Sol-gel technology for greener and more sustainable antimicrobial textiles that use silica matrices with C, and Ag and ZnO as biocides

Igal, Katerine; Zanotti, Karine; Zuin, Vania Gomes; Vazquez, Patricia

Published in:
Current Research in Green and Sustainable Chemistry

DOI:
10.1016/j.crgsc.2021.100177

Publication date:
2021

Document Version
Publisher's PDF, also known as Version of record

Current Research in Green and Sustainable Chemistry 4 (2021) 100177

Contents lists available at ScienceDirect

Current Research in Green and Sustainable Chemistry

journal homepage: www.elsevier.com/journals/current-research-in-green-and-sustainable-chemistry/2666-0865

Sol-gel technology for greener and more sustainable antimicrobial textiles that use silica matrices with C, and Ag and ZnO as biocides

Katerine Igal [a], Karine Zanotti [b], Vania Gomes Zuin [b,c], Patricia Vazquez [a,*]

[a] National Scientific and Technical Research Council (CONICET), La Plata University, Argentina
[b] Department of Chemistry, Federal University of São Carlos, Brazil
[c] Institute of Sustainable Chemistry, Leuphana University Lüneburg, Lüneburg, Germany

ARTICLE INFO

Keywords:
Antimicrobial textiles
Sol-gel method
AgO
ZnO
Green and sustainable chemistry

ABSTRACT

Based on the philosophy of Green Chemistry, in order to grant antimicrobial properties to fabrics, in this work a 100% cotton fabric was used impregnating silver (Ag) and zinc oxide (ZnO) with the addition of carbon extracted from disused batteries, in the intuition of reuse them in a conscious and relevant way. For this, a simple and greener chemical route that occurs at low temperatures was used, the silica-based sol-gel method, which requires a precursor, in this case, tetraethyl orthosilicate (TEOS), and a catalyst to generate the basic hydrolysis using ammonium hydroxide. To evaluate the durability of the coating on the fabric, it was subjected to several wash cycles. Finally, its antimicrobial activity against fungal and bacterial strains was evaluated by the modified standard method (DIN 53931) and the agar-based diffusion method (SN 195920–1992), respectively. The sol-gel green method was effective for obtaining coating for the inhibition of fungal and bacterial strains. In addition, there was a high degree of persistence of the additives after the washing cycles before the antimicrobial tests, registering inhibition up to 20 cycles, making not only the process but also the final alternative fabric greener and more sustainable.

1. Introduction

The development of antimicrobial textiles has been one of the most active and important research areas in recent years, involving activities in the discovery and applications of new agents with antimicrobial activity, new functional fibers, new chemical finishes and nanotechnologies [1–3]. Also, as part of a new movement related to greener and more sustainable textile chains based on the United Nations' Sustainable Development Goals (UN-SGDs) [4]. Due to their highly diversified applications, such antimicrobial fabrics are expected to face anticipated challenges for the future: from increasing, the spread of infectious diseases, especially drug-resistant ones, including bacteria, viruses and fungi, to personal hygiene problems (clothing) [5].

However, the vast majority of publications on this topic focus their research on viruses and bacteria, in the face of this pandemic is a scenario very good at the moment. Only some publications are about of fungi and the use of Ag and ZnO [6,7]. Once the problem of infectious agents is present and increasingly urgent, detailed investigations are necessary, mainly about the less studied topics. Because to providing advances in the development of new antimicrobial technologies, they prepare us to face possible future crises.

Biological pollutants are very versatile and can be transported through the air due to the formation of bioaerosols when partially or totally disseminated. They are living organisms or agents derived from them that manage to develop on substrates located inside buildings. Bioaerosols are linked to diseases such as asthma, allergic rhinitis, and infections [8]. In this sense, filamentous fungi, given their ability to grow on various substrates, are considered among the most deteriorating organisms. Among the fungi that are generally found in the environments inhabited by humans in urban areas are: *Alternaria, Aspergillus, Cladosporium, Penicillium, Chaetomium, Fusarium, Trichoderma, Phaecylomices, Aurebasidium, Phoma* and *Scolecobasidium* [9].

Bibliographic data link them to the deterioration of the materials and its negative effect on human health [10]. It can be said that the genera: *Aspergillus*, are pathogens of animals and humans that cause a group of diseases collectively called aspergillosis; *Chaetomium*, known to produce cellulolytic compounds and *Cladosporium* can be isolated from the air, soil, textiles, food, seeds, crops; being common in interior building

* Corresponding author. Center for Research and Development in Applied Sciences (CINDECA), National Scientific and Technical Research Council (CONICET), La Plata University, La Plata, Argentina.
E-mail addresses: vazquez@quimica.unlp.edu.ar, pgvazquez@hotmail.com (P. Vazquez).

https://doi.org/10.1016/j.crgsc.2021.100177
Received 11 May 2021; Received in revised form 7 September 2021; Accepted 18 September 2021
Available online 25 September 2021

Table 1
Nomenclature and composition of the synthesized samples.

	K3Bis	K3BIZn
TEOS (mL)	34.0	34.0
Ethanol (mL)	43.5	43.5
NH_4OH (mL)	23.5	23.5
H_2O (mL)	10.0	10.0
$AgNO_3$ (g)	0.4	0.4
ZnO (g)	–	1.0
Carbon (g)	1.0	1.0

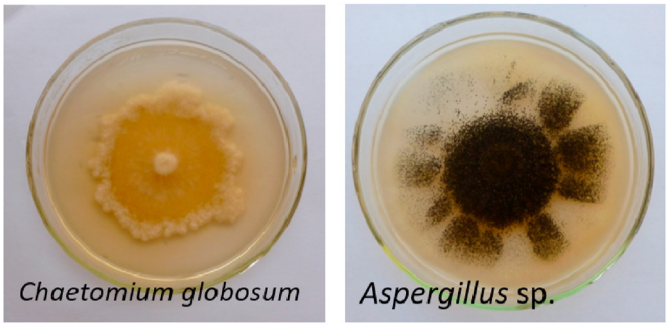

Fig. 1. Photographs of the fungal strains used in the assay.

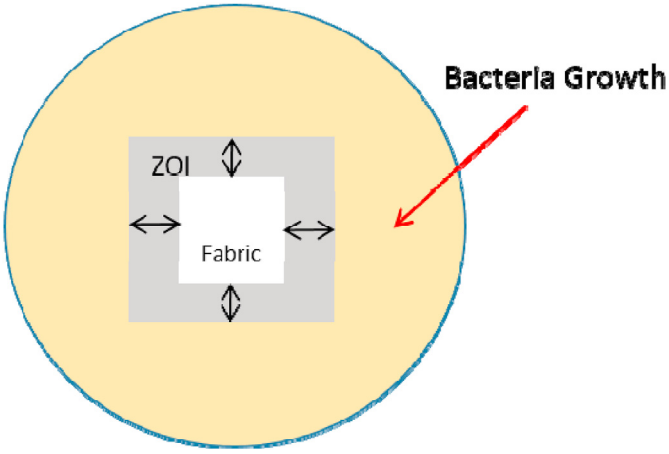

Fig. 2. Scheme of the measurements obtained after incubation.

environments. There are also bacteria that are dangerous pathogens, such as spore-forming ones. They have a great importance in food, industrial and medical microbiology.

Current advances in the field of biomedicine or biotechnology are focused on the preparation of nanoparticles [11–13]. Its morphology plays an important role in the resultant antibacterial activity.

