore confer a competitive advantage, allowing a better exploitation of the rich organic matter represented by diatoms. As a consequence, diatom-associated bacteria may have evolved tolerance to toxic PUAs released by diatoms. In general, contact of living cells with toxicants (below a specific threshold), induces changes in cell membrane fluidity, which bacteria counteract by modifying their membrane fatty acid composition so to maintain fluidity at a constant level. Another mechanism of regulating membrane fluidity against membrane-active substances consists in a modification of the degree of fatty acids saturation.

Based on these observations, we aimed at elucidating and quantifying the reactions of six bacterial strains isolated during a diatom bloom in the Northern Adriatic Sea (Mediterranean Sea) to different concentrations of PUAs, in terms of adaptive modifications of the degree of saturation of their fatty acids as an indicator of membrane rigidity.

Methodology

Water samples were collected from the Northern Adriatic Sea (Italy) during a diatom bloom (dominant diatom species were Skeletonema marinoi, Chaetoceros socialis and unidentified pennates) in April 2014. Enrichment cultures were prepared in mineral medium, in the presence of different concentrations of 2E,4E/Z-heptadienal (HEPTA), 2E,4E/Z-octadienal (OCTA), and 2E,4E/Z-decadienal (DECA). PUAs-resistant bacterial strains were and stored at -80°C with 30% sterile glycerol (v/v) added until further use. Amplification of 16S rRNA gene was performed using the primers 27f (5′-GAGAGTTTGATCCTGGCTCAG-3′) and 1495r (5′-CTACGGCTACCTTGTTACGA-3′). Consensus sequences of the polyunsaturated aldehydes-tolerant isolates were compared with those deposited in GenBank by using the BLAST program. For phylogenetic analysis, 16S rDNA sequences of the isolates, and related sequences retrieved from databases (GenBank and RDPII), were conducted using MEGA version 6.1. The phylogenetic trees were drawn using the neighbour-joining method.

The bacterial lipids were extracted from wet pellets from 20 ml cell suspensions (about 1.5 × 1010 cells) centrifuged 3 h after addition of PUAs and washed with phosphate buffer (50 mM; pH 7). Analysis of fatty acid composition was performed using a quadruple GC System (HP5890, Hewlett & Packard, Palo Alto CA, USA) equipped with a split/splitless injector. A CP-Sil 88 capillary column (Chrompack, Middelburg, NL; length, 50 m; inner diameter, 0.25 mm; 0.25 lm film) was used for the separation of the FAME.

Results and Conclusions

According to 16S rRNA sequencing, the six strains were assigned to the genera Pseudomonas, Sufflavibacter, Halomonas, Vibrio, Idiomarina, and Labrenzia. Growth of these strains was reduced by 50% (EC50) at PUA concentrations ranging from 600 to 1700 µM HEPTA, 400 to 800 µM of OCTA, and 70 to 400 µM of DECA. Membrane reactions to PUAs were investigated in two of these strains, Vibrio sp. and Halomonas, sp., testing membrane fatty acid composition in terms of adaptive modifications of their degree of saturation (ratio between saturated and unsaturated fatty acids) by GC-FID. As a result, a direct correlation between bacterial membrane hydrophobicity and PUA toxicity was observed, and these bacteria were also found to react to PUAs by increasing the degree of saturation of their membranes fatty acids. Tested PUAs act as very toxic and effective poison, probably accumulating in cytoplasmic membranes because of their high hydrophobicity.

Our data suggest that diatom PUAs act as contact poison, due to their high hydrophobicity, allowing to directly accumulate in the bacterial and animal membranes, causing toxic effects and also protecting diatoms from grazing. Hereby, PUAs cause an about four-times higher toxic effect on bacteria than corresponding n-alkanols which are known to be among the most toxic organic compounds. This is probably due to the PUA's ability to disrupt proteins by the formation of Schiff's bases, different than most known toxins known in the marine phytoplankton and involved in biotic interactions. Our study, thereby, brings novel information about the mode of action of these ecologically relevant compounds having such a strong impact on recruitment of copepods and therefore transfers of matter within the aquatic food webs. This also implies that bacterial growth inhibition and membrane adaptive reaction, and the direct relationship between PUAs hydrophobicity, bacterial toxicity and membrane adaptation, can be used as good bioindicators for the detection of PUA-induced stress in nature.

Na-Tech ACCIDENT RISK ANALYSIS OF TWO HAZMAT STORAGE FACILITIES AFFECTED BY FLOODS

Iulia Crăciun, Andrei Radovici, Alexandra Kovacs,
Alexandru Mereuță, Zoltán Török, Viorel Arghiuș,
Alexandru Ozunu*

Babeș-Bolyai University, Faculty of Environmental Science and Engineering, 30 Fântânele Street, 400294, Cluj-Napoca, România
: alexandru.ozunu@ubbcluj.ro

Introduction and study objectives

Floods are one of the most frequent natural hazards that produce significant socioeconomic losses every year, affecting population worldwide. Floods can also affect industrial plants and facilities located in flood prone areas, causing the release of hazardous substances, which can result in Na-Tech accidents (NAtural hazard triggering TECHnological disasters).

Even though the frequency of Na-Tech accidents is considered to be low, the analysis of such events is important giving the potential major consequences on population, infrastructure, economy and the environment. The process of Na-Tech risk analysis may prove more complex than the conventional approaches, mostly because of the different characteristics of the processes and methodology used along with the complexity of the possible outcomes that may occur. A database analysis of Na-Tech accidents shows that mostly atmospheric and pressurized storage tanks were damaged and the most frequent consequences registered were water and ground contamination.

In the case of Na-Tech events triggered by floods the consequences can be magnified by the fact that the prevention and mitigation measures and the utilities may be affected by the natural hazard and therefore not working properly. Some of the assets or systems that can be affected as a result of a Na-Tech event can be essential for the maintenance of vital societal functions at the local, regional or national level. The disruption or destruction of these critical infrastructures will have a significant impact on health, safety, security, economy, environment and also on other dependent infrastructures. Furthermore the natural hazard can increase the likelihood of multiple failures, triggering DOMINO effects. The importance of taking into account the natural hazard when analyzing the technological risks is revealed also by the SEVESO III Directive, by stating that external events must be considered and analyzed.

Methodology

In Romania floods are the most frequent natural hazards with high damage potential. At the end of year 2015 a number of 300 Seveso-type industrial site were registered by the authorities, from which a number of 15 were identified in this study to be situated in flood prone areas. In this study two sites containing hazardous substances were selected for further analysis in order to determine and compare the risk of possible Na-Tech scenarios.

The frequency of the two possible Na-Tech scenarios was determined by combining the frequency of the flood with a certain severity and the probability of failure of the process or storage equipment hit by the flood. This failure probability can be determined from fragility curves related to different Damage States (DS). On the other hand, the consequences of the Na-Tech event are determined by mathematical modeling and simulation of possible post-release scenarios. Usually, the flood event is characterized by the return period and severity parameters (maximum water depth and maximum water velocity). In this study the return period was obtained from historical data and the severity parameters were simulated using the HEC RAS hydraulic model.

Results and conclusions

In this study a procedure for Na-Tech risk assessment involving floods was developed. It has been highlighted that the technological accidents caused by floods can produce greater consequences compared to the hazards occurring separately, due to the interaction between flood characteristics and the technological equipment.

Preliminary results show an increase in the expected frequency of single accident scenarios as well as the overall impact registered on site. Furthermore, a significant increase of the values for individual and societal risk is expected when considering a technological accident scenario triggered by a severe flooding event.

The results reveal the importance of taking into consideration external events, such as natural hazards when analyzing the risk associated with technological accidents. In this way more complex procedures and methodologies for Na-Tech risk assessment can be developed. These types of analyses play a significant role in increasing the awareness of the population, authorities and stakeholders regarding Na-Tech risks.

NEW APPLICATIONS OF BEHAVIORAL SURVEY IN THE MONITORING OF POLLUTANTS EFFECTS UPON FRESHWATER FISH.

STUDY CASE: ACUTE TOXICITY OF METHYLMERCURY (II) CHLORIDE IN ZEBRAFISH MODEL

Stefan-Adrian Strungaru[1], Mircea Nicoara[2,*],
Madalina Andreea Robea[2], Elena Todirascu-Ciornea[2],
Gabriel Plavan[2]

[1)] *"Alexandru Ioan Cuza" University of Iasi, Department of Research, Faculty of Biology, Bd. Carol I, 20A, 700505, Iasi, Romania*
[2)] *"Alexandru Ioan Cuza" University of Iasi, Department of Biology, Faculty of Biology, Bd. Carol I, 20A, 700505, Iasi, Romania*
[*]: *mirmag@uaic.ro*

Introduction and study objectives

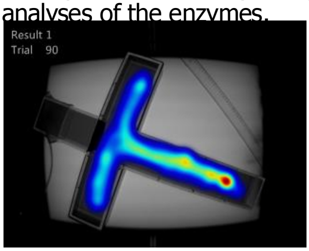
Mercury is an aggressive and potent neurotoxin that significantly increased within environment, leading to concern for human and wildlife health in many regions of the world. The most well-known case recorded in the history of mercury mass poisoning in human population is the Minamata disaster from the Japanese island of Kyushu, in 1956. The UNEP (United Nations Environment Programme) took a decision regarding reduction of the mercury emissions within environment based on its toxicity upon the life forms; it was named Minamata Convention on Mercury and signed by 128 countries and 35 parties. Romania signed it on 10.10.2013 as a member of the European Union. The convention contains a series of recommendations and tasks about the global mercury problem and its toxicological effects. The use of fishes as experimental animals has largely expanded over the past decade for a number of reasons, including the great request in aquaculture, which led to a variety of supporting basic studies in areas such as nutrition, disease, physiology, genetics, ecotoxicology and other toxicological research, as well as fundamental studies in genetics and immunology relevant for higher vertebrate groups, including mammals. The main objective of the study was the assessment of the toxicity upon zebrafish model species of the Methylmercury (II) chloride (CH_3HgCl) released within freshwater environment from anthropogenic activities on the one side, and the development of new ecotoxicological monitoring techniques through interdisciplinary approach, on the other side. The study used methods of behavioral analysis (memory, social interaction, swimming performance, anxiety and learning capacity) in order to gather information about zebrafishes ecology and their response to mercury toxicity.

Methodology

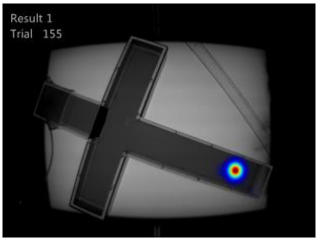
The quantification of behavior changes caused by CH_3HgCl toxicity was based on the software EthoVision XT ver.11.5, developed by NOLDUS. It is used in a wide range of fields, mostly related to neurosciences, such as toxicology, safety pharmacology, psychopharmacology, drug discovery, molecular biology, genetics, behavioral neurosciences, but also in applied ethology and animal welfare studies. This video tracking software is the core of the multiple purpose maze system that is recording with an infrared camera the organisms moving within the arena illuminated by an infrared light source. This type of maze is used in a series of tests for: swimming performance and muscle contraction, memory, learning skills, decision and social interaction. The software was calibrated according to the objectives of the study. The experiments were conducted on 3 fish groups consisting each of 3 males and 3 females of zebrafish adults. The groups were: Group I (1 µg L^{-1} CH_3HgCl), Group II (5 µg L^{-1} CH_3HgCl) and Control group (0 µg L^{-1} CH_3HgCl). The performance of each fish specimen was studied before and after the administration of mercury. Firstly, each fish specimen learned to decide in the water maze in order to avoid the negative stimulus and protect himself. This process needed one week for each group before the treatment. Three tests were used in this study, each one with 120 variables (e.g.: rotation, distance covered, velocity, acceleration) and these were: swimming performance and spatial memory, aggressiveness level and social skills, response to visual negative stimulus from environment. The measurements of the behavior changes were done at 2 h, 6 h, 12 h, 24 h and 32 h after the administration of the treatment and used the tests described above. The required time for each test trail was 4 minutes per subject. In the case of the control group same tests were run, but no treatment was added in the environment.

Results and conclusions

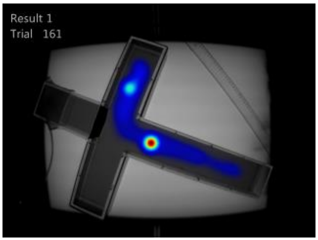
The experiment successfully simulated the effects of acute contamination with Methylmercury (II) chloride - a compound that may result from anthropogenic activities - upon zebrafish model. Though no mortality in the specimens under the treatment was recorded, their neuronal functions were damaged. The concentration of 1 µg L^{-1} CH_3HgCl is 14.28 times higher than the maximum concentration allowed: 0.07 µg L^{-1} (Directive 2013/39/EU, mercury compounds). This can be similar to a shock wave that may result from a pollution source. Very quick changes in the swimming performance and spatial memory of the groups were observed (see the figure below!) caused by the toxicity of the mercury compound. Observations were correlated with the biochemical analyses of the enzymes.



Control group
(0 µg L^{-1} CH_3HgCl)
Trial at 32 h



Group I
(1 µg L^{-1} CH_3HgCl)
Trial at 32 h



Group II
(5 µg L^{-1} CH_3HgCl)
Trial at 32 h

Acknowledgements

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ASSESSMENT OF THE WATER QUALITY OF THE DANUBE RIVER, ROMANIA, USING WATER QUALITY INDICES TECHNIQUE

Alhassan H. Ismail[1,*], **Diana Robescu**[1], **Laura Stanescu**[1]

(1) Faculty of Power Engineering Department of Hydraulics and Environmental Engineering, University POLITEHNICA of Bucharest, Bucharest, Romania
**: hassan19851988@yahoo.com*

Introduction and study objectives

One of the conventional ways of water quality assessment is based on the comparison of a measured value of a parameter, in a water sample, with an existing desirable limit of that parameter. In order to assess the quality of river water, a lot of parameters are required to be determined. The tabulation and interpretation processes of these parameters are sometimes difficult even for the specialists in the water field. Besides, it does not always give a comprehensive vision and integrated concept on the water quality status. Consequently, various tools have been used to overcome this issue such as water quality indices (WQIs).

The water quality index (WQI) can be defined as the aggregation of observed values of water quality parameters to obtain a single number that represents the overall description of the quality of water. Usually, the WQI has a scale from 0 to 100, the highest value representing better water quality and lowest value indicates poorest water quality. Moreover, it can be used to express the quality of water for different uses such as drinking, irrigation and industrial.

In this study, data sets of 13 water quality parameters obtained during 1 year (2008) in four sampling stations were subjected to six different WQIs. The paper aimed at exploring the usefulness of these indices in assessing the water quality of Danube River, to identify the effectiveness of the selected water quality index models through a comprehensive comparison and to get information on the spatial variations of water quality in a simple and easy way. The selected WQIs are Canadian Council of Ministers of the Environment Water Quality Index (CCME-WQI), Oregon Water Quality Index (OWQI), Aquatic Toxicity Index (ATI), Universal Water Quality Index (UWQI), Overall Index of Pollution (OIP) and Bascaron Water Quality Index (BWQI).

Methodology

Danube River was chosen as a case study for water quality assessment, as it is the second longest river in Europe. The calculation of the final value in all selected WQIs in this study was determined to produce a value between 0 and 100. This usually done by transforming the measurement of water quality parameters into a dimensionless number using sub-indices and represent them on a common scale. For the CCME-WQI, all the 13 water quality parameters were considered for the evaluation process. It has a totally different approach among others in which it comprised three factors (scope, frequency and amplitude) for calculating the final index, while other indices, OWQI, ATI, UWQI, OIP and BWQI uses different aggregation methods such as unweighted Harmonic Square mean function, unweighted additive aggregation function, weighted sum function, unweighted arithmetic mean function and weighted sum function, respectively. The number of water quality parameters included in the WQI calculations of OWQI, ATI, UWQI, OIP and BWQI were 6.0, 7.0, 6.0, 4.0 and 8.0 respectively.