It has been demonstrated that the antibacterial activity of the nanocoatings is increased with a high surface-to-volume ratio due to the decrease in size of the corresponding nanoparticles with antibacterial activity [14]. Metals or metal oxides are being used successfully as such nanoparticles with biocidal action against biological or chemical compounds in textiles (natural or synthetic) [15]. Studies show their advantages when used in sol-gel matrices, such as the excellent antimicrobial activity against bacteria, durability and stability due to the washing cycles and the highly cross-linked silica matrix on the textile surface, respectively [16].

The mechanism of the antimicrobial effect of Ag is not understood, it is proposed that it disturbs the permeability of the cell membrane and the respiration function of the cell [17,18]. The antibacterial activity of ZnO has been addressed in different investigations, but the exact mechanism is not fully clarified and is still controversial [19]. However, the literature already shows that the manner in which antimicrobial agents inhibit or kill bacteria could be associated to different biological or biochemical aspects. These could be cell wall damage, alteration of cytoplasmic membrane permeability, alteration of the physical or chemical sites of proteins, inhibition of enzyme action, and inhibition of protein or nucleic acid synthesis [20,21].

Given that the world is witnessing a crisis with devastating impacts on the environment and society, as can be seen in the appearance of infectious diseases. It is fundamental and consistent to analyze the best materials and methods to obtain the desired products in order to achieve sustainable advances, in theory and in practice. This is not an easy task [22–24]. To achieve this objective, the philosophy of Green Chemistry is very well as basis, which in the early 1990s born due to the need to reduce the negative impact of humanity on the planet [24].

Despite the benefits provided by the advancement of science and industrial development, the environmental cost has been very high, producing substances for which nature does not have efficient reconversion strategies [25]. Anastas & Warner created the 12 principles of Green Chemistry [24], which reflect more conscious ways of doing chemistry by efficiently using raw material, eliminating waste generation, avoiding the use of toxic and/or dangerous reagents and solvents in the production and application of chemical products, among others [26].

The growing interest and diffusion of Green Chemistry is part of an important worldwide advance in the discussions and implementations of new zero waste policies, which can be achieved through education for a sustainable future, where Chemistry is re-thought within and outside the laboratory in a context of circularity [27]. The circular model suggests a continuous flow of materials, avoiding the generation of waste by creating value so that they are reintroduced into the supply chain and/or exploring new processes, which use the products in their entirety, questioning current models [28,29]. Aligning this philosophy with the potential of metal nanoparticles with proven antimicrobial activity, Ag, ZnO and carbon recycled from alkaline batteries were used in this study, treating exhausted batteries as a resource and no longer as a waste. Batteries contain high concentrations of valuable metals, which, if thrown away, pollute the environment. When reused, they become an important raw material, avoiding their extraction in the mines and the consequent environmental impact that this activity entails.

In recent decades, so-called green methods have been introduced in order to develop and synthesize materials that serve to mitigate the problems that society has at the health, socio-economic and environmental level, one of these is the sol-gel method [30]. This opened a new way of synthesis at low temperature, since it allows controlling the properties of a material obtained from very pure liquid precursors [32]. It meets the necessary characteristics to be used as an eco-compatible synthesis, in addition to a selective oxidic network, such as an antimicrobial additive [33].

The term sol-gel is widely applied to describe the chemical route for the synthesis of inorganic oxides in a relatively simple way. The sol is a colloidal dispersion, where the dispersed phase is the dissolved substance that is found to a lesser extent, and the dispersion medium is that where the particles are dispersed [31]. Colloidal solutions or sols contain either large macromolecules, molecular aggregates, or small particles. A gel is a solid consisting of at least two phases: a solid phase that forms a network that traps and immobilizes a liquid phase [34] formed by the gradual loss of part of the liquid from the sol by evaporation. A polymeric gel is an infinite macromolecular network, which is swollen by solvent, and can be created when the concentration of the dispersed species increases. After the sol-gel transition, the solvent phase is removed from the pores of the interconnected network. Gelation can occur after the sol is introduced into a container, and in this way it is possible to obtain materials with a

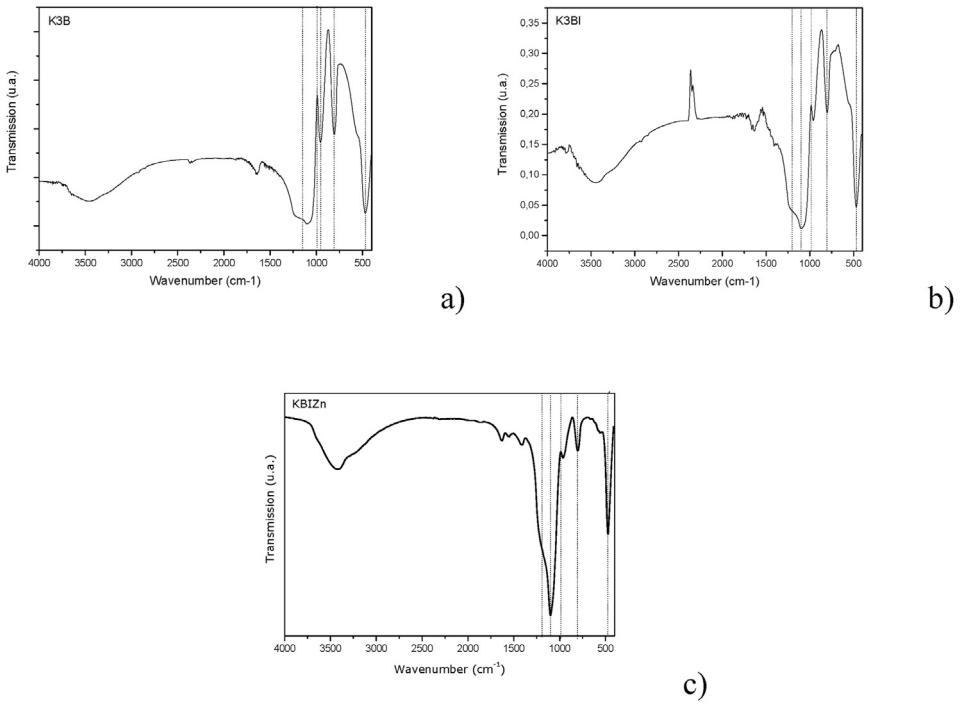

Fig. 3. FT-IR spectrum a) K3B; b) K3BI and c) KBZnAg.

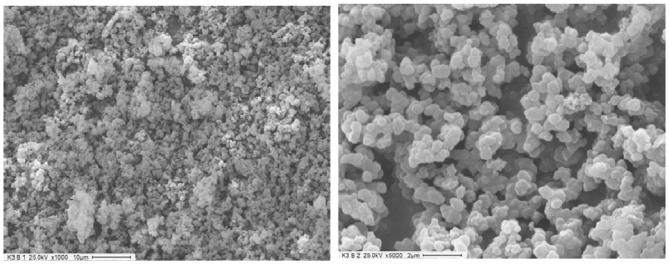

Fig. 4. SEM micrographs of K3B sample (Magnification: 5000× (10 μm), 5000x (2 μm)).

desired shape. Alternatively, gelation can occur from rapid evaporation of the solvent, as occurs during film or fiber preparation. The term aging is applied to the process of change in structure and properties after gelation.

Therefore, in this work, the sol-gel method was used to synthesize modified silicas through the inclusion of Ag and ZnO with the addition of carbon to later be added as antimicrobial additives to obtain antimicrobial fabrics – new materials that can provide solutions to the control of diseases and deterioration produced by different infectious agents, such as fungi and bacteria.

2. Material and methods

2.1. Sol-gel method

To carry out the synthesis of the impregnation of antimicrobial fabrics, pieces of fabric (4 cm × 4 cm) were immersed for 1 min, in the mixture that was prepared. Later, they are removed and left to dry for a week.

The general procedure for obtaining the mixture was to place a portion of the solvent used, ethanol (CH_3CH_2OH, 30 mL, Carlo Erba), in a beaker under a N_2 atmosphere. Later, ammonium hydroxide ($NHOH_4$, 23.5 mL, Anedra) was added as a catalyst, together, the TEOS precursor ($Si(OC_2H_5)_4$, 34 mL, Aldrich 98%) was incorporated. Finally, the rest of the solvent (ethanol, 13.5 mL) and 10 mL of distilled H_2O, continuing the work under an extractor hood under controlled environmental conditions. Then, carbon, extracted from disused batteries, commercial ZnO (Merck, 99,99%), and Ag nitrate ($AgNO_3$, Sigma-Aldrich 99.99%) were added while stirring the mixture.

The methodology for obtaining carbon from disused batteries is found in the following literature: [35–37].

The nomenclature of the samples obtained (K3BIs and K3BIZn) with the content of each compound in them can be seen in Table 1. These impregnated fabrics were exposed against the *Chaetomium globosum* (KU936228) and *Aspergillus* sp. strains to measure their antifungal

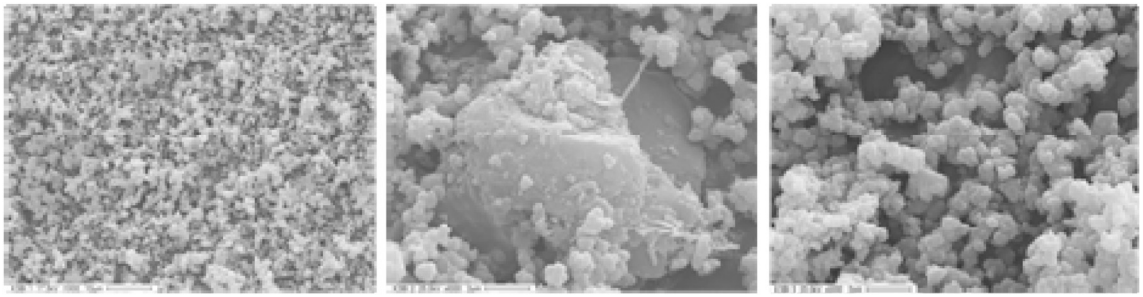

Fig. 5. SEM micrographs of K3BI sample (Magnification: 1000× (10 μm); 5000x (2 μm) and 5000x (2 μm)).

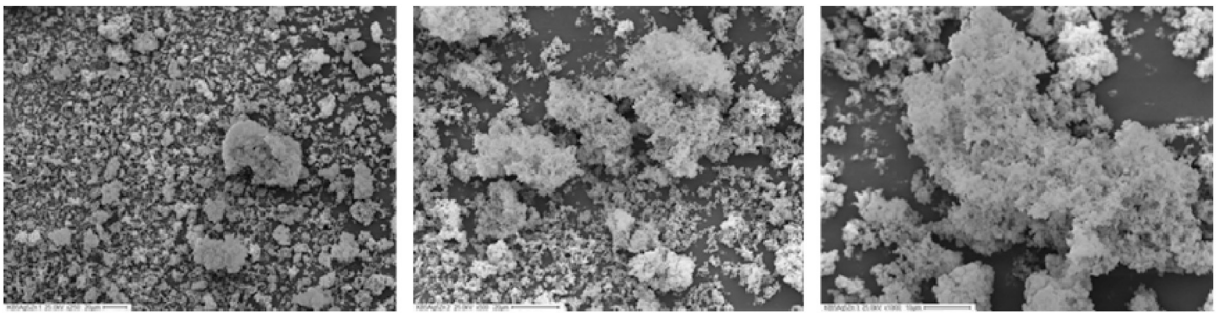

Fig. 6. SEM micrographs of KBZnAg sample (Magnification: 250× (20 μm); 500x (20 μm) and 1000x (10 μm)).

Table 2
Antifungal activity of fabrics impregnated by the sol-gel method against *C. globosum and Aspergillus* sp., according to the modified standard method (DIN 53931).

Sample	Wash cycles	Growth		Sporulation intensity	
		C. globosum	Aspergillus sp.	C. globosum	*Aspergillus*sp.
Control Fabric	0	5	5	+++	++
K3Bis	0	0	2 (10%)	++	++
K3Bis 1°wc	1	0	2 (10%)	++	++
K3Bis 5°wc	5	0	2 (10%)	++	++
K3Bis 20°wc	20	3 (30%)	3 (65%)	++	++
K3BIZn	0	0	2 (10%)	++	++
K3BIZn 1°wc	1	0	2 (10%)	++	++
K3BIZn 5°wc	5	2 (25%)	2 (15%)	++	++
K3BIZn 20°wc	20	3 (30%)	3 (75%)	++	++

activity. In addition, an antibacterial test was carried out against *Escherichia coli* and *Staphilococcus aureus*.

The different samples were characterized by Fourier Transform of Infrared (FTIR) and Scanning Electron Microscopic (SEM) techniques. FTIR spectrum was obtained using Bruker IFS 66 equipment (Germany), pellets of the sample in KBr (Aldrich, 99 wt% FTIR purity), at room temperature, were measured in a range between 400 and 4000 cm^{-1}. SEM was applied to obtain different micrographs of the solids using the JEOL equipment, JSM-6390LV (Japan), with a voltage of 20 kV.

2.2. Wash cycles

To assess the durability of the adhesion of the additives to the fabric, durability tests were carried out against washing. Each sample was subjected to 1, 5 and 20 washing cycles, of 15 min each. Each cycle consisted of placing the impregnated fabrics in a 400 mL beaker in contact with a solution of 2 g/L sodium lauryl sulfate (Biopack) for 15 min. The tissues were rinsed, removed with forceps, placed in another beaker with distilled water. This procedure was carried out twice; afterwards, each cloth was rinsed again with a water wipe, removing any trace of soap.

2.3. Evaluation of the antifungal activity of fabrics

The antifungal activity of the fabrics treated with the modified silicas was estimated with the bioindicators (Fig. 1): *Aspergillus* sp. *and C. globosum* (KU936228) according to the modified standard method DIN 53931 [38].

The culture medium used consists of 1 g of KH_2PO_4 (Anedra, analytical reagent), 1 g of KNO_3, 0.5 g of $MgSO_4$ $7H_2O$ (Anedra, analytical reagent), 0.5 g of KCl (Anedra, analytical reagent), 0.2 g of glucose (Anedra, analytical reagent), 0.2 g of sucrose (Anedra, analytical reagent) and 15 g of agar (Parafarm) per 1 L of distilled H_2O. It is a less nutritious culture medium, allowing more delicate colony growth and easier evaluation of the antifungal activity of the fabric. 100 μL of the previously obtained spore suspension (inoculum) were inoculated, spread with the Drigalsky spatula to obtain a homogeneous lawn of the strain and incubated in an oven at 28 °C for 24 h. The impregnated fabrics were sterilized by UV radiation. It placed in the center of the previously grown plate, working in laminar flow. Then, they were incubated in a 28 °C oven for 14 days. After that time, the antifungal activity was determined in terms of mycelial growth on the surface of the cotton fibers and the intensity of sporulation. To ensure statistical validity, the test was performed in triplicate.

The degree of fungal growth was ordered in degrees from 00 to 5:
(00) indicates no growth;
(0) fungal growth to the edge of the sample;
(1) fungal growth only above and below the edge of the fabric;
(2) fungal growth above and below the sample less than 25%;
(3) fungal growth above and below the sample between 25-75%;
(4) fungal growth above and below the sample greater than 75%;
(5) 100% sample growth.