Results and conclusions

The results of CCME-WQI showed that the water quality classification scheme for sampling stations was found to be "fair" in station 1, station 3 and station 4, whereas "marginal" in station 2. For OWQI, the water quality categorization for all sampling sites was found as "very poor" and the major parameters that affect the water quality are nitrate (NO3) and total phosphorous. ATI was used to assess the health of aquatic life, especially fish, in the river. The classification scale of the water quality for all sampling sites suggests that the river is of "suitable quality for all fish life" and NH4 was the major important parameter in this index. The results of UWQI revealed that the water quality categorization for all sampling sites was found as "good". Total phosphorous was the prominent parameter in this index. OIP has a scale ranged from 0 to 16; this scale has been converted to a scale ranged from 0 to 100 for comparison purposes. The categorization of water quality in all stations was found as "acceptable". In BWQI, the categorization of water quality in all stations was found as "good". The most important parameters that affect adversely on water quality are NH4 and the water temperature.

The selected water quality index models have different approaches in the implementation process. It was observed that CCME-WQI has a totally different approach and distinct characteristics among others. CCME-WQI has the ability to take into account all the water quality variables, in addition to its flexibility of selecting the water quality standards and comparatively tolerant in case of missing data. However, this index is not free of flaws, such as considering all the water quality variables have the same degree of importance, and it can be applied only when there are available guidelines on water quality parameters. The other WQIs models rely on sub-indices values in the calculation process with different aggregation methods. The CCME-WQI has provided realistic results in comparison to the raw data of the Danube River. The results of the other WQIs (OWQI, ATI, UWQI, OIP, and BWQI) did not introduce representative outcomes of the raw data of the river. Furthermore, it was observed that some of these indices were biased and others have an eclipsing problem. Therefore, CCME-WQI can be applied to assess the water quality in the Danube River as it can express the results more closely. However, other selected index models may be applicable to another water bodies.

ASSESSMENT OF SOIL EROSION USING FOURNIER INDEXES TO ESTIMATE RAINFALL EROSIVITY

Alina Maria Coman, Georgiana Lacatusu, Ana Maria Macsim, Gabriel Lazar[*]

Vasile Alecsandri" University of Bacau, Calea Marasesti, 157, Bacau – 600115, Romania
[*]: *glazar@ub.ro (G. Lazar)*

Introduction and study objectives

Landscape degradation through different processes has intensified and extended spatially to all geographical regions around the world. According to recent assessments, over 70% of the world's agricultural land suffers from erosion, inducing loss of productivity. The erosion by water affects soil productivity and quality by a decrease of infiltration rates, water holding capacity, nutrients, organic matter and soil depth. Soil erosion risk is different from region to region depending on the configuration of the watershed (topography), soil characteristics, local climatic conditions, land use and implemented management practices. Rainfall and land cover are important factors influencing soil erosion. Universal Soil Loss Equation (USLE) is an empirical equation widely used to estimate soil erosion, providing a clear perspective from which to understand the interaction of erosion and its influencing factors.

In this context, it seems necessary to develop a soil erosion model for the study area based on factors influencing erosion. The objective of the study is to determine USLE's parameters and to estimate the erosion, due to rainfall drops impact in a representative area using spatial database GIS techniques. Until now this issue wasn't studied before although it affects vast areas.

Racaciuni watershed is located in the north-eastern part of Romania, in the north part of the administrative border of the Bacau county. It is bordered by Carpathian hills and right bank of the Siret River, being left tributary. The area of the basin is 78.83 km^2; the total length of the river is 17.35 km. The elevation of the study area ranges from 137 to 720 m above sea level. The annual average rainfall of 544 mm and exhibits a wet climatic condition with a minimum mean and maximum temperature of 4.6 ^{0}C and 20.6 ^{0}C, respectively. The soil erosion in the vicinity of the hydrographic network and its main tributaries intensify soil degradation as well as agricultural management practices. The clayey soil in the north-eastern part of the area is most susceptible to erosion.

Methodology

The USLE model (Universal Soil Loss Equation) groups variables that influence the erosion process into five categories including climate, soil profile, relief, vegetation-land use, and land management practices. This empirical assessment has been widely used for both agricultural and forest watersheds to predict the average annual soil loss by introducing improved means of computing the soil erosion factors. The model includes the following factors: rainfall erosivity factor (R), soil erodibility factor (K), topographic factor (Ls), cover and management factor (C), support practice factor (P).

The rainfall factor is a measure of the erosive force of a specific rainfall. This is determined as a function of the volume, intensity, and duration of rainfall and can be computed from a single storm, or a series of storms to include cumulative erosivity from any time period. Rainfall data of 30 years, between 1962 and 2007, collected from Romanian Meteorological Department were used to calculate R-factor. Because the watershed has no record of daily rainfall intensity, for estimating the pluvial aggressiveness on the soils in the study area, Modified Fournier index was determined based on monthly and annual average value, data recorded at the stations which are representative for the basin. Differentiated altitudinal positions of the stations allow the correlation of these indices with altitude, and the position in space allows the analysis of spatial distribution of rainfall aggressiveness index. Soil erodibility factor was obtained from the soil map, taking into account the texture of every soil type, classified with values from national studies, five classes of erodibility being established. The effect of topography results from the combination of two parameters, slopes length and slopes inclination degree, using a digital elevation model, which was created by digitizing contour from the topographic map on 1:5,000 scale. C factor was determined from Corine Land Cover data set (2012), after reclassification, resulted in a number of five classes of vegetation: built area (0), forest (0.1), pastures (0.30), vineyards (0.20) and arable land (0.4). All factors have been measured and integrated into a geographic information system. The USLE equation was implemented in ArcGIS 10.2 software supposing the multiplication of the five involved factors, at the level of each grid cell with 10 m spatial resolution, using Raster calculator tool.

Results and conclusions

The entire database was converted to a raster format, using the Raster Calculator function from the Spatial Analyst extension, the value of potential soil erosion being computed for every pixel. After the combination of all these five factors, the soil loss in t/ha/year was obtained. In this approach, the combination of annual rainfalls, elevation, monthly and mean annual rainfall, and Fournier index was used. Rainfall erosivity factor map showed values ranging from 47 to 108 $MJ \cdot mm \cdot ha^{-1} \cdot h^{-1} \cdot yr^{-1}$. Hence, the value for the annual soil erosion in the Racaciuni basin lies between 0 and 50 $t \cdot ha^{-1} \cdot yr^{-1}$, but are also small areas higher than that.

The lower value has a significant predominance (36.6 %) in the area with a high degree of forestation, resistance to high erosion and a lower degree of anthropic influence. High erosion values area associated with areas characterized by high degree slope and deforested piedmont areas in the neighborhood of settlements. The surfaces affected by high erosion are 22.3 % of the watershed and 41.1 % of the surface have a medium erosivity factor. In this study, the importance of USLE equation is well recognized, in which R factor plays the most important role.

IMPACT OF RISKS ON RESOURCE MANAGEMENT FOR A ROAD PAVEMENT SYSTEM USING MONTE CARLO SIMULATION

Raluca Arba*, Lucia Rusu, Dan Sitar-Taut, Sergiu Jecan

Babeș-Bolyai University of Cluj Napoca, Romania
58-60 Theodor Mihaly Street, Cluj-Napoca, Romania,
**: raluca.arba@econ.ubbcluj.ro*

Introduction and study objectives

Road pavement construction and maintenance are responsible for a considerable amount of resources and energy consumption. Resource management is in this case a complex case with limited options to forecast due to the fact that projects have different sizes, are taking place in regions with various types of soil, landforms or types of distress. Risk and uncertainty are in this case variables that need to be considered and can influence the development of any road pavement project.

The objective of this paper is to offer a solution for risk management using Monte Carlo simulation and by taking into consideration three key aspects for any project management: costs, time and quality. For each one of these factors we will be using a scale of prioritization based on the impact a certain risk may have on them. Besides the above mentioned risk scales in pavement management projects, during the maintenance process it is also important to detect and analyze the types of road distress. This paper uses Monte Carlo simulation procedures with evaluation of risk scales and type of road distress and specifications of correlations between the simulated variables.

We compare then the above method with the results of other projects that use Monte Carlo simulation for road pavement risk management in order to emphasize on its efficiency when taking into account more than one factor that influences a budget. While some of the analysed authors and projects are focusing on conducting a simulation on costs, others use Monte Carlo method to determine the amount of distress a project may involve or the roughness of road pavement. One of the most notable projects is LCCA (Life-Cycle Cost Analysis) in Pavement Design conducted by The Federal Highway Administration in 10 states of US. It uses a model that includes all possible inputs, like real costs for initial construction, rehabilitation and maintenance into the analysis and weighs the probability of occurrence of each in order to determine future costs for risk pavement management. The advantage of the proposed method resides in using a model that involves more than one factor that influences risk management

Methodology

Road pavement projects are characterized by the diversity of situations, dimensions of projects and budgets. Risk scale prioritization is used in decision-making analytical techniques or prospect theory and will be used to determine how resources should be managed in order for a budget to be adapted as to cover the potential risks and for the project to achieve its goals. Any potential risk that is overlooked may lead to an exceeded budget or a failure in complying with performance and quality of road pavement. The present study uses a scale from 1 (very low impact on a considered factor) to 5 (very high impact on a factor) to calculate the levels of risk impact on three major factors – costs, time schedule and quality. A vector of risk prioritizations results and it is used to calculate the global impact (Ig) as a function of maximum from risk prioritization computed for the impact on costs (Rc), prioritization of risks depending on the project time span level (Rt) and quality risk (Rq) -

$$Ig = Max \{Rc, Rt, Rq\}$$

We use the Pavement Condition Index (PCI) and the Long-Term Pavement Performance Program (LTPP) in order to identify and classify risk based on the type of road distress. PCI is used to measure the pavement surface condition using a scale from 1 (very poor) and 5 (very good) and LPTT offers descriptions and measuring methods for all types of distresses (cracks, potholes, rutting, and spalling) in pavement.

Results and conclusions

Taking into consideration the scales presented in the previous section, we have created 50 scenarios of risk analysis by type of distress, level of risk and scales for risk prioritization computed for the impact on costs (Rc), prioritization of risks depending on the project time span level (Rt) and quality risk (Rq). The result is a matrix of scenarios.

We have used this matrix in a Monte Carlo simulation procedure that determines a random number from 1 to 50 and associate this number with a certain road project scenario. The table below show the first three results out of 5000 simulations experiments.

Experiment no	**Random no - Scenario chosen**	**Type of distress**	**Risk**	**PCI**	**Rc**	**Rt**	**Rq**	**Ig**
1	2	Edge Failure	low	3	2	1	2	2
2	6	Edge Failure	high	1	5	2	4	5
3	21	Potholes	moderate	2	3	4	2	4

Considering that a project is considered to be successful and delivered on time when Ig is below or equal to 2 and a project may be finished with reasonable budget and time adjustments when Ig is equal to 3, we have determined with a 95% of certainty that the probability for a project to be successful is 17,78% and 44,72% to be finished with reasonable adjustments. When taking into consideration the type of distress we have determined that there is a probability of 14,32% for a project to experience cracking and out of this percentage there is a probability of 43,72% for the project to be delivered successfully.

This paper presents an efficient method for risk prioritization and resource management involving the examination of a series of simulation experiments. Important factors such as costs, time, quality and the impact of risks on them are used to determine degrees on which a project should efficiently adjust its budget.

Acknowledgements:

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SIMULTANEOUS AND SELECTIVE ELECTROCHEMICAL DETECTION OF PARAQUAT AND CARBARYL PESTICIDES FROM WATER ON BDD ELECTRODE

Aniela Pop, Florica Manea*, Lacrima Ighian, Rodica Pode

Politehnica University of Timisoara, Department of Applied Chemistry and Engineering of Inorganic Compounds and Environment, Faculty of Industrial Chemistry and Environmental Engineering, V. Parvan 6, 300223 Timisoara, Romania,
**: florica.manea@upt.ro*

Introduction and study objectives

The Priority List of Hazardous Substances is revised and published by Agency for Toxic Substances and Disease Registry once at two years, in order of prioritizing the chemical compounds that exert a significant potential threat to the people health. The list is released based on a combination between frequency, toxicity and potential exposure of humans to chemical compounds released into environment. The 2015 Substance Priority List (SPL) include a wide range of pesticides. Among them, paraquat dichloride, reffered as paraquat (PQ), is a toxic herbicide even in traces, with a long resistance time into environment. Carbaryl (CR), known as the first succesfull carbamate pesticide with insecticidal action over 100 species is a hazardous compound listed also on SPL. Due to its indiscriminate use, the bioaccumulation of CR in water sourses could occur. The European Commission established a maximum residue limit of 0.1 $\mu g \cdot L^{-1}$ for any single pesticide in drinking waters, and less than 0.5 $\mu g \cdot L^{-1}$ for the sum of all present pesticides.

In general, pesticides are usualy quantitatively analysed through chromatographic techniques by different detection systems, known as laborious procedures. The electrochemical techniques could be a viable alternative, having in view the fast and easy operation, high sensitivity and reproducibility, but specific electrode material and/or advanced electrochemical techniques are required.

In this paper, simultaneous and selectively detection of PQ and CR pesticides from water samples using amperometric and voltametric techniques on boron-doped diamond (BDD) electrode was successfuly achieved.

Methodology

The electrochemical experiments were performed using an Autolab Pontentiostat/Galvanostat PGStat 302 (EcoChimie, The Netherlands), with a conventional three-electrode cell with saturated calomel electrode as reference, platinum electrode as counter-electrode and BDD electrode as working electrode. Cyclic voltammetry (CV), square-wave voltammetry (SWV) and chronoamperometry (CA) techniques were applied in order to find elaborate the detection protocol for simultaneous and selective determination of both pesticides. PQ and CR were purchased as analytical standards from Sigma-Aldrich (PESTANAL) and freshly prepared.

Results and conclusions

The electrochemical behavior of BDD electrode of each PQ and CR characterized by CV in acetate buffer supporting electrolyte showed that CR is oxidized at the potential value of +1.356 V/SCE and PQ is reduced at the potential value of -0.662 V/SCE.

The mechanism aspects elucidated for each oxidation and reduction process exhibited a great potential for simultaneous/selective detection of these pesticides. The detection protocols are proposed in relation to the potential range that is determining parameter in simultaneous detection of CR and PQ. In Figure 1 are exemplified the recorded chronoamperograms for the simultaneous and selective detection of PQ and CR, with a recorded lowest detection limit (LOD) of $2.7 \cdot 10^{-3}$ µM for PQ and 0.5 µM for CR. Very good electroanalytical performance was achieved also for SWV technique, envisaging direct detection in water sample without supporting electrolyte, which informed about valuable potential practical applications.

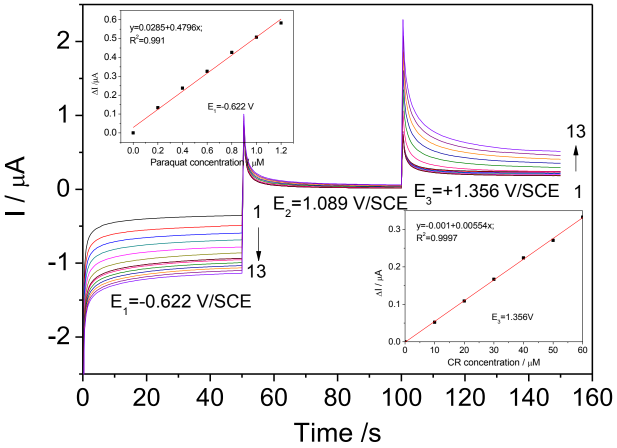

Figure 1: Chronoamperograms recorded on BDD sensor in acetate buffer supporting electrolyte (1) on BDD electrode and in the presence of different CR and PQ concentrations: 2-0.2 µM PQ; 3-0.4 µM PQ; 4-0.6 µM PQ; 5-0.8 µM PQ; 6-1.0 µM PQ; 7-1.2 µM PQ; 8-1.2 µM PQ+10 µM CR; 9-1.2 µM PQ+20 µM CR; 10-1.2 µM PQ+30 µM CR; 11-1.2 µM PQ+40 µM CR; 12-1.2 µM PQ+50 µM CR; 13-1.2 µM PQ+60 µM CR.