The intensity of sporulation was evaluated using the following symbols:
- clear, no mycelium;
+ weak, only mycelium;
++ marked growth, partly spores;
+++ strong growth, extensive spore formation.

The inoculum consists of a spore suspension of known concentration obtained from a specific fungal culture. To obtain the inocula, 10 mL of a solution containing 0.85% (p/v) of NaCl and 0.005% (p/v) of Tween 20 were taken, they were deposited on the corresponding cultures and, with the help of using a loop, spores were gently removed to mix with the solution. 5 mL of the suspension obtained were taken with an automatic pipette and were taken to a sterile tube. The mixture was homogenized with the help of a vortex and an aliquot was taken to determine the concentration of the spores present. The concentration of spores (10^5 spores/mL) in the inocula was adjusted by means of a Neubauer chamber and the aid of an optical microscope (OM), with which it was possible to directly quantify the spores. After the counting chamber was seeded, the spores present in each square were counted, an average was taken among the 4 and this value was multiplied by the volume of the cell (0.001 cm^3).

2.4. Agar diffusion method (SN 195920–1992)

To study the antibacterial efficacy of the impregnated fabrics, the agar-based diffusion method was used (SN 195920–1992). The bacterial strains to carry out the test were *E. coli* and *S. aureus*, selected for being abundant in the environment and being related to pathologies that affect

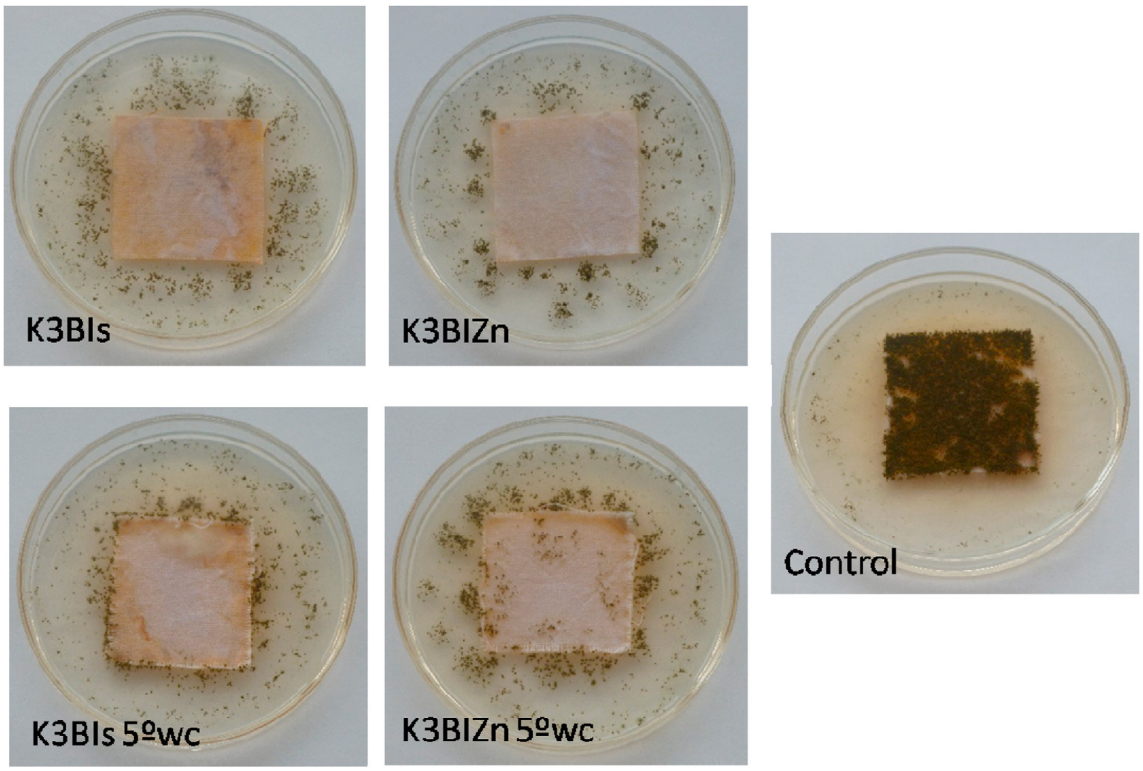

Fig. 7. Antifungal test of fabrics impregnated with the sol-gel method against *C. globosum*.

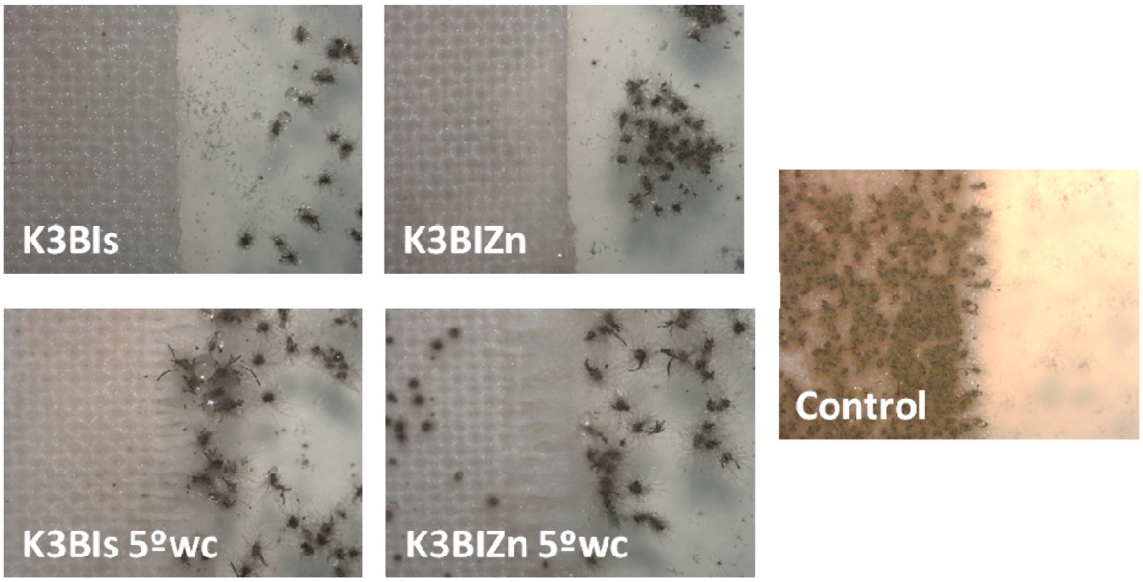

Fig. 8. Images observed with a magnifying glass of the control fabric and the fabrics impregnated with the sol-gel method, tested against *C. globosum*.

human health. The composition of the agarized culture medium (MCAB) used consists of 5 g of NaCl (Anedra, analytical reagent), 5 g of yeast extract (Oxoid), 10 g of casein peptone (Oxoid) and 15 g of bacteriological agar (Biokar) for 1 L of distilled water. Then, plates with 15 mL of the MCAB culture medium were prepared and inoculated with the previously prepared inoculum, which was spread throughout the plate with sterile swabs. Lastly, the treated and untreated fabrics were added. Plates were incubated for 24 h at 37 °C [39,40].

The inoculum was made from 24 h cultures that were in an oven at 37 °C. Suspensions with physiological solution were obtained by adjusting the turbidity to 0.5 of the Mc Farland scale (1.5×10^8 Ufc/mL) [41]. Then a dilution was made to obtain a bacterial suspension of 1.5×10^6. Once the incubation period of the plates inoculated with the selected strains had elapsed, the zone of inhibition (ZOI) was recorded [42]. The results were obtained from the average of four measurements taken in each triplicate as shown in Fig. 2. In addition, the standard deviation between measurements was determined.