Acknowledgements

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PERFORMANCE OF DYNAMIC VOC$_S$ ADSORPTION ONTO HYPERCROSSLINKED POLYMERIC RESINS COMPARED TO ACTIVATED CARBON

Adela Marilena Buburuzan*

Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73 Prof. dr. docent Dimitrie Mangeron Street, 700050, Iasi, Romania,
**: adelahaleta@ch.tuiasi.ro*

Introduction and study objectives

Volatile organic compounds (VOCs) are known as one of the major contributors to the formation of photochemical ozone and secondary organic aerosol (SOA), which are also considered one of the major air pollutants. Many countries have formulated relevant laws to reduce pollutant emissions and developed corresponding reduction targets. The choice of VOCs control technology depends on the actual operating conditions and the physical and chemical properties of organic compounds. Adsorption is a reliable alternative to eliminate organic compounds from industrial waste gases because of the flexibility of the system, low energy and cheap operation costs, which is favored by the majority of researchers. Activated carbons are generally used in many adsorption processes because of their higher adsorption capacity and low cost. However, their efficiency is limited by their sensibility at high temperatures, the self-firing of the adsorbent in the bed, pore blocking and the difficulty in the regeneration of the spent adsorbents. Therefore, the most research is focused to select the adsorbent with a good stability and regeneration performance recently. For this purpose, in ours previously work, the potential of two non-functionalized hypercrosslinked polymers type Macronet, MN 202 and MN 250, in the adsorption of *n*-hexane vapors was studied. The experiments were performed comparative with adsorption of *n*-hexane vapors on granular activated carbon, AC 20 and the results indicated that these polymeric adsorbents record good efficiency for *n*-hexane vapors removal, greater than GAC - AC 20.

The purpose of this work is to study the efficiency of two non-functionalized hypercrosslinked polymers resins, type Macronet, MN 202 and MN 250 on toluene vapors removal, in dynamic conditions, compared to adsorption onto granular activated carbon AC 20. The principle objective is to find the percent adsorption and breakthrough curve of toluene vapors on the MN 202, MN 250 and AC 20 adsorbents.

Methodology

The dynamic experiments of toluene vapors adsorption were carried out in a column of quartz with 1.0 cm diameter using different bed heights of adsorbents (MN 250, MN 202 and AC 20), concentrations of toluene–air mixture, and temperature at a constant flow rates. The temperature of the adsorbent bed was controlled and measured by a thermocouple placed as close to adsorber column as possible. The concentration of toluene vapor in the air stream, before and after the adsorption column, was measured by a gas chromatograph (Carlo Erba 4200 Series) equipped with a six-way valve. The GC is equipped also with a column with 10% DC-200 Chromosorb PNAW, a flame ionization detector (FID) and an integrator. The injector, oven and detector temperature were maintained at 170, 110 and 170°C, respectively. The hydrogen gas was used as the fuel and nitrogen was used as the carrier gas. The calibration curve was prepared by injecting know amounts of the VOC into a sealed bottle equipped with a Teflon septum according to the standard procedure.

Results and conclusions

Performance of adsorption process was quantified by efficiency of toluene vapors removal from gaseous stream, the adsorption capacity and by analyzing the breakthrough profile curves, for each adsorbent studied, in the same experimental conditions. Also, the influence of some operational parameters, like VOCs concentration, the bed depth of adsorbent and temperature of adsorption process, onto breakthrough curves was studied.

To study the effect of concentration on the breakthrough time and adsorption capacity the concentration of toluene vapors in the gaseous stream was varied at 3, 3.5 and 4.5 mg/L at the flow rate of 130mL/min, a temperature of 30°C and at 1 cm bed length of adsorbents in the column, for all three adsorbents studied. It was observed that the adsorption capacity at equilibrium for toluene, q_e (mg/g) was recorded in order MN 250 > AC 20 > MN 202. In the same time, the values of characteristics parameters of the breakthrough, time when breakpoint appear, t_b (considered when the outlet concentration is 20% of the inlet concentration) and the quantity of the adsorbent pollutant at breakpoint, q_b show that the efficiency of toluene removal from gaseous stream is achieved in order MN 250 > MN 202 > AC 20.

To find out the effect of bed length on the breakthrough and adsorption capacity of toluene vapors, the experiments were carried out in 6 mg/L of toluene passed at the flow rate of 130 mL/min at different bed lengths i.e. 1, 1.5 and 2 cm of MN 202, MN 250 and AC 20 respectively. It was observed that increase in length of the bed provides a better adsorption percentage and higher breakpoint time.

To examine the effect of the temperature on the toluene vapor adsorption process, the temperature of the adsorption process was varied from 30, 40 and 50°C, at 3 mg/L of toluene in gaseous stream, the flow rate of 130 mL/min and 1 cm bed length for all three adsorbents. With increasing temperature decreases the adsorption capacity of MN 202, MN 250 and AC 20 for toluene vapors indicating exothermic nature of adsorption process. Also, with increasing the temperature the breakpoint time was reached earlier.

In conclusion, this study showed that hypercrosslinked polymeric resins MN 202 and MN 250 are very suitable for toluene vapors adsorption from gaseous streams, MN 250 also performing the removal of toluene vapors greater than GAC – AC 20.

SOURCES APPORTIONMENT OF AMBIENT AIR POLLUTANT PM10 IN IASI CITY

Ana-Maria Şchiopu[1,2,*], **Ion Apostol**[2],
Adela Marilena Buburuzan[1,*]

[1] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. dr.doc. D. Mangeron Str., 700050 Iaşi, Romania,
[2] Soc. Salubris S.A. Iasi, 43 National Road, Romania
[*]: anamariaschiopu@yahoo.com (A.M. Schiopu); adelahaleta@ch.tuiasi.ro (A.M. Buburuzan)

This study intend to evaluate the air quality in Iasi and to evaluate the consequences of Suspended particulates passing through a size selection port as defined by the PM (10) reference sampling method and SR EN (Romanian Standard – English version) 12341 with a 50% separation efficiency for a 10 µm aerodynamic diameter (PM10) pollutant emissions for the purpose of completing the air quality plan for the City and its substantiation specific measures to reduce emissions of PM10.

According to Order no. 1206/2015 for the approval of lists of administrative units drawn from regimes of employment in areas of zones and agglomerations provided in Annex. 2 of the law no. 104/2011 on ambient air quality, Iasi is engaged in the evaluation scheme I for particulate suspended matter (PM10).

Iaşi fall into Annex I for the I – st management regime – in the List of administrative units in the classification drawn up following I-st management regime for particulate suspended matter (PM10).

Emissions of particulate suspended matter (PM10) in the territory of the city are released into the atmosphere especially in urban areas (residential areas) and industrial platforms. Once released into air pollutants due to the leakage can be transported to different areas depending on weather conditions present. The combination of unfortunate weather conditions, the topology of the region and the concentrations of pollutants can lead to concentrations above target levels / limits with effects on human health.

Air quality monitoring in Iasi agglomeration is achieved by monitoring four automated stations that are part of the National Network for Monitoring Air Quality.

In order to monitor air quality, sanitation operator conducts biannual physico-chemical analyzes regarding PM10 pollutant in 8 big junctions in the city, in two factions:

- In periods when do sanitation (sweeping, spraying and washing mechanized);
- In periods where there is no sanitation (sweeping, spraying and washing mechanized).

The physico - chemical analyses from the sanitation operator are performed in conjunction with instant indicator values registered in the network of air quality monitoring stations, is continually analyzed, taking steps to minimize them.

Table 1: The evolution of air quality to the suspended matter PM_{10} (µg/m^3) from the automatic network monitoring station in Iasi city, into 2008-2015

No	Indicator	PM_{10} Limit values	Medium anual concentration							
			2008	2009	2010	2011	2012	2013*	2014*	2015
1	PM_{10} aut.	50	48,07	39,06	27,40	26,32	26,68	37,13	26,89	27,58**
2	PM_{10} grv.	50	41,59	48,85	28,42	29,86	33,69	30,79	29,93	30,78***

PM_{10} aut. - Automatic measurement

PM_{10} grv. - Measurements using gravitational methods

There were also implemented a series of measures to minimize increases indicator values for PM 10 in the city:

- Invasive real-time skid material used to treat the road in winter.
- Use priority means of mechanized cleaning.
- Sprinkling streets in Regulation hygiene on the health of the population.

In every semester were taken air samples, both during sanitation mechanized and no sanitation, and were analyzed (by a accredited laboratory) and the results indicated that sanitation does not influences the amount of particulate matter. This is due to the height of sampling air taller than that to which the effectiveness watering / street washing which confirms once again that the main cause of overtaking indicator PM10 in the area is not because of missing of the sanitation actions in the area but the traffic that generates particulate suspended matter.

Table 2: The evolution of air quality to the suspended matter PM_{10} (µg/m^3) from the sanitation company made in Iasi city, in 2016 - in 8 big cross-roads

No	Indicator	Concentraction of polluant 2016															
		Int 1		Int 2		Int 3		Int 4		Int 5		Int 6		Int 7		Int 8	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
1	PM_{10}	29	32	37	38	46	47	25	37	35	41	32	36	29	31	31	34

PM_{10} aut. - Automatic measurement

Int – intersection (cross-roads)

a) With sanitation; b) without sanitation

Thus, although analyzes revealed that the activity of splashing / washing area does not have a significant impact on the indicator PM10, sanitation company has not stepped up sanitation mechanized in adjacent stations monitoring air quality in Iasi and will continue this work with all available technical resources.

SO_2 REMOVAL FROM RESIDUAL GASES BY SOLID ADSORBENTS

Oanamari Daniela Orbuleţ[1], Cristina Modrogan[1,*], Pandele Andreea Mădălina[1], Cristina Orbeci[1], Dăncilă Madelene[1], Constantin Bobirică[1]

[1)] Analitycal Chemistry and Environmental Engineering Department, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, str. Polizu, no.1-7, Bucharest Romania,
[*] : c_modrogan@yahoo.com

Introduction and study objectives

One of the main challenges in the power and chemical industries is to remove generated toxic or environmentally harmful gases generated. To comply with stringent environmental and pollutant emissions control regulations, coal-fired power plants must be equipped with new technologies that are efficient and less energy-intensive than status quo technologies for fuel gas cleanup.

In this research, the adsorption equilibrium of sulfur dioxide on various sorts sorbents was studied. Thus, the authors studied the performance of the following sorbents: macroporous resins and highly cross-linked styrene–divinylbenzene (DVB) resins (MN-macronets), which are used as ion exchangers. In order to assess the effects of advanced cross-linking on the various sort of sorbent properties of styrene–divinylbenzene copolymers, two sorts of resins were used as references: an inert macroporous resin, PC 150, with a cross-linking degree of 7% (which represents the equivalent of the highly cross-linked resin MN 200), and the resin C 150, which is obtained by adding sulfonic (HSO_3-) functional groups (which represents the equivalent of the highly cross-linked resin MN 500).

Methodology

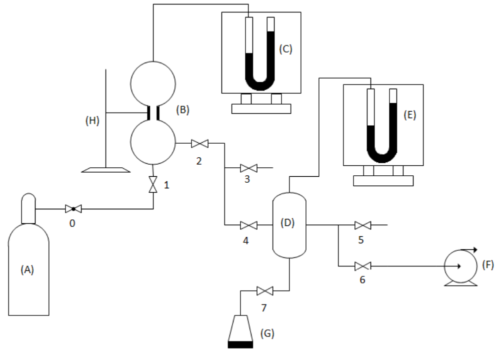
The experiments were conducted in a laboratory plant shown in Figure 1. The operation mode of the plant is as following: the storage tank (B) is fed with sulfur dioxide gas through the opening of the gas tank (A) and of valves 0, 1 and 2, while valves 3 and 4 remain closed. The initial pressure difference is established through vacuuming the plant using the vacuum pump (F) by opening valves 6 and 7 (while all other valves remain closed), and an amount of sulfur dioxide gas equal with the established initial pressure difference is inserted (the pressure difference varies from 40 mmHg to 400 mmHg). Then valves 6 and 7 must to be closed and valve 4 opened.

After the insertion of sulfur dioxide in the vessel (D) valve 4 must be closed and valve 7 opened. Thus, the sulfur dioxide mixed with the adsorbent (that is in the vessel G). It is waiting for the required adsorption time (time set to one hour).

During the adsorption process an increase in the hihgt of the mercury column of the manometer 2 is observed.

After the equilibrium is reached, the valve 7 must be closed and the sample analyzed. Analysis is carried out by adding excess 0.1 N iodine in in the adsorption vessel, and then keep the mixture in contact for 30 minutes.

After 30 minutes, the content of the vessel is filtered and the vessel is washed with distilled water. An amount of starch is added to the liquid sample obtained and then titrated with sodium thiosulfate until no blue coloration is observed



- Gas tank with SO_2 used to feed the plant (A);
- Storage tank for SO_2 (B);
- Laboratory stand (H);
- Manometer 1: the pressure of sulfur dioxide in the storage tank B (C);
- Reactor: composed of a vessel (D) and a laboratory balloon with sample (G);
- Manometer 2: the initial pressure difference (E);
- Vacuum pump (F);
- Laboratory balloon with sample (G);
- Valves (0 ÷ 7)

Figure 1: The physical model used for the gas adsorption process

The difference in volumes of iodine and thiosulphate represents the volume of iodine used in the reaction. The amount of sulfur dioxide adsorbed on the adsorbent mass is calculated based on the amount of iodine consumed in the reaction.

Results and conclusions

Because of the insertion of functional sulfonic groups (HSO_3^-), the sorption capacity of the MN 500 resin is strongly decreasing, due to the decrease of its pore volume and of its specific area. Experimental results establish the equilibrium diagrams in order to determine the adsorption degree of sulfur dioxide on the above mentioned sorbents, by using Langmuir and Freundlich models, at a temperature of $25^{\circ}C \pm 2^{\circ}C$ and a partial pressure of SO_2 in the range 40 mmHg ÷ 400 mmHg.

In the above mentioned range of partial pressures of SO_2 it can be observed that MN 200 resin has an adsorption capacity which is very close to the adsorption capacity of PAC, reaching a value of 290 mg SO_2/g of sorbent at a partial pressure of 300 mmHg. The high sorption capacity of MN 200 resin is due to the cross-linking process, which leads to a 3D molecular network with a high specific area (about 1000 m^2/g). The resins C 150 (inert) and PC 150 (sulfonic cation exchanger) have small adsorption capacities, compared with MN resins and activated carbons, because of their low specific area.

KINETICS STUDY ON CATALYTIC OXIDATION OF AROMATIC VOLATILE ORGANIC COMPOUNDS OVER V_2O_5-WO_3/TiO_2 CATALYST

Liliana Lazar[1,*], **Heinz Koeser**[2]

[1] Gheorghe Asachi Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 73 Prof. dr. docent Dimitrie Mangeron Street, 700050, Iasi, Romania
[2] Otto-von-Guericke University Magdeburg, FVST / IAUT Environmental Engineering, Universitatplatz 2, Magdeburg 39106, Germany
[*]: lillazar@ch.tuiasi.ro

Introduction and study objectives

Volatile organic compounds (VOCs) are responsible for atmosphere pollution due to their contribution to ozone and photochemical smog. As a result of specific properties (high volatility, specific odour, toxicity, carcinogenic character), VOCs represent a potential risk for human health as well. Emissions of gases containing VOCs result from different anthropogenic sources. Alongside major pollutants of municipal waste thermal incinerators (NO_x, SO_2, HCl, HF, CO, heavy metals, mineral pollutants) gas emissions contain different VOCs consisting in hydrocarbons, derivatives containing oxygen, halogenated derivatives, dioxins and furans. Several traditional technologies have been employed to control VOCs emission with many advantages and limitations. Catalytic oxidation has been evidenced to be one of the most reliable and suitable technology for the post-treatment emissions at low VOC concentration. It usually requires lower temperatures that thermal oxidation, due to the use of catalysts. Low-temperature catalysts involving noble metal and metal oxides provide the possibility of fast and selective production of the targeted chemical products (CO_2 and H_2O) under relatively mild conditions. Vanadia-based catalysts have been applied industrially, such as V_2O_5-WO_3/TiO_2 and V_2O_5-MoO_3/TiO_2, which are commercially employed for the reduction of NOx known as SCR-DeNOx catalysts.

In this study, experimental data concerning kinetic investigations of catalytic oxidation of aromatic VOCs over industrial V_2O_5-WO_3/TiO_2 catalyst with low content of active component (0.53 %wt. V_2O_5), is presented. This industrial SCR-DeNOx catalyst (by IHI-Japan) is specific for processes concerning removal of NOx in high-dust system. For kinetic study, benzene and its mono-halogenated derivatives (chlorobenzene and bromobenzene) were chosen as model molecules of the aromatic VOCs. Preliminary tests were performed to determine any limitations by mass transfer and thermal effects, and to evaluate the apparent activation energy of the reaction.

Methodology

The kinetic experiments were performed in a continuous-flow fixed-bed microreactor. The catalytic reactor consists in two concentric quartz tubes, in an electrically heated oven. The incoming gas was heated in the outer ring cylinder to the required reaction temperature before its flow was reversed and returned in the inner cylinder of the reactor were the honeycomb shaped catalysts test element was placed. The catalyst was used in a monolith form, with straight channels. Inside the monolith catalyst a thermo-element was inserted, which was connected to a computer, the reaction temperature being thus monitored on-line. Each catalytic oxidation test conducted in this study was under isothermal operation. Benzene (or its mono-halogenated derivatives) was supplied by a liquid-injection system called controlled evaporation and mixing. Here the liquid aromatic hydrocarbon, controlled by a liquid flow controller, is transported by a carrier inert gas, into the evaporator-mixer and flows as vapour into the system. Catalytic oxidation reaction was conducted in air stream, in the presence and absence, respectively, of water vapour (5 %vol. H_2O) and for low concentrations aromatic VOC in the initial gas-phase (< 100 ppm). The tests were performed at atmospheric pressure and reaction temperature in the range of 150 – 350 °C. The total gas flow rates through the reactor were controlled for establishing the area velocity of 11.5 m/h. The catalytic activity was evaluated in terms of aromatic VOC conversion by gas chromatography equipped with FID and ECD (ParkinElmer, USA). A continues non dispersive Binos 1001 infrared analyser (Rosemount, Germany) was used to determine the CO and an Infralyt 4 (VEB Junkalor, Germany) for the CO_2 concentration of the gases.

Results and conclusions

The studies regarding oxidative destruction of aromatic VOCs on commercial V_2O_5-WO_3/TiO_2 catalyst with low content of active component (0.53 %wt. V_2O_5) may constitute an alternative for treatment of gas emissions with a low content of VOC, taking into account the fact that gases resulted from municipal waste incinerations which undergo a SCR-DeNOx process. The value of conversion increases with temperature, and is influenced by water vapours. The reactivity of aromatic VOCs decreases in order: bromobenzene > chlorobenzene > benzene. Independent of VOC nature and concentration, initial gas phase composition, all the studied aromatic hydrocarbons participate in catalytic oxidation reaction starting with temperature of 150 °C. The catalytic conversion in oxidation reaction in non-humid air stream exceeds the value of 85 % at temperature of 350 °C.

The aromatic VOC catalytic oxidation reaction rate in the presence of oxygen can be described as power law model was chosen as a first approximation. This model is the simplest kinetic equation that describes the rate of aromatic VOC as a function of the concentration or pressures of VOC. Moreover, catalytic oxidation was previously reported to be following the first order reaction. The apparent rate constant (k) follows the Arrhenius equation and thus connect the reaction temperature with the reaction rate. The plot of ln k vs. $1/T$ calculated from the experimental data for different aromatic VOCs. Thus, according to the Arrhenius law both the dimensionless apparent activation energy (E_a/R) and pre-exponential factor (k_0) related to the parameter k have been calculated from these data. The correlation coefficient R^2, obtained for the Arrhenius equation is 0.95 – 0.98 and shows a good fit to the experimental data. The activation energy for the benzene and its derivatives catalytic oxidation has values ranged between 25 – 30 kJ/mol. This values were under the value equal to 42 kJ/mol considered in literature as being the limit at which mass transformation is the limiting rate step for a chemical process. The relative small values of activation energy suggest that the catalytic process rate is influenced by elementary processes of reactants mass transfer through catalyst pores (intern diffusion) and by chemical transformation.

STUDIES ON PHYSICAL ABSORPTION OF CO_2 IN WATER IN AIRLIFT REACTORS (ALRs)

Petronela Cozma[1], Ioan Mămăligă[2],
Manuela Olga Pogăcean[1,3*], Raluca-Maria Hlihor[1,4],
Camelia Smaranda[1], Maria Gavrilescu[1,5*]

1) Department of Environmental Engineering and Management,
2) Department of Chemical Engineering,
"Gheorghe Asachi" Technical University of Iasi, 73 Prof.dr.docent D. Mangeron Street, 700050 Iasi, Romania
3) Phytosanitary Office Mureş, 80 Dezrobirii Street, Târgu Mureş, Romania
4) Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, 3 Aleea Mihail Sadoveanu, 700490 Iasi, Romania
5) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
*****: *manuelapogacean@yahoo.com; mgav@tuiasi.ro*

Although a main component of the carbon cycle, CO_2 is also a major cause of global warming being one of the most important greenhouse gases (GHCs) since it represents 72% of the totally emitted GHCs. CO_2 toxicity generates a variety of syndromes and effects on human health, depending on the initial concentration in air. Anthropogenic CO_2 is emitted from the combustion of fossil fuels (e.g. oil, natural gas, diesel, organic-diesel, petrol, organic-petrol, ethanol). The emissions of CO_2 have sharply increased during the last 50 years and still expects a rise in its amount since it increases by 3% each year. Earth global warming is emerging as a risk all over the world generating public concern mainly due to the appearance of some dangerous meteorological phenomenon like hurricanes, tornados, higher and unexpected floods etc. CO_2 is a component of biogas resulting from anaerobic digestion of organic waste, which reduce the heat capacity of biogas. It is therefore a priority to enhance the energy efficiency of processes and to remove CO_2 from flue gases as essential measures to reduce CO_2 emissions and the Earth global warming issue.

This research focuses on the application of *environmentally-friendly* technologies for the decontamination of CO_2 gas streams (in particular, biogas). As a consequence of biogas purification the carbon intensity can be reduced by use of renewable energy. In this sense, the potential application of airlift reactors for the removal of CO_2 from polluted gas streams by physical absorption in water was investigated. A complex experimental program was elaborated and accomplished, which allowed the evaluation of various operating and design parameters that can affect the efficiency of the process. These parameters are as follows: gas distributor geometry, pneumatic contactor type, the downcomer to riser cross sectional area (*Ad/Ar*) ratio, bottom and top clearances internal baffle height and superficial gas velocity. Both absorption and desorption studies were addressed. From our knowledge, **this is the first study in literature on the removal of CO_2 from biogas using physical absorption with water in airlift reactors.**

The reactor performance is expressed in terms of maximum CO_2 concentration achievement in water after a specific period of time and overall CO_2 volumetric mass transfer coefficient in the liquid phase. Both absorption and desorption studies were employed. It was observed that small downcomer to cross sectional area and large riser (low A_d/A_r ratio) improved the mass transfer of CO_2 from the gas phase to liquid phase.

Finally, the best conditions for effective CO_2 removal from gas stream and baseline data on absorption of carbon dioxide from gas mixture are obtained. Our results demonstrated that airlift reactor is a promising gas liquid contactor showing a high potential for CO_2 mass transfer from a gaseous mixture to water.

Acknowledgements

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ENVIRONMENTAL ASSESMENT OF SURFACE WATERS BASED ON MONITORING DATA AND NEURO-EVOLUTIVE MODELLING

Elena Dragoi[1], Zsófia Kovács[2,*], Silvia Curteanu[1],
Ákos Rédey[2], Igor Creţescu[1,*]

[1)] "Gheorghe Asachi" Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, 73 Prof. dr. Dimitrie Mangeron Blvd, Iaşi 700050, Romania,
[2)] University of Pannonia, Institute of Environmental Engineering, 10 Egyetem St., Veszprém, 8200 Hungary
[*]: icre@tuiasi.ro,

Introduction and study objectives

The quality of surface waters has a high impact on a multitude of social and economic aspects. Consequently, many policies were adopted in order to ensure a good quality of surface waters such as 2000/60/EC Water Framework Directive and 2008/105/EC on environmental quality standard in the field of water policy.

In this context, a series of quality indicators can be used to measure (in a general and transparent manner) the quality of surface water: pH, electrical conductivity (EC), dissolved oxygen (DO), oxygen saturation (OS), chlorophyll-a (Chl-a), turbidity (NTU), biological oxygen demand (BOD), chemical oxygen demand (COD), ammonium-N (NH_4-N), nitrate-N (NO_3-N), total nitrogen (TN), orthophosphate-P (PO_4-P), total phosphorus (TP).

Using the measurements of these indicators in set of 350 water bodies and lake (chosen based criteria like position relative to typology (hydrogeology, catchment area) and different pollution, gathered over a period of time, a local indicator is determined for each point. Based on these local indicators, a general indicator describing the quality of the body of water is determined.

In order to model the variation of water quality over time and to generate predictions that can provide a general picture for this aspect (when the ideal situation is considered: no pollutants or other disruptive effects occur), a neuro-evolutive approach combining a modified version of Differential Evolution algorithm (DE) and Artificial Neural Networks (ANNs) is applied.

DE is a bio-inspired optimizer that mimics the Darwinian principle of evolution and in this context, was used to determine the optimal characteristics (topology and internal parameters) of the ANN (which acts as a model for the considered system). This combination is applied based on the considerations that: i) ANN topology is difficult to determine; ii) good predictions can be generated by the ANN once its optimal characteristics are identified; iii) DE is a powerful optimizer that can provide good solutions in a multitude of cases.

Methodology

The methodology applied in this work include: i) determination of local indicator based on the measurements taken at specific moments of time on specific locations; ii) determination of the general quality indicator at specific moments on time based on the local indicators; iii) generation of a model that correlates the measures taken with the local and general indicators (Figure 1).

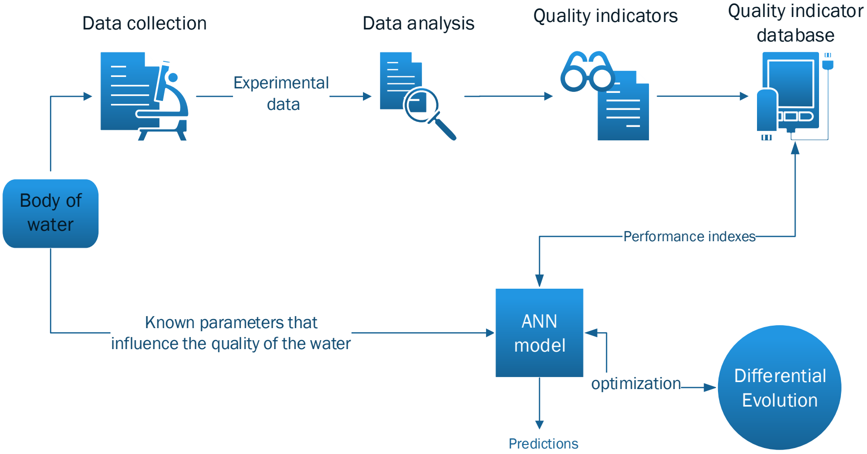

Figure 1: General methodology for quality indicators determination and modelling

Results and conclusions

By employing the proposed methodology, it is possible to perform the water quality assessment and to identify the water bodies which not exhibit a good quality of water. Therefore, this evaluation could predict the future evolution of the water quality status of the water body.

Acknowledgement:

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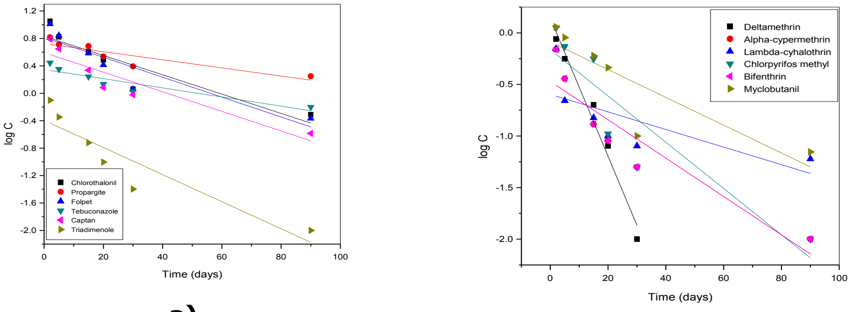
KINETIC MODELLING OF PESTICIDE DEGRADATION IN APPLES

Raluca Maria Hlihor^{1,2}, Petronela Cozma^{1,*},
Manuela Olga Pogăcean^{3}, Isabela Maria Simion^{1,2},
Laura Carmen Apostol^{4}, Maria Gavrilescu^{1,5,*}

$^{1)}$ "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
$^{2)}$ "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, 3 Aleea Mihail Sadoveanu, 700490 Iasi, Romania
$^{3)}$ Phytosanitary Office Mureş, Regional Laboratory for Quality Control of Pesticides, Târgu Mureş, Romania
$^{4)}$ "Stefan cel Mare" University of Suceava, Faculty of Food Engineering, 13 Universitatii Str., 720229 Suceava, Romania
$^{5)}$ Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
*: petronela_cozma@ch.tuiasi.ro, mgav@ch.tuiasi.ro

Determination of pesticides in fruit and vegetables is a priority to assess the quality of food and to avoid possible risks to human health. These compounds are widely used to control pests affecting crops before and after harvest and can easily reach the human population. After applying treatments with pesticides, is considered that they suffer degradation in all compartments: environmental compartments (atmosphere above soil, the soil layer, root-soil layerzone) and vegetation compartments (deposit on the surface of leaves and fruits, leaves, fruit, the thickness of stem and root). Photochemical oxidation, photolysis, hydrolysis and metabolism could contribute to the general degradation of pesticides. Degradation refers to various biological processes, chemical and photochemical decomposition for all considered compartments, leading to reduction of a chemical, and is assumed to follow first order kinetics. The objectives of this work were to study the kinetic behavior of 12 pesticides applied in single and double doses in apples and to assess 6 mathematical models which determine the statistical parameters that describe pesticide behavior. Modeling was performed considering different treatments with pesticides for BBCH (Biologische Bundesanstalt, Bundessortenamt and CHemical industry) scale 76-79 (2/3 of normal size) and given the concentration of pesticides in time from 2 days to 2 months after harvest. In order to evaluate the degradation of pesticides in time and to determine the statistical parameters that describe these processes we used the following kinetic models: first-order, 1.5th – order, second-order, RF-first-order, RF-1.5th – order, RF-second-order. Fig. 1 shows the first-order kinetic model applied for pesticides degradation in apples considering single dose treatments. For most pesticides, the degradation didn't follow the first-order kinetic model as is otherwise often emphasized in literature. Taking this into account, the models described above were applied with good values of correlation coefficients, R^2.



a)

b)

Figure. 1: First-order kinetic model applied for pesticides degradation in apples (single dose treatments)

The half-lives, $t_{1/2}$ resulted from the regression equations considering single dose treatments are between 0.01 (for lambdacyhalothrin) and 74.90 (for myclobutanil) days. Regarding double dose treatments, the half-lives of pesticides have values between 1.51-17.91 days.