3. Results and discussion

The structural and morphological characterization was carried out using different techniques, here we will present by means of SEM and FT-

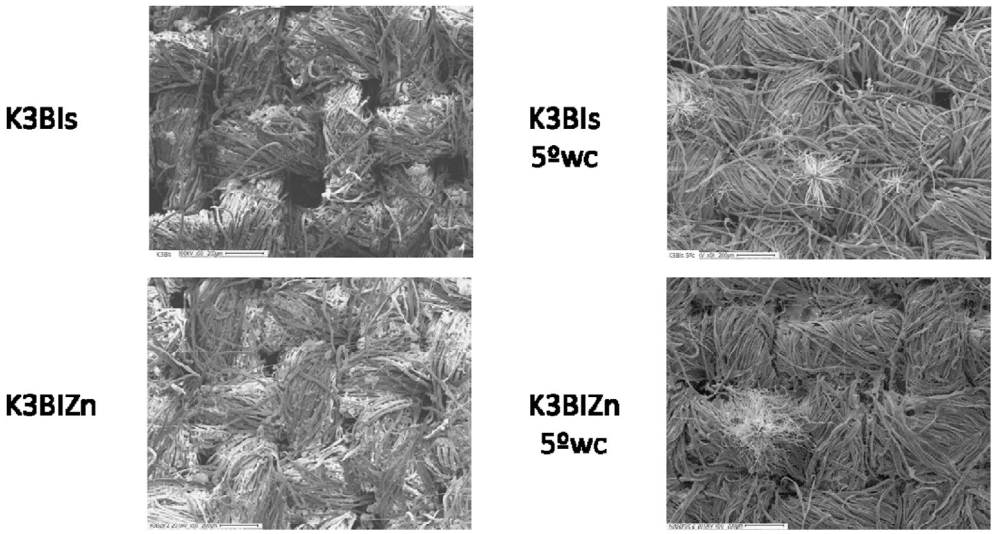

Fig. 9. SEM micrographs of the control fabric and the fabrics impregnated with the sol-gel method, tested against *C. globosum*.

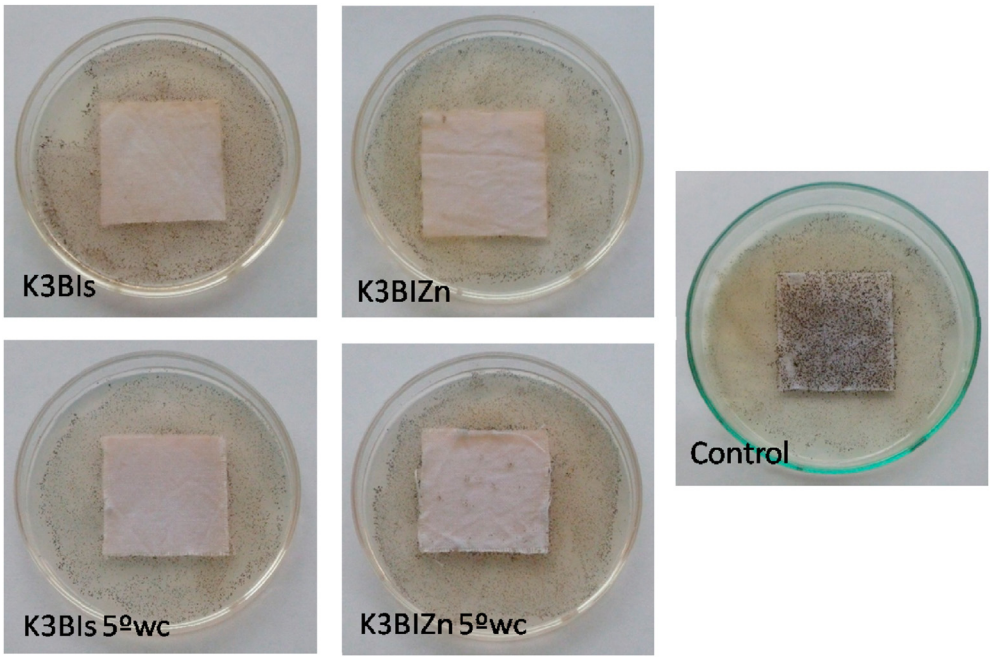

Fig. 10. Antifungal test of fabrics impregnated with the sol-gel method against *Aspergillus* sp.

IR, the evolution of the additives depending on the components. The samples K3B, K3BI (with C and Ag content) and KB5Ag5Zn (without C content, but with Ag and OZn) will be presented as examples.

Regarding the characterization carried out by FT-IR, the bands corresponding to pure silica can be observed in all the samples, which are found at 460, 800, 1080 and 1220 cm^{-1}, respectively, as can be seen in Fig. 3 (a, b and c). The bands at 1220 and 1080 cm^{-1} are assigned to the Si–O–Si bond asymmetric stretching modes. The vibration at 800 cm^{-1} is associated with the symmetric stretching of the Si–O–Si bond or vibrational modes of ring structures. The band at 460 cm^{-1} is assigned to the bending mode of the Si–O–Si link, although it can be associated with defects caused by non-symmetric links. Samples containing C show the same bands as pure silica. As long as Ag is added to the additive there is a small shift in the bands 1220 and 1080 cm^{-1} assigned to the Si–O–Si bond asymmetric stretching modes. These same bands suffer a notable shift when the synthesis is carried out with Ag and OZn and is compared with the samples containing C.

In the SEM micrographs (Figs. 4 and 5 and **6**), it can be seen that the particles have a mostly rounded morphology. These particles form clusters of variable size due to the action of ammonium hydroxide (basic hydrolysis), which reduces the stability of the silica obtained with TEOS as a precursor (see Fig. 6).

As detailed in the **Introduction** section, the fungi that were tested belong to the genus *Aspergillus* and *Chaetomium globosum* (KU936228), taking into account that the last-mentioned is widely known for its cellulolytic activity [43,44].

Chaetomium species produce ascospores, which are characteristic and relatively easy to identify. They have spherical to pyriform (pear-shaped) asci (spore-producing sex cells of ascomycete fungi), covered with characteristic hairs, which may or may not be branched, wavy or spirally wound. Asci typically produce eight cylindrical or rough-shaped ascospores. Ascospores are asept, smooth, dark, with variations in shape and size, but limoniform in most indoor species, and released in a dark mass. One of the most common indoor species is *Chaetomium globosum*, a

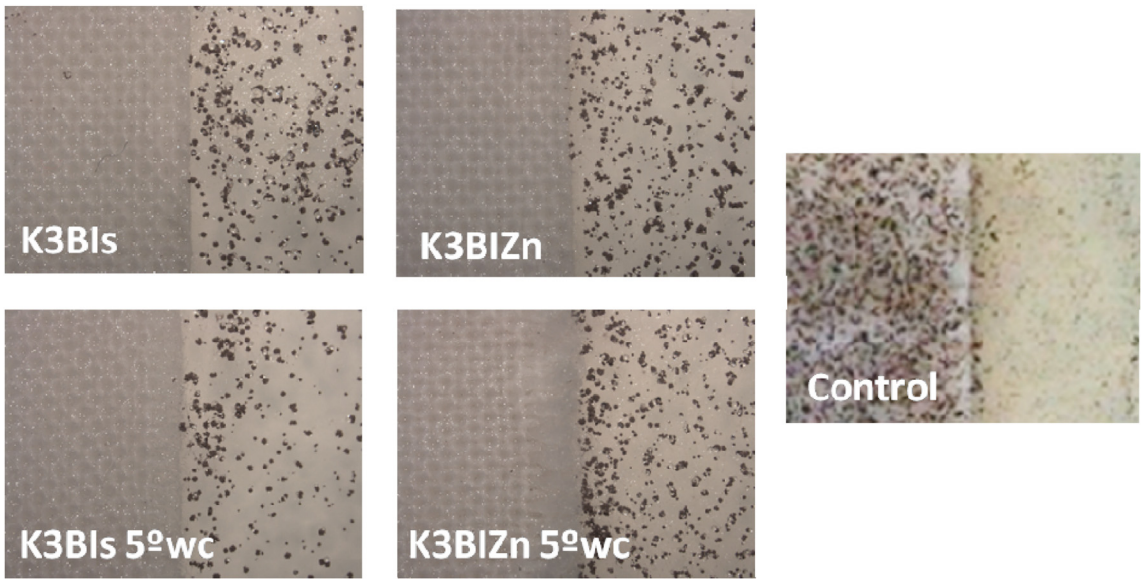

Fig. 11. Images observed with a magnifying glass of the fabrics impregnated with the sol-gel method, tested against *Aspergillus* sp.