Understanding the degradation of pesticides in relation to other factors and evaluation of pesticide residues is very important not only for a correct estimation of food risks, but also to optimize pesticide application techniques in order to improve pesticides monitoring programs. Estimating the degradation of these substances is important for estimating the risk to human health and to optimize pesticide application.

Acknowledgements

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INQUIRY ON PESTICIDES RESIDUES IN PLANT BASED PRODUCTS AT NATIONAL AND INTERNATIONAL LEVEL

Mihaela Rosca[1,2,*], Raluca Maria Hlihor[1,3,*],
Isabela Maria Simion[1,3], Petronela Cozma[1], Maria Gavrilescu[1,4]

[1)] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
[2)] University of Minho, CEB – Centre of Biological Engineering, Campus de Gualtar, 4710-057 Braga, Portugal
[3)] "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania
[4)] Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
[*]: m.rosca@ch.tuiasi.ro, raluca.hlihor@ch.tuiasi.ro

Different types of pesticides are regularly used to maintain a positive balance between supplies and demand for food plants consumption and a high quality of fruits, vegetables and cereals. Commonly, pesticides are classified by International Agency for Research on Cancer (IARC) as carcinogenic or probably/possibly carcinogenic to humans. In this context, consumption of food plants treated with pesticides represents a high potential risk for human health. Our paper examines the situation of pesticides occurrence in plant products in Europe and Romania and actions to mitigate their environmental and human health impacts and risks.

For the reduction of negative effects induced by pesticide residues, different organizations or authorities such as Pesticide Action Network for worldwide, U.S. Department of Agriculture's (USDA), European Food Safety Authority (EFSA) and others, elaborated and implemented several monitoring and control programmes. Based on the information provided by EFSA in 2014 in the annual report about the pesticide occurrence in food plants, in approximately 97.1% of the analyzed samples (82,649 samples totally) were not found pesticide residues or the concentrations were below the maximum residue levels (MRLs). At the European Union level, through the control programme of pesticides residues in fruits, vegetables and cereals, the member countries reported that in the analyzed samples from food plants were identified, a total of 778 different pesticides. The origin of the samples was: 69.4% from food plants produced in EU and EEA countries, 25.7% from third countries, while for 4.9% of the samples the origin was unknown. The highest MRLs were found in spinach, beans, mandarins, carrots, rice, pears, oranges and cucumbers.

In Romania, the control programme of pesticides residues in fruits, vegetables and cereals is implemented and elaborated by National Sanitary

Veterinary and Food Safety Authority (NSVFSA), Ministry of Agriculture and Rural Development (MARD) and Ministry of Health (MH). According to data compiled by the National Multiannual Control Programme of pesticides residues, the samples were taken from food plants with origin from domestic market, EU Member States and third countries. The samples were analyzed to identify the presence of 247 possible active substances. Comparing the results reported by NSVFSA in 2013, 2014 and 2015 it can be observed that the number of samples with residues below MRL decreased (from 30% in 2013 and 33% in 2014, to 26% in 2015), while the number of samples with concentrations above the MRLs increased (from 0.2% in 2013 and 0.9% in 2014, to 1.9 in 2015) (Fig. 1). The origin of all food plants from which samples were taken in 2013 (4528 samples - 1828 vegetables, 1859 fruits and nuts, 224 cereals), 2014 (1711 samples - 491 fruits, 1055 vegetables and 165 cereals) and in 2015 (1737 samples - 581 fruits, 935 vegetables and 221 cereals) was from domestic market, EU, third countries or the origin of the country was unknown (Fig. 2). In Romania, the highest concentrations concerning different pesticide residues in samples were 7.830 mg/kg chlorothalonil in lettuce (in 2013), 3.080 mg/kg for thiophanate-methyl in strawberries (in 2014) and respectively 16.851 mg/kg thiophanate-methyl in parsley (in 2015), which are much higher than the MRLs and could pose high risks for human health.

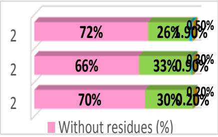

Figure 1: Results concerning pesticides residues in samples taken in Romania between 2013 – 2015 years

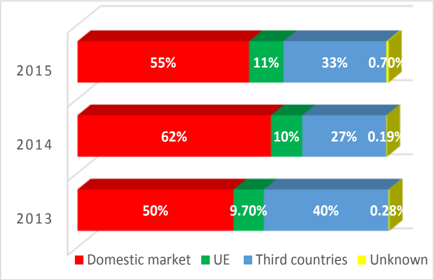

Figure 2: Origin of the food plant samples taken for identification of the pesticides in Romania between 2013 – 2015 years

Therefore, based on the information provided by IARC about pesticides and the data reported by EFSA and national authorities, a careful monitoring and an assessment of the potential risk on human health due to the consumption of food plants containing various types and concentrations of pesticides is required.

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AEROBIC COMPOSTING OF MIXING SEWAGE SLUDGE WITH GREEN WASTE FROM LAWN GRASS

Oana Acatrinei – Insuratelu[1], **Gabriel Buftia**[1],
Iuliana-Mihaela Lazar[2], **Lacramioara Rusu**[2,*]

1) "Vasile Alecsandri" University of Bacau, Doctoral School, 157 Marasesti Str, Bacau 600115 Romania
2) "Vasile Alecsandri" University of Bacau, Department of Chemical and Food Engineering, Marasesti Str. 157, Bacau 600115, Romania
**: lacraistrati04@yahoo.com*

Introduction and study objectives

Waste management is important in practice in terms of reduced pollution. For the organic waste management, different techniques are used: incineration, pyrolysis and gasification, waste disposal in landfills, composting and anaerobic digestion. According to the directive of the European Union, organic waste will have to be reduced to a certain extent; it implies a choice of one of the several methods for their treatment. Among the organic waste treatment processes, the cheapest and most effective is considered to be the composting process.

Generally, the composting process is defined as a biological decomposition process of the heterogeneous organic waste in controlled conditions of moisture, temperature, and aeration. By composting, the organic waste can be converted into compost and can be used to improve the soil quality, for agricultural purposes; also, it can be used in bioremediation of contaminated soils.

Monitoring method was generally used for simulation and optimization of the process in order to develop an efficient composting process. The modeling is an efficient tool for the understanding of the dynamic interaction between the composting mechanisms, to modify the composting process, in order to predict the stability of compost products, and then assuring the obtaining a good quality compost for agriculture use.

The present study aimed to evaluate the behavior during composting of materials such as sewage sludge and green waste and their compatibility in mixtures and the quality of the end product. Also, this study highlights the technical and operational characteristics of a composting system on a laboratory scale.

Methodology

EcoZone^{TM} system was used in the experimental procedure. It consists of three rooms, where compostable organic matter (green waste, anaerobically stabilized sludge) was introduced in different ratio. Before the composting process, the material within each chamber was homogenized and analyzed in triplicates in order to determine the following parameters: the moisture content, the organic matter content, pH, electrical conductivity, dried matter content and the volatile substance content. Each room is equipped with perforated rubber stoppers to allow the insertion of sensors used for measuring the temperature, the oxygen and carbon dioxide concentration during the composting process. To ensure the conditions of carrying out of the process is required every two days mixing and aerating every day. The use of this type of experimental stand allows both observation and monitoring in detail of all phases of composting and correction of the parameters when is necessary (the quantity of water, the temperature, the degree of aeration). Three variants of compost were obtained as follows: Variant 1 (the material was made up of sludge that has been subjected to a heat pretreatment at a temperature of 120°C for 20 minutes and untreated green waste); Variant 2 (sludge and green waste subjected to the same treatment); Variant 3 (sludge and green waste without treatment, considered version control).

The variables used for investigated the model at laboratory scale were: the oxygen and carbon dioxide content, the temperature of the mixture and the time. These parameters were monitored for a period of 21 days.

Results and conclusions

The main characteristics of the final compost obtained for each experimental variant are presented in Table 1.

Table 1: Relationship between composting variant and the characteristics of final compost.

Parameters/ Characteristics	Variant 1	Variant V2	Variant V3
C/N	19	18	18
pH	8.2	8.6	8.7
Moisture content (%)	25.3	35.7	30.5
Dry matter (%)	74.6	64.2	69.4

The use of compost in agriculture requires a C/N ratio between 12 and 18; taking into account this fact, can be concluded that the end products obtained in the three variants comply with this requirement.

The temperature variation during composting process followed a typical pattern exhibited by many composting systems thus; it is found that after 15 days, the temperature was relatively constant, 37 – 42 °C. The highest concentration of carbon dioxide (10.7%- 25.5%) was recorded in the days 2 - 6, after that, the concentration remained relatively constant for all 3 variants until the end of the composting. The maximum value for the oxygen concentration was obtained on the 14th day (23%) in the case of variant 1.

The main advantage of this laboratory scale experiment is the reduced processing time and the fact that it can be fast adapted to different experimental conditions. This concept at pilot scale experiment permits us to investigate the dynamics of main parameters during the composting process and to provide the basis for an efficient design process.

ECOTOXICITY OF FOAMING AGENT CONDITIONED SOILS ON TWO TERRESTRIAL ORGANISMS

Emanuela Galli[1,*], **Valerio G. Muzzini**[1], **Antonio Finizio**[2], **Pietro Fumagalli**[2], **Paola Grenni**[3], **Anna Barra Caracciolo**[3], **Jasmin Rauseo**[3], **Luisa Patrolecco**[3]

[1] IBAF-CNR, Area della Ricerca di Roma 1, Via Salaria Km 29,300;
00015 Monterotondo (Roma) Italia;
[2] Università di Milano Bicocca;
[3] IRSA-CNR
[*]: emanuela.galli@ibaf.cnr.it (E.Galli)

Introduction and study objectives

Commercial foaming products are used as lubricants to facilitate the excavation process in mechanized tunnelling by means of tunnel boring machines (TBMs). These foaming mixtures contain anionic surfactants (AS) as the main component and other additives, generally polymers, not always of a known chemical composition. Sodium lauryl ether sulphate (SLES) is one of the most used AS in foaming agents, in a concentration ranging from 10 to 50% of the overall commercial product. The possible re-use of the huge amount of soil debris produced during the excavation process as by-products (e.g. land covering) or its discharge as a waste depends on the residual concentration of AS in the soil. The first option has the undoubted advantage to lower the costs of disposal. However, concerns are present about the potential environmental risk related to the re-use of conditioned soil. In fact, even if anionic surfactants are generally considered biodegradable and not toxic, information on their biodegradation rates in soil as well as on the ecotoxicological effects of the commercial formulations of foaming products are quite scarce. Recently, some authors tested both foaming agents containing SLES on some plant species and conditioned standard soils on the earthworm *Eisenia foetida*; they did not find any ecotoxicological effect at the dose used in the tunnelling excavation. However, environmental and ecotoxicological data on foaming agents conditioned soil from the construction site are not available so far and an improvement in knowledge of these aspects would be very relevant for the decision making processes of stakeholders.

In the present work, we report some results regarding the biodegradation and ecotoxicological effects of some foaming agents. In particular, we performed two ecotoxicological tests using terrestrial organisms such as the plant *Lepidium sativum* and the earthworm *Eisenia foetida.* The tests were conducted following the traditional OECD protocols, but using two soils conditioned with foaming agents collected from the tunnel excavation area.

Methodology

Two soils with different geopedological characteristics (Soil 1: gravel 56.7% sand 23.1%, silt 14.1%, clay 6.1%; Soil 2: gravel 88.3%, sand 9.1%, silt 2.0%, clay 0.6%), collected (50 m depth) from the tunnel excavation area, were conditioned using three common commercial foaming agents (P1, P2, P3), at concentrations used for mechanized drills. The final concentration of the surfactant SLES in the two soils ranged from 100 to 250 mg/kg. The conditioned soils were put into 1 m^3 mesocosms used to simulate the temporary storage of soil debris produced during the tunnel excavation in the construction site. For each foaming agent (P1, P2, P3) two replicate mesocosms were set up using the Soil 1 and the Soil 2. Moreover, some mesocosms containing Soil 1 were conditioned with a Polymer (PR) in addition to the foaming agent P2, and finally lime was added to Soil 1 conditioned with P1. All the three foaming products (P1, P2, P3) and the Polymer (PR) contained SLES, as the main chemical component of the commercial product (ranging from 10 to 50%), water and minor unknown substances. Soil sub-samples were collected from mesocosms at different times (0, 7, 14, 28 days) and used to perform both the ecotoxicological tests and chemical analysis.

Cress (*Lepidium sativum*) was grown in a greenhouse under controlled conditions, in pots (10x10x22 cm with 20 seeds) filled with treated soils from the mesocosms. At day 21, the growth index (plant dry weight) was measured, comparing it with the control soil.

The earthworm (*Eisenia foetida*) tests were performed in glass boxes filled with 700 g of soil using a double control (artificial soil prepared according to OECD guideline n. 207 and untreated Soil 1 or Soil 2 from mesocosms). At the start of the tests, 20 worms were added in each box then incubated at 20°C. The growth and survival in the soils were tested after 28 days; the effect on reproduction was determined at day 56.

At the same times, aliquots of soil from the mesocosms were used for obtaining elutriates (ratio 1:10 w:v, UNI 14735.2005) to perform the germination test on cress seeds and the acute toxicity test on earthworms. SLES residual concentrations in soil and elutriate were also measured by using the methylene blue active substances (MBAS) method (Standard Methods 5540C, 2012).

Results and conclusions

The overall results showed that both Soil 1 and Soil 2 were not suitable neither for plant growth nor for earthworm reproduction. This negative effect covered the effect of the foaming products. On the contrary, the cress tests performed on elutriates obtained from the conditioned soils did not show any toxic effect on seed germination seven days after the treatment with the foaming agents. In general, the earthworm test performed using the conditioned Soil 1 and Soil 2 elutriates did not cause any toxic effect on these organisms. As expected, a high level of mortality was evident only in soils added with lime due to the high pH value of the samples. The initial SLES content ranging from 78 to 368 mg/kg soil (depending on the product used) corresponded to the environmental concentrations used for tunnelling. Chemical analyses showed that SLES concentration at day 7 was slightly decreased compared to its initial values; a reduction of 30 - 60% was detected, with differences due to the different soils and different foaming products. However, since both the Soil 1 and Soil 2 were excavated from a depth of about 50 m, they were not suitable for plant and earthworm growth and this aspect has to be taken into consideration for their possible re-use as by-products.

STUDIES ON ORGANIC POLLUTANTS TRANSPORT AND DIFFUSION IN VARIOUS ENVIRONMENTAL COMPARTMENTS

Camelia Smaranda[1,*], **Petronela Cozma**[1], **Ioan Mămăligă**[2], **Adrian Catalin Puitel**[3], **Teodor Malutan**[3], **Maria Gavrilescu**[1,4]

1) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. dr.doc. D. Mangeron Str., 700050 Iași, Romania,
2) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Chemical Engineering, Iași, Romania
3) "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Natural and Synthetic Polymers, Iasi, Romania
4) Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
**: betianuc@ch.tuiasi.ro*

The present work was undertaken to explore the mechanism of Congo red (CR) acid dye sorption on three Romanian soils collected from the central and NE regions of Romania. Generally, the sorption process has a complex nature and can be described by the following consecutive steps: transport in the bulk of solution, diffusion across the liquid film surrounding the sorbent particle, and particle diffusion in the liquid contained in the pores and in sorbate along the pore walls. In order to study the mechanism of sorption process and identify the rate controlling factor various diffusion models as intraparticle diffusion, film diffusion and pore diffusion model was applied in the investigated system.