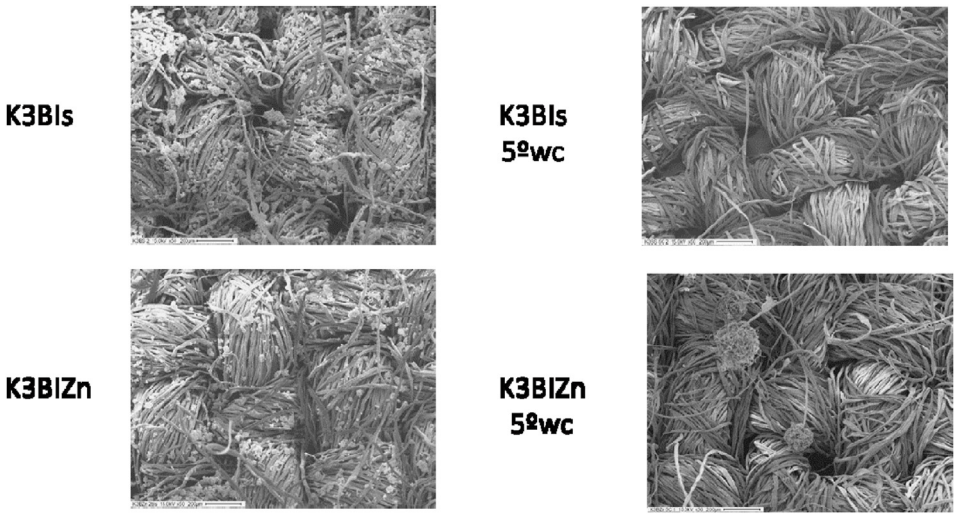

Fig. 12. SEM micrographs of the control fabric and the fabrics impregnated with the sol-gel method, tested against *Aspergillus* sp.

hydrophilic species, which often grows in long-term water-damaged environments; they grow on wood or paper products, related to humidity or with high water activity.

They are common in drywall damaged by water, wood, or materials with high cellulose content. *Chaetomium* spores detected indoors are excellent indicators of moisture damage. This species is known in the bibliography for its cellulolytic activity and is widely used for testing fabrics.

On the other hand, *Aspergillus* is a filamentous fungus belonging to the *Ascomycota phylum.* It is made up of septate hyaline (colorless) hyphae and they reproduce asexually, with the formation of conidia (asexual spore). It is characterized by the production of specialized hyphae, called conidiophores, on which are the conidiogenic cells that will give rise to the asexual spores or conidia. The conidiophore characteristic of *Aspergillus*, although it is a unicellular structure, has three well differentiated parts: vesicle (swollen apical end), stipe (cylindrical section located below the vesicle) and foot cell (final section, sometimes separated by a septum, which joins the conidiophore with the mycelium). Conidiogenous cells, commonly called phialides [45], are arranged on the vesicle. The different species differ in size, growth rate, texture (velvety, granular, cottony) and colony color: yellowish-green (*A. flavus*), black (*A. niger*), brown (*A. terreus*). The coloration appears almost always in all aerial structures, both in the mycelium and in the conidial heads. *Aspergillus* is one of the main mycotoxin-producing fungi.

Mycotoxins are secondary metabolites produced and secreted by the fungus during the degradation process of organic matter, as a defense mechanism against other microorganisms [46]. *Aspergillus* species are able to use a wide variety of substances as nutrients due to the large number of enzymes they produce. Several species grow on the hides and fabrics used daily reducing their commercial value. *Aspergillus niger* and other species are frequently found in food causing them to spoil. *Aspergillus fumigatus, Aspergillus flavus, Aspergillus niger*, and other species are pathogens of animals and humans, causing a group of diseases collectively called aspergilloss [47].

This section shows the values obtained from the antimicrobial fabrics from the impregnation method used, the sol-gel method. Table 2 presents the data of the tests of the antifungal activity of the fabrics against *C. globosum and Aspergillus* sp., according to the modified standard method DIN 53931. Previously, the growth and intensity of sporulation was expressed as evaluated after being incubated for 14 days at 28 °C.

Table 3
Antibacterial activity of the fabrics impregnated by the sol-gel method against *E. coli* and *S. aureus*, according to the agar-based diffusion method (SN 195920–1992).

Sample	Wash cycles	Inhibition Zone (mm)	
		E. coli	S.aureus
Fabric Control	0	0	0
K3Bis	0	2,1 ± 0,3	2,4 ± 0,2
K3Bis 1°wc	1	1,5 ± 0,2	1,9 ± 0,5
K3Bis 5°wc	5	1,0 ± 0,2	0,9 ± 0,3
K3Bis 20°wc	20	0,8 ± 0,1	0,9 ± 0,2
K3BIZn	0	1,8 ± 0,2	2,1 ± 0,2
K3BIZn 1°wc	1	1,6 ± 0,3	2,1 ± 0,1
K3BIZn 5°wc	5	0,9 ± 0,3	0,8 ± 0,3
K3BIZn 20°wc	20	0,8 ± 0,1	0,6 ± 0,2

As can be seen both in the values presented in Table 2 and in the Fig. 7 and Fig. 10, there was no growth of fungi on the fabric for most of the samples and a weak sporulation, being able to conclude that this method had positive results against the evaluated fungi. Despite the washing cycles, the growth on the impregnated fabric in the K3BIZn sample was only noticeable for the 5th washing cycle, giving 25% for *C. globosum* and 15% for *Aspergillus* sp.

Fig. 8 and Fig. 9 show the photographs obtained from the test with *C. globosum* through the magnifying glass and the scanning electron microscope (SEM), respectively. In Fig. 8, a noticeable difference of the impregnated fabrics with respect to the control fabric can be observed (last photograph, third column). For Fig. 9, the SEM micrographs show the results analyzed above, where there is no growth for the *C. globosum* fungus, in some samples the growth is 0 and only the texture of the cotton cloth used is observed.

It must be taken into account that this fungus, for *Aspergillus* sp, commonly has an invasive growth and occurs on all sides of the sample under evaluation when the inhibition is not good. This observation allows us to conclude that truly acceptable results were obtained in the tested fabrics (Fig. 10). For *Aspergillus* sp, the growth inhibition on the impregnated fabrics, which contained silica with Ag and ZnO, could be

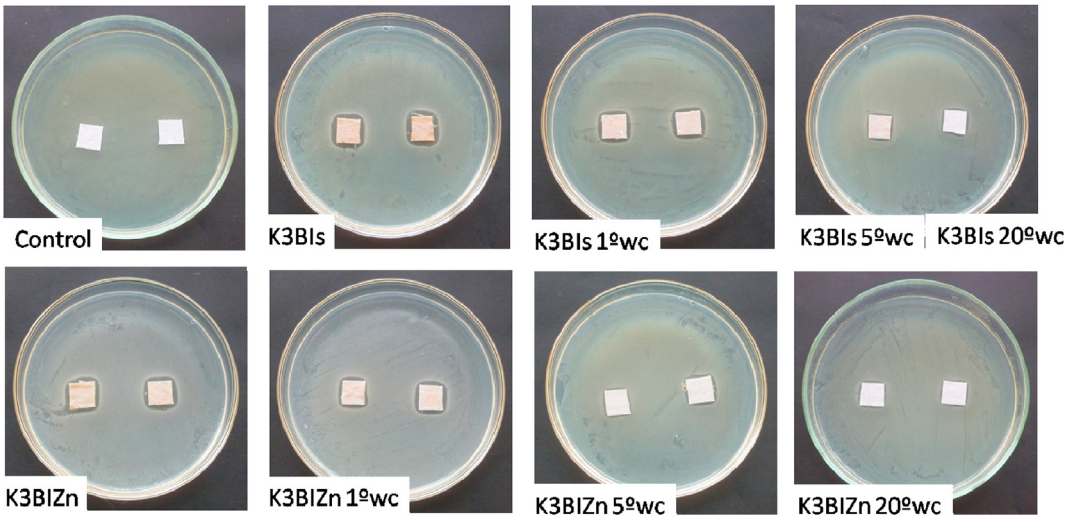

Fig. 13. Antibacterial test of fabrics impregnated with the sol-gel method against *Escherichia coli*.

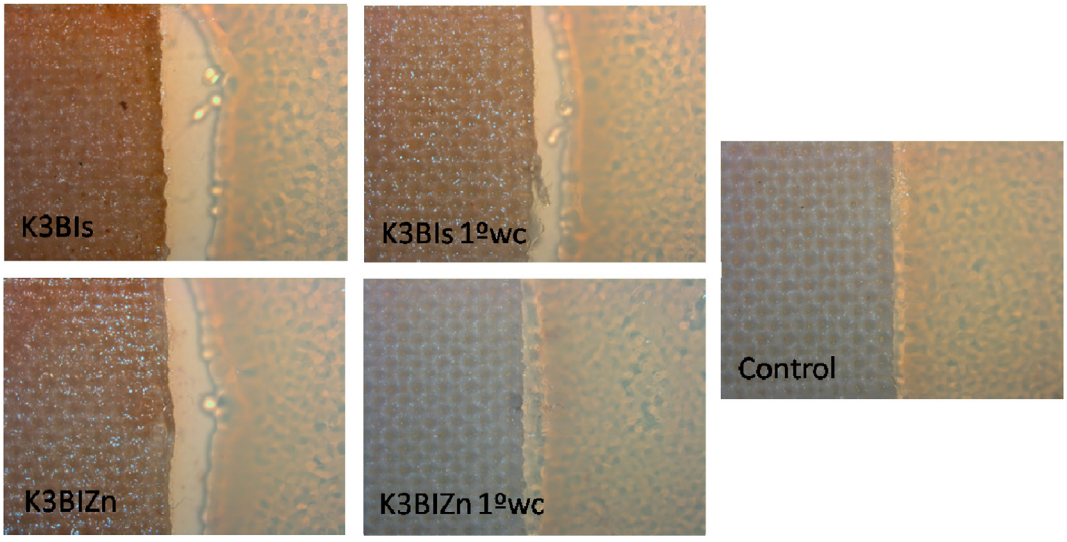

Fig. 14. Images observed with a stereoscopic microscope of the control fabric and the fabrics impregnated with the sol-gel method, tested against *Escherichia coli*.

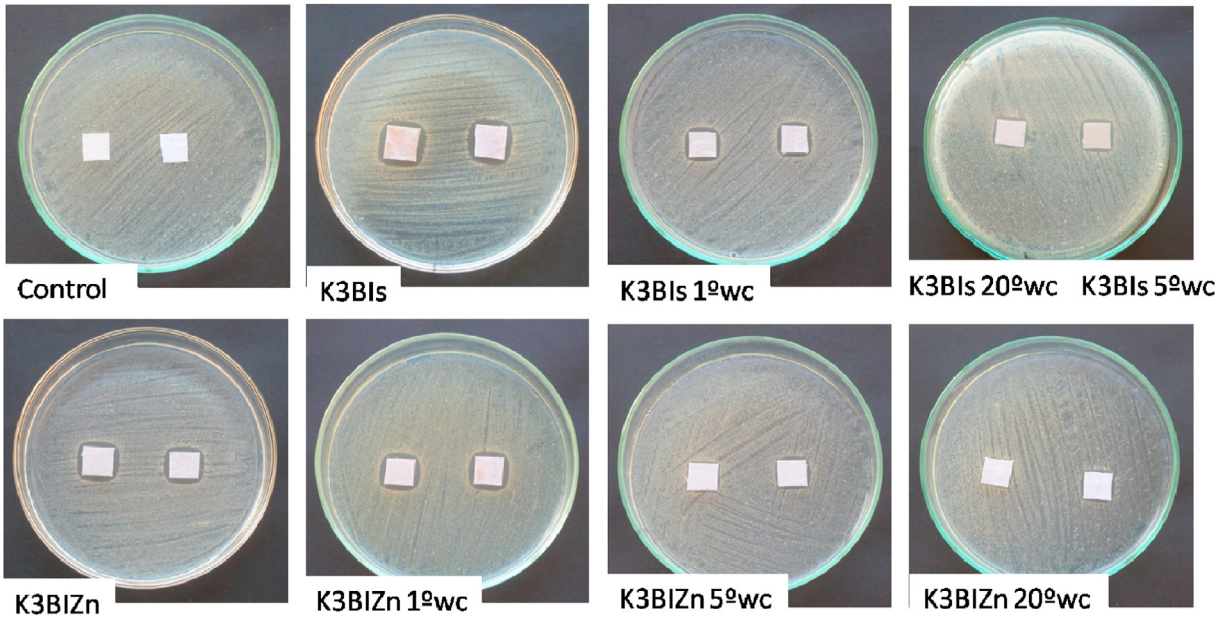

Fig. 15. Antibacterial test of fabrics impregnated with the sol-gel method against *Staphilococcus aureus*.