Based on the intraparticle diffusion analysis of pollutant sorption onto soils, the depicted two phases plot suggests that the process occurs by surface sorption and intraparticle diffusion in macro, meso and micropores. The linearity of the plots suggests that intra particle diffusion might have an important role in the sorption of the organic dye on soil particles. The sorption of the dye on the three soils could not be described by simple mechanism of surface only, and it is likely that the sorption on the external surface was followed by diffusion into the pores as well as to the large number of steps on the surface. The first stage takes place during 2 to 20 min and may be considered as the effect of intraparticle diffusion. The second portion of the slope refers to the final equilibrium stage in which the intra-particle diffusion starts to slow down and level out as the extremely low dye concentration remains in solution or maximum sorption was attained. Also, the linear portion of the curves did not pass through the origin, indicating that the intraparticle diffusion is involved in the sorption process, but is not the single rate controlling step of CR sorption on studied soils. It was observed that the values of intraparticle diffusion coefficient k_{id} generally increased with the increase of the initial pollutant concentration from 10 to 100 mg L^{-}

^{1}, which shows that the sorption rate is governed by the diffusion of the dye within the pores of the adsorbent. Our results show an increase of k_{id} values in the following order: Soil-1> Soil-2> Soil-3.

The values of intercept I give information on the boundary layer thickness, and the results shows an increasing of I in the range of 0.318 to 1.116 mg g^{-1} for Soil-1, 0.330 to 0.558 mg g^{-1} for Soil-2 and 0.192 to 3.498 mg g^{-1} for Soil-3. In concordance with these results it can be concluded that boundary layer effect is better at higher initial dye concentration. As the double nature of the intraparticle diffusion plot confirms the presence of film and pore diffusion, the kinetic data for sorption CR on soils Soil-1, Soil-2 and Soil-3 were further analyzed applying Boyd film model. This model was applied to identify whether external transport or intraparticle transport control the rate of sorption.

In order to find out the nature of process responsible for sorption of azo dye Congo red in soil were calculated the diffusion coefficient of the process. The values of pore diffusion coefficient (D_p) and film diffusion coefficient (D_f) and the time for half change ($t_{1/2}$) were calculated under the given set of operating condition and the results are presented in the Table 1. The values of D_p and D_f are ranged from 10^{-9} to 10^{-11} cm^2 s^{-1} indicating that pore diffusion has some influence in the sorption rate limiting step.

Table 1. Pore diffusion (Dp) and film diffusion (Df) coefficients for CR sorption on soils

Soil	***CR (mg L^{-1})***	***t ½ (s)***	***D_p (cm^2 s^{-1})***	***D_f (cm^2 s^{-1})***
Soil-1	10	987.858	0.7592 x 10^{-11}	0.3282 x 10^{-11}
	20	632.049	0.1186 x 10^{-10}	0.5522 x 10^{-11}
	50	679.556	0.1103 x 10^{-10}	0.4424 x 10^{-11}
	100	461.073	0.1626 x 10^{-10}	0.1002 x 10^{-10}
Soil-2	10	2376.504	0.1136 x 10^{-9}	0.1565 x 10^{-9}
	20	1026.884	0.2629 x 10^{-9}	0.1164 x 10^{-9}
	50	531.147	0.5083 x 10^{-9}	0.3521 x 10^{-9}
	100	365.776	0.7381 x 10^{-9}	0.7752 x 10^{-9}
Soil-3	10	529.794	0.1415 x 10^{-10}	0.3532 x10^{-9}
	20	1103.152	0.6798 x 10^{-11}	0.1044 x10^{-10}
	50	852.230	0.8800 x 10^{-11}	0.3688 x10^{-10}
	100	1311.950	0.5716 x 10^{-11}	0.3522 x10^{-10}

We concluded that the sorption mechanism of Congo red on the three studied soils is very complex; intraparticle diffusion is not the only rate controlling step for the sorption of organic pollutant onto the investigated soils. Also, liquid film and pore diffusion are involved in the sorption of CR onto soil matrices, but the results suggest that pore diffusion is the rate limiting step.

Acknowledgement:

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PHOTO-FENTON DEGRADATION OF ORGANIC COMPOUNDS BY IRON(II)-EMBEDDED ACTIVATED CARBON COMPOSITES

M.S. Secula*, A. Vajda, L. Lazar*, I. Mamaliga

Gheorghe Asachi Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 73 Prof. dr. docent Dimitrie Mangeron Street, 700050, Iasi, Romania

**: mariussecula@ch.tuiasi.ro; lillazar@ch.tuiasi.ro*

Introduction and study objectives

One of the most important classes of pollutants is represented by dyes. The synthetic character and complex molecular structure make them more stable and difficult to be biodegraded. At present, there are more than $1 \cdot 10^5$ commercial dyes with an estimated production of $7 \cdot 10^5 - 1 \cdot 10^6$ tons per year. Also, it was reported that about 10 to 40 % of used dyes are evacuated in wastewaters, and 10 to 15 % of dyes reach the environment. The treatment of wastewaters containing dyes in order to separate/degrade dyes is of major importance. The aim of the present work is to investigate the efficiency of a cheap Iron-impregnated activated carbon (AC) Fenton like catalyst towards the photo-Fenton degradation of organic compounds in aqueous solutions. As model pollutant, Indigo Carmine anionic dye is considered.

Methodology

Using the wet impregnation procedure, 5 g of L27 AC material were contacted with Fe(II) solutions of $FeSO_4$ precursor at a theoretical iron content in the resulted composite of 1 %. The L27 AC was impregnated for 3 h at 45 °C, then filtered, washed several times with water and ethanol and dried at 55 °C for 24 h. The obtained composite is noted further herein as Fe-L27. Thermogravimetric analysis (TG/DTG), Fourier transform infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used to investigate the structural, textural, and micromorphology of the catalyst. Total iron content in the obtained composites and iron leakage were determined by spectrophotometric method using phenantroline. Photocatalytic tests were carried in batch mode. In each run, 1 L of 100 mg L^{-1} Indigo Carmine solution was placed in the photoreactor (UV – Consulting Peschl Laboratory Reactor System). The mixture was stirred in dark until the adsorption – desorption equilibrium between the pollutant model and the catalyst surface was established. Then UV irradiation was performed for 2h using a Pen-Ray-Power Supply lamp. 4 mL of reaction mixture were systematically sampled, separated by centrifugation and then 1mL was diluted and analyzed by means of UV–Vis Hitachi spectrophotometer following the absorbance at 261 nm. After the analysis, the undiluted solution was added back into the photocatalytic reactor to minimize the loss in total volume and maintain the solid/liquid ratio.

Results and conclusions

Different Advanced Oxidation Processes (AOPs) such as simple UV, UV/O_3 and heterogeneous photo-Fenton processes are evaluated for the degradation of Indigo Carmine (Fig.1). The Iron(II)-embedded AC composite enhances significantly the degradation process and the complete removal of Indigo Carmine molecule is reached after 10 min of irradiation.

Thermogravimetric analysis, Fourier transform infrared, X-ray diffraction, transmission electron microscopy and BET analysis were employed to investigate the structural, textural, and micromorphology of the catalyst.

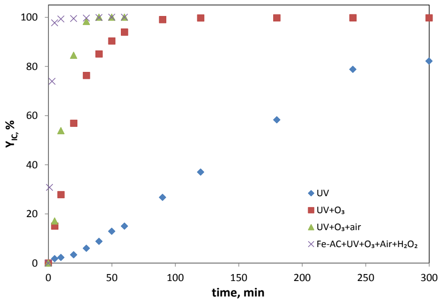

Figure 1: Degradation of Indigo Carmine by different AOPs

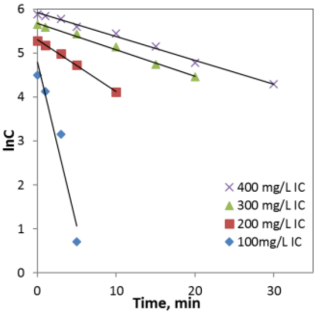

Figure 2: Pseudo-first order kinetics of Indigo Carmine photo-Fenton degradation at different values of initial concentration (0.1 g L^{-1} Fe-L27, 100 mg L^{-1} H_2O_2, pH = 3).

Photocatalytic tests were performed using an UV – Consulting Peschl Laboratory Reactor System. UV light irradiation tests were carried out to determine the performance of the prepared Iron-impregnated composite towards the degradation of Indigo Carmine in aqueous solution using different conditions (17 watts UV lamps, simple or provided with *in-situ* generation of O_3; different values of H_2O_2 concentration, different values of Indigo Carmine initial concentration, different values of pH, different doses of NH_4-OH enhancer). These tests were conducted after the adsorption equilibrium has been established. Fig. 2 shows the pseudo-first order kinetics of photo-Fenton degradation at different values of initial concentration. The obtained results emphasize an enhancement of Indigo Carmine degradation in case of the heterogeneous photo-Fenton process conducted with an O_3 generating UV lamp in the presence of hydrogen peroxide.

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ANALYSIS OF PESTICIDE FATE AND BEHAVIOR IN FRUIT AND VEGETABLES AND ASSOCIATED HUMAN HEALTH RISKS

Raluca Maria Hlihor[1,2], Isabela Maria Simion[1,2,*], Petronela Cozma[1], Manuela Olga Pogăcean[3], Mihaela Roșca[1], Maria Gavrilescu[1,4,*]

[1] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
[2] "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, Faculty of Horticulture, Department of Horticultural Technologies, 3 Aleea Mihail Sadoveanu, 700490 Iasi, Romania
[3] Phytosanitary Office Mureş, Regional Laboratory for Quality Control of Pesticides, Târgu Mureş, Romania
[4] Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
[*]: teslaru.isabel@ch.tuiasi.ro, mgav@ch.tuiasi.ro

Pesticide residues started to be a serious concern to consumers since they are known to have harmful effects not only for pests or diseases aimed by their application, but also for human health. Therefore, the problem of human health risks posed by pesticides is gaining worldwide attention. Major concerns address the presence of pesticides in fruit and vegetables and their toxic effects, since they act as endocrine disruptors, interfere with reproductive systems and development of the fetus, and generate serious diseases like cancer and asthma. Although several studies can be found in literature concerning pesticides in different vegetable products samples from markets, very few are focusing on the pesticide behavior during their application according to vegetables phenological growth phases.

In this context, the present study aims to develop an analysis of current information about pesticide residues in fruit and vegetables and associated human health risks comparative to our results on this subject. The fundamental objective of this work is closely linked with national and international social policies aiming at improving the quality of life. The paper addresses two specific objectives: 1) problem formulation and analysis of data on pesticide residues in fruit and vegetables; and 2) evaluation of human health risks induced by the action of pesticides present in vegetable crops. The objectives are developed according with today's approach which addresses both the long-term moderate exposure to pesticides and towards adopting methodologies for analyzing and monitoring pesticide residues so as to diminish the human health risks.

The line adopted for the study of pesticides fate and behavior in fruits and vegetables considers the fact that, for the estimation of pesticide residues belonging to different classes of compounds, researchers apply different methods of extraction and quantification. The main criterion we used in choosing any methodology is that the analysis method applied to various matrices is quick, easy, cheap, efficient, robust and secure. Materials and methods selected and applied in this work were essential tools for the accomplishment of experimental research program, entailing: the evaluation of the situation of plants exposure to the action of pesticides on a predetermined area given the latest treatments used and applied; investigation of selected pesticides effect on plants when applied both in the recommended normal dose and overdose (double dose); assessment of pesticides effects and their degree of accumulation in the various stages of plant and fruit developments; risk assessment induced by the presence of pesticides in fruits and vegetables for human health.

The risk for human health was characterized as the probability of potentially adverse health effects as a result from human exposures to environmental hazards and included four steps: (i) hazard identification (likelihood to generate damage to humans), (ii) dose-response assessment (analysis of quantitative correlation between exposure and effects), (iii) exposure assessment (frequency, duration, intensities of contact with pesticides) and (iv) risk characterization (analysis of the nature and magnitude of the risk resulted from exposure to pesticides, based on data collected during the development of previous steps). During the analysis, data from literature are related with our data on pesticides hazards and risks acquired based on the study developed in a Romanian site, where diverse pesticides (fungicides, insecticides, acaricides) were applied on plants at various time intervals, in simple and double doses.

Although pesticides use has numerous beneficial effects (e.g. crop protection, preservation of food and materials and prevention of vector-borne diseases), our work highlighted major potential threats of human exposure to pesticides residues in different plant products. Moreover, our study advocated on the prerequisite for surveillance and monitoring programs for pesticide residues in fruits and vegetables so as to protect the final consumers from exposure to this category of persistent organic pollutants.

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THE SEASONAL IMPACT OF PRECIPITATION AND AIR TEMPERATURE ON THE VARIATIONS IN GROUNDWATER LEVELS

Georgiana Lacatusu[1], Alina-Maria Coman[1],
Ana-Maria Macsim[1], Iuliana-Mihaela Lazar[1,*]

[1)] *Vasile Alecsandri" University of Bacau, Calea Marasesti, 157, Bacau – 600115, Romania*
[*] *: ilazar@ub.ro (I. M. Lazar)*

Introduction and study objectives

Since ancient time, the importance of water for people led to interest for its use and improvement. Nowadays, the modern technologies and the overgrowth population contribute to the climate change. The future effects of climate change will be reflected also in water domain. Therefore, the changing type of rainfall, long dry periods, higher evaporation, dry soils - because of the dry climate, all will lead to a low piezometric level, to a low quantity of infiltrated water in rivers and soil. Therefore, in worldwide, were established rules for hydrosphere protection and conservation. Groundwater levels show all the modifications that occur in an aquifer system. The groundwater quantity can be influenced by meteorological parameters like rainfall (it can rise or decrease the piezometric level), temperature (when the temperature is higher, the piezometric level is lower), atmospheric pressure. Rainfall has an important role in the infiltration process and presents two significant steps: the first one is the penetration of the precipitation water into the soil (infiltration), and the second step is percolation (it begins an influx into the groundwater aquifer when the soil is saturated with water). The study focuses on the relationship between precipitation, air temperature, and groundwater level, in period 1973-2014.

Methodology

The study area is located in the east part of Romania, in the south of Bacau city, near the industrial zone. Hydrogeological, the area has two surface water: Bistrita River (the lower water) and Siret River (middle water). From a geological point of view, the wells are placed in an area which belongs to coarse silt, sandy dust, sandy clay, clayey sands, formed in lower and higher Holocene and they are used for drinking water and agricultural activities. Geomorphological, the study area has a fluvial relief (Pliocene-Quaternary) terraces by 1-2 m and terraced slope by 5-7 m (Pliocene-Quaternary). From a meteorological point of view, Bacau city has a temperate- continental climate, with cold winters and hot summers. In the south of Bacau city, where the groundwater was collected, a micro-climate is formed because of natural factors (general circulation of the atmosphere, solar radiation, relief) and anthropic factors (industry, traffic, green spaces, etc.). Meteorological information about monthly temperature and quantity of precipitation from the study area were obtained from the Meteorological National Administration and the hydrogeological data are from the National Institute of Hydrology. The monitored wells are named „FH1", „FH2", „FH3", „FH4", with depth 12 m, 8 m, 8 m, respectively 24 m.

Using mathematical statistics and graphic-analytic methods it is concluded that autumn and winter precipitation have the dominant impact on groundwater level fluctuations, whereas summer season fluctuations are more dependent on the air temperature. Using various climate models it has been proven that with the increase of the air temperature in the future, the levels of groundwater could increase also during the winter.

Results and conclusions

In general, on the study wells, the groundwater level presents the same tendency in spring and autumn: is bigger than in the summer. This happens because in spring and autumn rains, even the rains are small quantitative (approx. 52.18 l/m^2, respectively 46.32 l/m^2) they are long and quiet, and it is easy to infiltrate. In summer, the quantity of precipitation is bigger (79.85 l/m^2), but they are fast and strong, and enters in soil only a part of them; also the air and the soil have a high temperature, a good part of water is evaporating; for this, the water enters only in the surface. During the end of the winter season (February), when a thaw and positive air temperatures occur, the level of groundwater tends to increase, for this the medium of groundwater level measured at monitored wells have the great values compared to the other seasons (Table 1).

Table 1: The average of monthly groundwater levels (cm) for monitored wells in every season and the average of monthly quantity of precipitation (l/m^2)

	FH1 (cm)	FH2 (cm)	FH3 (cm)	FH4 (cm)	Precipitation (l/m^2)
winter	292.484	235.817	185.421	1269.033	34.354
spring	279.762	227.904	169.699	1266.099	52.184
summer	270.238	223.889	172.432	1266.455	79.859
autumn	279.239	227.349	183.639	183.639	46.328

The well FH1 has the highest values of groundwater levels, compared to FH2 and FH3, because it is located very close to Bistrita River and for this, the recharge is also from the river. We discuss separately about FH4 because it is the deepest well - 24 m.

The results highlight the predominant impact of seasonal precipitation on the groundwater level fluctuations.

MASSIVE OPEN ON-LINE COURSES IN OPEN EDUCATIONAL RESOURCES FOR TOXICOLOGY LEARNING. DRUGS AND PERSISTENT ORGANIC POLLUTANTS AS XENOBIOTICS

Ileana Manciulea[1], Stefano Girotti[2], Luca Ferrari[3],
Michele Protti[2], Laura Mercolini[2], Lucia Dumitrescu[1],
Anca Vasilescu[4], Camelia Draghici[1,*]

1) Department of Product Design, Mechatronics and Environment, Transilvania University of Brasov, 29 Eroilor Blv, 500036 Brasov, Romania,
2) Department of Pharmacy and Biotechnology FaBiT, Alma Mater Studiorum – Università di Bologna, Italy
3) Dipartimento di Scienze dell' Educazione 'G.M. Bertin', Alma Mater Studiorum – Università di Bologna, Italy
4) Department of Mathematics and Computer Science, Transilvania University of Brasov, Romania
**: c.draghici@unitbv.ro*

Introduction and study objectives

Due to the lack of European Massive Open On-line Courses (MOOCs) in the field of the Toxicology and major differences in the teaching and learning of this important subject within various European biologically oriented faculties, we proposed and designed the European Erasmus+ project "Learning Toxicology through Open Educational Resources (TOX-OER)". Considering the complexity and heterogeneity of toxicology field, TOX-OER aims to develop and share toxicology-related knowledge and skills among 7 countries, which promote the internationalization of Higher Education Institutions in Europe but also in countries from other continents. The project is coordinated by Universidad de Salamanca (Spain), and the partners are: Space Research and Technology Institute (Bulgaria), Univerzita Karlova V Praze (Czech Republic), South-Eastern Finland University of Applied Sciences (Finland), Università di Bologna (Italy), Universidade do Porto (Portugal) and Universitatea Transilvania din Brasov (Romania).

The aim of this study is to present part of the TOX-OER outcomes developed by the project partnership, especially the modules related to the drugs and persistent organic pollutants, as principal groups of xenobiotics.

Methodology

The TOX-OER European project develops a scientific and pedagogical joint between research in the field of toxicology and MOOC pedagogical design. This will consist in guidelines to support partners for: a) the creation of accessible Open Educational Resources (OER); b) course & modules management; c) the implementation, monitoring and evaluation of individual and social learning activities. This procedure will contribute to the promotion of the learning outcomes in the design and delivery of educational programs and activities in favor of pupils, students, young people, trainees, adult learners, represented by professionals in the field and interested general audience.

The project consortium developed 7 modules: Module 1: General Concepts; Module 2: Pharmaco-Toxicokinetics; Module 3: Principal Groups of Xenobiotics – Prescription Drugs and Drugs of Abuse; Module 4: Environmental Pollutants; Module 5: Target Organ Toxicity and Biomarkers; Module 6: Environmental Toxicology; Module 7: Patents and Patent Application.

Module 3, Principal Groups of Xenobiotics, describes the main toxicological features of prescription and drugs of abuse~~,~~ and their differences from legal and scientific points of view. Analytical methods for their qualitative and quantitative determination in different biological and non-biological matrices will be described and discussed. The most important aspects of regulations in the pharmaceutical sector will be provided and explained.

Module 4, Environmental Pollutants describes the impact of some pollutants (gaseous pollutants, heavy metals, persistent organic pollutants and pesticides) on human health, as well as on the environment, with focus on the persistent organic pollutants.

Results and conclusions

The TOX-OER project creates the conditions for the recognition and certification (ECTS) of learning achievements, at least between partners. Finally, throughout the duration of the project, 01.09.2015 – 31.08.2017, the partners involved in the educational tasks will manage a virtual space (server) within which the MOOC platform will be installed, and where all the Open Educational Resources will be available.

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VALIDATION OF A MULTIRESIDUE METHOD FOR PESTICIDES DETERMINATION IN APPLES BY GAS CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY WITH FLIGHT TIME

Manuela Olga Pogăcean[1,2,*], Raluca-Maria Hlihor[1,3,*],
Lidia Favier[1,4], Maria Gavrilescu[1,5]

[1] "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. Dr. Docent D. Mangeron Str., 700050 Iasi, Romania
[2] Phytosanitary Office Mureş, 80 Dezrobirii Street, Târgu Mureş, Romania
[3] "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine of Iasi, Faculty of Horticulture, Department of Horticultural Technologies, 3 Mihail Sadoveanu Alley, 700490 Iasi, Romania
[4] Superior National School of Chemistry in Rennes, UMR CNRS 6226, Institute of Chemical Sciences Rennes,
Department of Chemistry and Process Engineering, 11 Beaulieu Str., CS 50837, 35708 Rennes Cedex 7, France
[5] Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
[*]: manuelapogacean@yahoo.com, raluca.hlihor@ch.tuiasi.ro

The application of multiresidue analysis has been a common procedure for many laboratories for simultaneous pesticide residues identification and quantification.

The present work reported on the evaluation and validation of a new analytical procedure for pesticides residues quantification in apples samples using gas chromatography coupled with mass spectrometry with flight time (GC-TOF-MS). A modified mini-Luke method was developed and successfully applied for the analyte extraction followed by GC-TOF-MS for separation and quantification purposes. According to the procedure, the pesticides were extracted from the vegetable matrix with a mixture of acetone, dichloromethane and petroleum ether. After evaporation, the extracts were redissolved in isooctane/toluene and further analyzed by GC-TOF-MS using an Agilent 7890 gas chromatograph with a TOF MS Pegasus 4.34 mass spectrometer with two columns of different polarities. The analysis method on GC-TOF-MS developed in the laboratory was validated for a representative matrix (apple blank sample) according to SANCO/825/00. Further, the proposed methodology was validated according to SANCO/10684/2009 in terms of: linearity, matrix effect, limit of quantification, specificity, repeatability, reproducibility, and accuracy. According to the guidelines, an analytical method for pesticides analysis is validated if it meets the following criteria: has recovery values in the range of 70-120%; the relative standard deviation (RSD) does not exceed

20% and the limit of quantification (LOQ), which is the lowest level at which an analyte can be quantified, is smaller or equal to the maximum residue levels (MRLs). Exceptionally, where regressions do not fall within the range of 70-120%, deviations between 60-140% may be accepted, provided that the standard deviation does not exceed 20%. It should be noticed that for method validation, blank samples without pesticide residues, selected from untreated trees were used.

The calculated recoveries, repeatability standard deviation (RSD) and limit of quantification (LOQ) for each analyte obtained under optimized analytical conditions are shown in Table 1. In general, recoveries of all considered molecules were higher than 80.1 %, and the relative standard deviations are less than 20% except one (deltamethrin, 31%). In addition, the correlation coefficients (R^2) of the calibration curves of all targeted pesticides were higher than 0.98. Alpha-cypermethrin did not meet the validation criteria, so it could not be validated for the apple matrix.

Table 1: The performance of the proposed method for the determination of pesticides in apples

Pesticides	***Recovery (%)***	***RSD* (%)***	***LOQ (mg/kg)***	***MRL (mg/kg)***	***R^2*****
Bifenthrin	114.3	18.4	0.01	0.3	0.997
Captan	116.7	19.7	0.02	3	0.984
Chlorothalonil	109.5	14.35	0.02	1	0.993
Chlorpyrifos methyl	100.3	17.3	0.01	0.5	0.997
Deltamethrin	101.3	31	0.05	0.2	0.985
Folpet	81.5	11.8	0.02	3	0.990
Lambda-cyhalothrin	91.8	7.4	0.01	0.1	0.997
Myclobutanil	101.3	14.5	0.02	0.5	0.994
Propargite: 2	112.6	8.4	0.01	3	0.991
Tebuconazole	90.9	8.5	0.05	1	0.996
Triadimenole	107.4	8.9	0.01	0.2	0.995
Alpha-cypermethrin	134	19.6	0.02	1	0.983

**RSD < 20%*

***$R^2 > 0.98$*

These results demonstrated that the analytical strategy prosed in this work can be a promising alternative in the field of the food safety for the assessment of toxic organic compounds.

Acknowledgements

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INFLUENCING FACTORS IN URBAN LAKE WATER QUALITY MONITORING

Cristina Liana Popa[1], **Elfrida M. Carstea**[1,*], **Erika Levei**[2],
Cristian I. Ioja[3], **Roxana Savastru**[1]

[1] National Institute of Research and Development for Optoelectronics, INOE 2000, Magurele, Atomistilor 409, 077125, Romania;
[2] National Institute of R&D for Optoelectronics, Research Institute for Analytical Instrumentation Subsidiary, Donath 67, 400293, Cluj-Napoca, Romania
[3] University of Bucharest, Faculty of Geography, Center for Environmental Research and Impact Studies, Bd. Nicolae Balcescu 1, 010041, Sector 1, Bucharest
: elfrida.carstea@inoe.ro

Introduction and study objectives

Urban environments can contribute greatly to the contamination of lakes and rivers by sewage discharges, industrial effluents or nutrients runoff. Urban lakes are especially under high risk because large quantities of pollutants lead to increased eutrophication, which affects wildlife habitat and population quality of life. Lakes are "ecological barometers of the health of a city". Therefore, complex spatial and temporal evaluation of lake water quality is needed.

Fluorescence spectroscopy has been frequently applied to study the quality of water from different sources and was related to the bacterial composition of water samples. The intensive application of the technique emerged from its multiple advantages: no reagents or sample preparation needed, high sensitivity, small quantities of sample, short measuring time. In the past two decades, research has proven that fluorescence spectroscopy is a valuable technique in evaluating organic matter, off- and on-line. So far, characterization of temporal variation of lake organic matter fluorescence has been intensely studied. Little research has been done on the spatial distribution of lake organic matter.

The aim of this study was to determine the spatial variability of lake organic matter and to assess the contribution of particular water quality parameters in establishing the monitoring plan of urban lakes. Samples from several lakes, located in Bucharest, were measured using conventional methods and fluorescence spectroscopy to determine the characteristics of organic matter. Principal component analysis and Pearson correlation were used to assess the relationship between individual parameters.

Methodology

Lake water samples were collected in July and October 2016 from 19 lakes, located within Bucharest: Grivita, Baneasa, Herastrau, Floreasca, Tei, Plumbuita, Fundeni, Pantelimon, Circului, Tineretului, Carol, Cismigiu, Titan, National, Morarilor, Vacaresti, Morii and Drumul Taberei lakes. In total, 43 samples were measured for total organic carbon, inorganic carbon, dissolved organic carbon, total inorganic carbon, dissolved inorganic carbon, total carbon, dissolved carbon, nitrogen, nitrate, sulfate, phosphate, pH, electrical conductivity, fluoride, chlorine, fluorescence components and pesticides.

The anions were analysed by ion chromatography (IC) with conductivity detection and chemical suppression using a 761 Compact IC (Methrom), equipped with a Metrosep A Supp 5-100/4 mm (polyvinyl alcohol with quaternary ammonium groups, 5μm particle size) column and a Metrosep A Supp 4/5 mm guard column, operating at a flow rate of 0.7 mL/min. The ICP-MS measurement were carried out using an ELAN DRC II (Perkin Elmer) spectrometer equipped with dynamic reaction cell. Total organic carbon (TOC) was determined by catalytic combustion and non-dispersive infrared detection using a 2100S Multi N/C Analyser (Analytic Jena).

Fluorescence measurements were undertaken using a FLS920 spectrofluorimeter (Edinburgh Instruments). Emission spectra were recorded at two excitation wavelengths, 260 nm and 340 nm, in the wavelength emission ranges of 300 – 500 nm and 360 – 500 nm, respectively, with step of 1 nm and dwell time 0.2 s.

Correlation and factor analysis were performed with IBM SPSS software. Factors were extracted using Principal Component Analysis with Varimax rotation and Kaiser normalization. A four-factor solution was chosen and the components with little variability in the data were removed.

Results and conclusions

The protein-like and humic-like fractions of organic matter were detected in the fluorescence spectra of urban lake samples. Peaks T and B, representing the protein-like fraction, were detected within the regions: peak T – excitation wavelength *260 nm*, emission wavelength range *325 – 345 nm*; peak B – excitation wavelength domain *260 nm*, emission wavelength range *300 – 310 nm*. Peaks A and C, designating the humic substances, were observed in the regions: peak A – excitation wavelength *260 nm*, emission wavelength range *405 – 430 nm*; peak C – excitation wavelength *340 nm*, emission wavelength range *410 – 435 nm*. The samples collected from Tineretului lake presented the highest values for protein-like fluorescence, nitrate, sulfate, conductivity and nitrogen. The highest humic-like fluorescence intensity was observed at Vacaresti lake samples, which also contained high quantity of total organic carbon. Circului lake sample showed high intensity at the fluorescence peak associated with recent production of organic matter. The same sample contained the highest quantities of total and dissolved inorganic carbon.

These results indicated a different spatial distribution of organic matter components between the lakes and even between samples from the same lake. This study proved that particular lake areas, with high accumulation of organic matter, from both allochthonous and autochthonous sources, required extensive water quality management to improve and preserve the ecological state.

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PROFILES OF VOCATIONAL INTERESTS FAVORABLE FOR THE INTEGRATION OF ENVIRONMENTAL ENGINEERING STUDENTS

Carmen Cătălina Ioan[1,*], Ileana Maria Carcea[2],
Andrei Dumencu[3], Brindusa Mihaela Sluser[1,*]

1) "Gheorghe Asachi" Technical University of Iaşi, Department of Environmental Engineering and Management, 73 Prof. Dr. Doc. Dimitrie Mangeron Blvd., 700050, Iaşi, Romania
2) "Gheorghe Asachi" Technical University of Iaşi, Department of Teaching Staff Training, 73 Prof. Dr. Doc. Dimitrie Mangeron Blvd., 700050, Iaşi, Romania
3) *"Gheorghe Asachi" Technical University of Iaşi,* Department of Mechanical and Automotive Engineering, 43, Prof.dr.doc. Dimitrie Mangeron Boulevard, 700050 Iasi, *Romania*
**: carioan@ch.tuiasi.ro; brobu@ch.tuiasi.ro*

This study approaches the vocational interests of students as a determinant factor of performance in academic work and also essential premise of personal career strategy, of professional insertion and integration upon graduation. In line with the literature, the vocational interests are defined as manifestations of personality (Holland) as educable dimensions, expressions of the individual's preferences against certain types of activities, for example innovative / conventional, theoretical / practical, individual / team, and certain media of professional work, such as industrial / laboratory, and natural / built in space, institutional space / employee option etc. The integration of these two variables, the type of working environment preferred by the person, outlines ten general professional themes (Jackson). On previous investigations the problem of vocational interests of students in terms of scientific interests and general occupational themes evaluated according to the Jackson Vocational Interest Survey (JVIS) have been studied. The results were interpreted using the theoretical models of the Vocational Requirements of various occupations (TMVR) built on the basis of deductive reasoning. In this paper the requirements of vocational nature of various occupations in the field of environmental engineering through the views of the practitioners, professionals working in those fields to determine the Practical Patterns of Vocational Requirements (PPVR) were approached. The opportunity of this investigation comes from the finding that the interpretation of results through the TMVR indicates that 34% of the evaluated students have non-crystallized profiles of vocational interests, being considered as risk factors both in the personal development during academic studies and for a debut in their career. For this purpose we submit to the evaluation of professionals in the Environmental Engineering Field the ten occupational themes defined by Jackson and tested through the validated tool for the population of Romania, with the possibility of estimating the importance on basis in the practical occupation on five levels - essential, very important, important, desirable, welcomed - or labeling as irrelevant. The general

occupational themes under evaluation are: expressive, logical, curious, practical, assertive, conventional, entrepreneur, communicative.

Similarities between the TMVR and PPVR are further analyzed as well as some differences that they induce in interpreting the profile of the vocational interests of undergraduates in the first and third year and of a group of MS students specialized in environmental engineering obtained by JVIS scale; the identified dominant themes based on responses from professionals, the logical approach and effective communication are common for engineering as a profession and are sufficient to guide high school graduates towards technical faculties. In what concerns the themes that provide information to the specifics of specializations and especially the occupations in the field of environmental engineering there are differences between the two models; TMVR considers curiosity as a defining preference for occupations such as researcher and counselor in environmental issues, which appears only in 40% of respondents according to the professionals' opinion; also the preference for activities involving assertiveness is considered essential in the job of environmental commissioner, but perceived so by only just over 40% of active professionals. One can appreciate that the quantitative analysis at the time of data collection is not relevant, and will be deepened through a qualitative analysis, by broadening the samples investigated.

The conclusions and proposals of this paper show the way in which the knowledge of the extended structure of the profile of vocational interests is useful to guide students towards certain occupations in the field of environmental engineering for their counseling in terms of personal development during their studies and comments upon the content of curricula which can contribute to the crystallization of vocational interests on the cognitive dimension of professional competencies - cultivating logical and creative approaches - on the attitude dimension, of cross skills - the cultivation of efficient professional communication, of responsible and constructive socialization, of an assertiveness specific to the management functions of guidance, management and control. Among the quantitative processing performed so far we have identified the following occupational themes that over 50% of respondents considered essential or very important; communication defined as "clear and detailed development of their own ideas, exposing complex reasoning, evidence and exhaustive argumentation" indicated by over 70%, logical approach to work problems by ' abstract rational thinking, oriented towards testable generalizations, deductive reasoning and precision " rated as critical and very important by over 69% of respondents and conventional attitude " attention to detail, strict compliance to procedures and algorithms" indicated by over 55% of respondents. Further on, we analyze the similarities between MCTV and PPVR and some differences that they induce in interpreting the profile of vocational interests in undergraduate students in the first or third year or a group of MA students specialized in environmental engineering obtained by JVIS scale; the dominant themes are common to engineering as a profession and are sufficient to guide high school graduates towards technical faculties. In what concerns the themes that provide information to specifics of specializations and especially in the field of environmental engineering occupations such as environmental consultant, environmental commissioner, researcher and others, there are differences between the two models, differences analyzed in the paper. Knowing this extensive structure of vocational interests profile, is necessary to guide students towards certain occupations in the field of environmental engineering, for their counseling in terms of personal development while learning.

THE EFFECT OF ENVIRONMENTAL MONITORING ON THE ENVIRONMENTAL LEGISLATIVE PROCESS

Cristina Salcă Rotaru[1]**, Ileana Manciulea**[2]**, Camelia Drăghici**[2]

[1)] Department of Law, Transilvania University of Brasov, Romania
[2)] Department of Product Design, Mechatronics and Environment, Transilvania University of Brasov, 29 Eroilor Blv, 500036 Brasov, Romania,
[*]: c.draghici@unitbv.ro

Introduction and study objectives

For specialist coming from various fields of environmental protection, the specific legislation can't be easily understood because there is a conjunction between many related regulatory actions, legislative acts issued by the national legislation, as well as from both European Union institutions and legal bodies. For law specialists, understanding the environmental legislation is more than a juridical interpretation, due to the particular technical approach of legal standards, but also due to its connection with other law areas.

Regarding the environmental protection field, where the superior interest of the state and the supranational bodies are involved, a more accurate surveillance of the judicial regulation is required, through monitoring and assessment of the necessary amendments, as well as their deployment. This mechanism, generally exceeds the legislative force, especially because it needs to be more flexible but also recognized by law and by those who apply and assess the law enforcement. A brief approach into the juridical field, presented as a whole from both points of view, issuer and legal power, assigned to any law area or to any field of interest, leads to the development of generally aplicable legislative scheme. According to the environmentalists' opinion, the specific monitoring elements can be added to the existing legislative scheme combined with the requirements for a final recognition by the legislation in force. In this respect, we observed that specific parts of the monitoring system flow elements determine the need of legislative scheme transformation.

The aim of his study is to emphasize a need and to turn the environmental legislative scheme into a legislative flow. This flow is useful to specialist from both legal and environmental field to undestand the interactions between both mechanisms, finally they could reach the ultimate goal regarding the environmental protection and the legislation compliance. An extention of this aim is an application of the use of environmental related legislation on Open Educational Resources for toxicology courses.

Methodology

The development of the legislative scheme is specific for each state, based on the internal regulatory mechanism, as well as on the type of documents drawn up by lawmaking powers.

In order to develop the environmental legislative scheme, we have taken into consideration: (i) the Romanian Constitution, establishing the legislative powers and the normative documents recognized at national level; (ii) provisions that regulate the effect of the international treaties on the national legislation; (iii) provisions of the constitutive EU treaties and mandatory regulations and the influence on the EU legislation on the national legal system. According to these provisions, we developed a generally available scheme for any regulatory field.

To design the new proposed environmental legislative flow, we have taken into account: (i) atypical elements from environmental legislation; (ii) the high importance of the standards of environmental monitoring and assesment, imposed by institution with no regulatory competence; (iii) developing the majority of the environmental legal norms that introduce technical terms.

Checking the implementation, the correct application and the real effect (not the expected one) of the legislation, is part of the mechanism stipulated by standards. Collecting data and information obtained by these standards is the basis of feedback mechanism which change the legislative scheme into a legislative flow. Checking the compliance with the normative documents occurs, but if non-compliance is registered, the feedback is applying civil, administrative or criminal legal sanctions.

We observed that even if the normative document is respected, there is no established feedback for the assessment of the achieved targets, as it is in the environmental protection legislation. No other regulation field has such a mechanism, identified as a result of an engineering interpretation of the law.

Results and conclusions

The actual study developed and checked the legislative scheme and the related new flow, emphasizing that the legislative scheme has general applicability, while the legislative flow is less applicable, limited to domains with emergency situations, as the environment protection is.

It came out that where applying the specific legislation is not enough for the environment protection, monitoring mechanisms are useful to streamline the legislation system. The use of the environmental monitoring mechanism, on a larger scale, at the environmental legislation development, is not only welcome, but also needed. This occurs without complicating the legislative process, but used to verify both its real effect and its efficient intervention on the regulations.

Both the legislative scheme and flow, were considered important inputs for educational purpose, therefore were used these to design one module as part of a Toxicology course as Massive Open Online Course, develop within Learning Toxicology through Open Educational Resources – TOX-OER project.

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IPS INFESTATION – A GLOBAL PROBLEM FOR CONIFEROUS

Simona Andrei[1, *], Bran-Elena Petronela[1],
Gabriel-Octavian Lazăr[2]

[1)] *Doctoral School in Environmental Engineering, "Vasile Alecsandri" University of Bacau, 157 Marasesti Str., 600115- Bacau Romania*
[2)] *Faculty of Engineering, "Vasile Alecsandri" University of Bacau, 157 Marasesti Str., Bacau- 600115 Romania*
[*] *: simonaa_andrei@yahoo.com (S. Andrei)*

Introduction and study objectives

Bark beetle infestation (Coleoptera: Curculionidae, Scolytinae) is a relevant issue for forestry sector at global scale. In Europe, the average wood lost because infestations was approximately 2.9 million m^3/year in the last half of the twentieth century. In present, at a global scale, insects affects 30 million hectares of forest annually. The intensity of the bark beetle attack increases in temperate forests worldwide, in Europe, Asia, in southern parts of North America as Mexic, Florida, California and in the north of the continent. In Colorado, from 2009 to 2014, the area affected by bark beetle increased rapidly, from 46,000 ha to 196,000 ha of damaged forest. In Alaska, during the period 1990-2000, spruce mortality was spread over an area of 1,19 million hectares. From 1990 to 2000, in Tatra Mountains, in Poland and Slovak Republic (Central Europe), more than 118,000 m^3 of trees were damaged by Ips typographus infestation.

Although it is the most important agent of tree mortality, bark beetle is considered a secondary pest because it has favorable conditions for development only in damaged trees. Climate warming and drought conditions have led to an unprecedented intensity of infestation. The spatial and temporal dynamics of bark beetle population outbreaks varies according to host species and insect aggressiveness.

In Romania, the largest infested areas with bark beetles, primarily including Ips typographus, are located in the Oriental Carpathians (70%), in Meridional Carpathians where these attacks represent 20% of the affected area and in Occidental Carpathians (10%).

The Vanatori-Neamt Natural Park, located in northeastern Romania, is a protected area which corresponds to category IUCN V. It covers an area of 30,818 ha, including 26,322 ha of forest (85%). In recent years, in terms of unfavorable weather conditions which involves decreasing the amount of rainfall (starting in 2011) and the rise in temperatures, the spruce forest in Targu Neamt area was strongly affected. This coniferous were planted outside of their natural area, for cellulose production, but with lower requirements, in this sector were not done the necessary deforestation. Trees, aged 60-70 years, showed signs of redness needles due to bark beetle attack. It was imposed the works to remove infested trees or even complete deforestation in areas that were affected almost all coniferous.

The aim of this paper is to identify the level of bark beetle infestation and to determine which factors (natural and/or human) favors infestation in Vanatori-Neamt Natural Park.

Methodology, results and conclusions

The study started with the identification of the affected areas. In this sense were made field inspections to assess the health of the ecosystem and infestation of bark beetles. Information on administrative-territorial boundaries was processed using ArcMap application (Figure 1). In Baile Oglinzi area measurements of soil physicochemical properties (pH, conductivity, volatile substances) were made. PH values are in the range 5-6, which is normal for spruce forests.

Following the inspection field, it was observed that Pomete was the most affected area (imposing deforestation). A high degree of drying coniferous was observed in Targu Neamt, also in Oglinzi village (Baile Oglinzi and border areas with Brusturi village). A lower level of damage was observed in villages Agapia, Cracaoani and Vanatori. Near the village Pipirig is the area with the lowest percentage of drying coniferous (in this area predominates pine and fir).

Initial results indicate that the spread of infestation is not directly affected by human activity but only indirectly, because of climate change.

In conclusion, it can be said that the cause of drying coniferous in Vanatori-Neamt Natural Park is not anthropic (the area is not industrial developed) but is based on climate change that started with decreased precipitations from 2011 to present and increasing temperature averages, especially in summer.

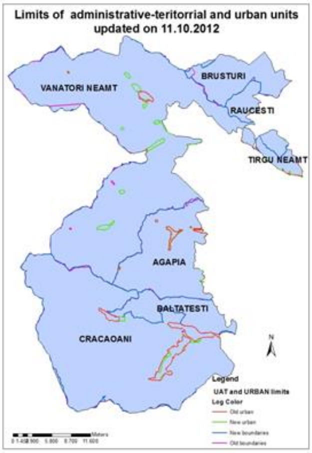

Figure 1: Limits of administrative-territorial and urban units in Vanatori-Neamt Park

A COMPUTER MODELING OF AQUATIC POLLUTANT DISPERSION IN ORDER TO ESTABLISH THE WATER QUALITY UPSTREAM AND DOWNSTREAM OF HOUSEHOLD SETTLEMENTS

Lorand Toth, Angela Călămar, Marius Kovacs, Sorin Simion, Alexandru Simion

INCD INSEMEX Petroşani
Str. G-ral. V. Milea nr. 32-34, 332047, Petroşani, jud. Hunedoara,
*: lorand.toth@insemex.ro

Introduction and study objectives

One of the most important environmental issues in Romania is aquatic pollution, which is an extremely complex phenomenon. Fast industrial development and increased standards of living led to a corresponding increase in water supply capacity, but along with this increase, the amounts of discharged contaminated waters also grew significantly. Many rivers and particularly those crossing inhabited areas are subject to pollutants discharge. Therefore, decision makers managing aquatic environmental need the support of reliable tools for assessing water quality and for predicting consequences of their decisions. This issue can be addressed through the use of computational tools for predicting the concentration of pollutants.

This paper is a dissemination of a project achieved through Nucleu program, implemented with the support of National Authority for Scientific Research and Innovation (NASR), project no. PN 16 43 01 15, with the following objectives: introduction to tributary streams of Jiu river, water sampling methodology, methods of studying the concentrations of water pollutants, water quality analysis on aquatic pollution, correlation of pollution phenomenon with household activities generating water pollutants and not least computer modelling of pollutant dispersion.

Methodology

To investigate the quality of surface waters we chose watercourses sited around Petroșani, thus achieving a comprehensive view of the status of natural receptors of Jiu river tributaries, according to household activities that may cause water pollution.

Monitoring points were chosen both upstream and downstream of household settlements on Slătinioara and Maleia watercourses (tributaries of Jiu river) to perform the analysis of water quality in terms of its pollution. We have chosen comparative sampling which required the identification of sampling locations by fixed points and GPS coordinates. The sampling frequency and timing were set according to water quality, distribution system and not least the source flow.

Before starting the sampling process a number of parameters considered to be of interest, the sampling technique, the types of bottles and conservation methods used were listed. Markers targeted for measurements were: pH, BOD, Sulphates (SO_4^{2-}), Chlorides (Cl^-), Magnesium (Mg^{2+}), Sodium (Na^+), Potassium (K^+), Ammonium (NH_4^+), Nitrite (NO^{2-}), Nitrate (NO^{3-}), Iron (Fe), Phenols (C_6H_5OH). The sampling was carried out so that contamination of samples was avoided. Conservation of the samples was carried out by storing them in the refrigerator at a temperature of at least 4 ° C until performing their analysis.

To gather preliminary information necessary for computer modelling of water pollutant dispersion, sampling points positioned upstream and downstream of household settlements and discharge areas were chosen, thus demonstrating the desideratum regarding the discharge of pollutant - effluent into the environment, at a given angle, by producing a jet whose confluence mainly it depends on the specific weight ratio of the effluent and emissary.

Results and conclusions

Several methods have been used to measure the level of pollution, namely: optical emission spectrometry with inductively coupled plasma, ion chromatography method as well as the spectrophotometric method in the UV-VIS range, with the help of which were obtained representative results for the monitoring program used.

Measurements performed during September-December 2016 showed/revealed that in some sampling points pollutant concentrations are higher than the reference values (background pollution), coincident with the discharge area. Measurements performed at sampling points downstream of household settlements revealed the presence of certain quantities of pollutants, characteristic to household activities as follows: ammonium indicator (27,1 mg / l), nitrite indicator (15,6 mg / l), nitrate indicator (75,2 mg / l), phenol indicator (0,53 mg / l), CBO5 indicator (32 mg / l) and pH indicator (6,1) on one hand and iron (0,009 mg / l), sulphate (57,6 mg / l) and magnesium (0,03 mg / l) indicators on the other hand, confirmed the background pollution and geological features of the area crossed by the stream.

Values of indicators analyzed upstream of household settlements accounted for input data for assessing the watercourse background pollution.

In the case of this paper, the Surface Water Solution (SMS) software was used to monitor the dynamics and properties of pollutants as well as to analyze their dispersion.

In order to achieve the mathematical model of water movement, we used the Reynolds form of Navier-Stokes equations system, in x and y Cartesian coordinates, along with the continuity equation for incompressible fluids in free-flowing turbulent motion by running the RMA2 subprogram within the SMS software. The numerical simulation of advection-diffusion processes at an average depth in the studied aquatic system was performed using the RMA4 subprogram.

Measurements performed as well as the use of specialized software for simulation of pollutants dispersion in the aquatic environment revealed the anthropic impact on the environment.

ICEEM 09 Organizers

Department of Environmental Engineering and Management,
Faculty of Chemical Engineering and Environmental Protection
"Gheorghe Asachi" Technical University of Iasi, Romania

DICAM - Department of Civil, Chemical, Environmental and Materials Engineering
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