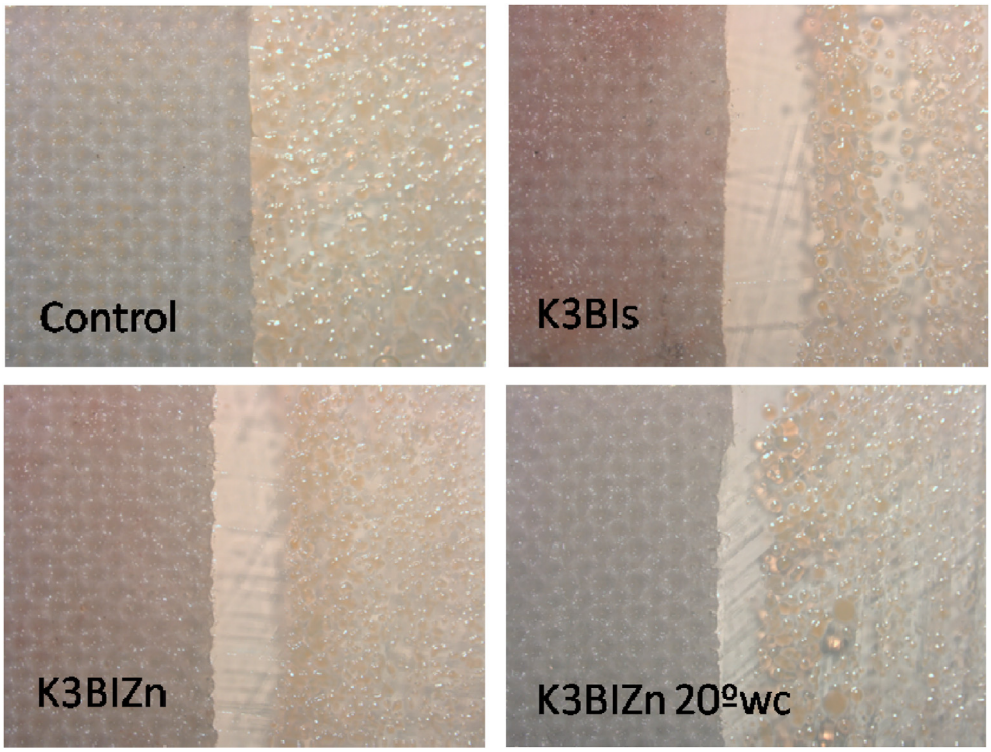

Fig. 16. Images observed with a stereoscopic microscope of the control fabric and the fabrics impregnated with the sol-gel method, tested against *Staphilococcus aureus*.

observed in more detail in the magnifying glass compared to the control fabric (Fig. 11).

SEM micrographs are shown in Fig. 12, which it can be seen that in most of the impregnated fabrics there are no specialized growing hyphae. As for *C. globosum*, it can be concluded that there were better results for acid hydrolysis than basic, using the impregnation technique for the case of Ag.

Table 3 presents the data of the tests of the antibacterial activity of the fabrics impregnated by the sol-gel method against *E. coli* and *S. aureus*, according to the agar-based diffusion method (SN 195920–1992). Previously, the zone of inhibition (ZOI) was expressed as evaluated after being incubated for 24 h at 37 °C. It is important to note that the number of samples tested reflected the results without mediating error in the measurements. As well as the numerous washing cycles, that allowed observing the adhesion of the sample to the fabric with its subsequent evaluation.

Fig. 13 and Fig. 15 show the photographic records of the tests of the antimicrobial fabrics obtained by the sol-gel method against *E. coli* and *S. aureus*, respectively.

The images observed with a stereoscopic microscope are shown in Fig. 14 and Fig. 16 for both *E. coli* and *Staphylococcus aureus*, in which the interface of fabric-culture medium-bacterial growth can be clearly observed in comparison with the control fabric.

4. Conclusions

In recent years, there has been an effort to increase research on antimicrobial fabrics, but the vast majority of these publications focus on research with bacteria and only a few carry out resistance tests against fungi. However, taking into account the impact of fungal infections on human health and their increasing incidence, such as, for example, the group of diseases called aspergillosis – which are produced by some species of the genus *Aspergillus* – added to the high health costs, studies should also focus on this field and interest in antifungal fabrics should be increasing, given their importance. It can be concluded, in general terms, that the proposed objectives have been achieved, once it was possible to synthesize antifungal materials through a green and environmentally friendly method of simple and fast obtaining, such as the sol-gel method, which allowed the inclusion of the biocide in oxidic matrices. In addition, the synthesized solids could be incorporated effectively in the preparation of the antimicrobial fabrics.

The perspectives derived from this study is that these fabrics can be used for many applications, for instance, in the health system to reduce problems currently faced and perhaps more severe from now on – such as, for example, hospital infections – in a way that add value to what was considered waste. In a first stage derived from this study on antimicrobial tissues is that they could be used in the health system, such as hospital infections in a way that adds value to what is considered waste, such as the C of disused batteries. This also means to adopt a broader greener and more sustainable chemical approach in the textile supply chain, following the UN SUSTAINABLE DEVELOPMENT GOALS (UN-SDGs). In 2015, the UN set out 17 goals that are a blueprint to achieving a better and more sustainable future for us all, addressing the challenges our world and the people in it face on a daily basis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank the National Scientific and Technical Research Council (CONICET), Scientific Research Commission of the Province of Buenos Aires (CICPBA) and the La Plata University (UNLP) for the financial support. Special thanks to N. Bellotti and the Center for Research and Development in Paint Technology (CIDEPINT) for the collaboration in this study.

References

[1] S. Riaz, M. Ashraf, Recent advances in development of antimicrobial textiles. Textile science and clothing Technology book series (TSCT), 2020, https://doi.org/10.1007/978-981-15-3669-4_6.
[2] S. Kanagasubbulakshmi, K. Kadirvelu, Green synthesis of iron oxide nanoparticles using Lagenariasiceraria and evaluation of its antimicrobial activity, Defence Life Sci. J. 2 (2017) 422–427, https://doi.org/10.14429/dlsj.2.12277.
[3] K. Murugesh Babu, N. Sahana, D.V. Anitha, B.S. Kavya, Silk fibroin coated antimicrobial textile medical products, J. Textil. Inst. 112 (8) (2021) 1199–1207, https://doi.org/10.1080/00405000.2020.1806634.
[4] A. Parmar, S. Kapil, S. Sachar, S. Sharma, Design of experiment based methodical optimization and green syntheses of hybrid patchouli oil coated silver nanoparticles for enhanced antibacterial activity, Current Research in Green and Sustainable Chemistry 100016 (2020), https://doi.org/10.1016/j.crgsc.2020.100016.
[5] H. Khanzada, A. Salam, M.B. Qadir, D.-N. Phan, T. Hassan, M.U. Munir, K. Pasha, N. Hassan, M.Q. Khan, I.S. Kim, Fabrication of promising antimicrobial aloe vera/PVA ElectrospunNanofibers for protective clothing, Materials 13 (2020) 3884, https://doi.org/10.3390/ma13173884.
[6] M.E. El-Naggar, T.A. Khattab, M.S. Abdelrahman, et al., Development of antimicrobial, UV blocked and photocatalytic self-cleanable cotton fibers decorated with silver nanoparticles using silver carbamate and plasma activation, Cellulose 28 (2021) 1105–1121, https://doi.org/10.1007/s10570-020-03537-4.
[7] L. Jin, F. Zhou, S. Wu, et al., Development of novel segmented-pie microfibers from copper-carbon nanoparticles and polyamide composite for antimicrobial textiles application, Textil. Res. J. (2021). https://doi:10.1177/0040517521993484.
[8] M Viegas Dias, C fungal prevalence on waste industry – literature review, Encycl. Mycol. 2 (2021) 99–106, https://doi.org/10.1016/B978-0-12-809633-8.21053-4.
[9] A.A. Haleem Khan, S. Mohan Karuppayil, Fungal pollution of indoor environments and its management, Saudi J. Biol. Sci. 19 (4) (2012) 405–426. https://doi:10.1016/j.sjbs.2012.06.002.
[10] Dennis Allsopp, Kenneth J. Seal, Christine C. Gaylarde, Introduction to biodeterioration, Cambridge university press, 2010, https://doi.org/10.1017/CBO9780511617065 online ISBN:9780511617065.
[11] K. Nienhaus, H. Wang, G.U. Nienhaus, Nanoparticles for biomedical applications: exploring and exploiting molecular interactions at the nano-bio interface, Materials Today Advances 5 (2020) 100036, https://doi.org/10.1016/j.mtadv.2019.100036.
[12] Z. Adamczyk, N. Dan, Editorial overview: theory and simulation of proteins at interfaces: how physics comes to life, Curr. Opin. Colloid Interface Sci. 41 (2019) A1–A3, https://doi.org/10.1016/j.cocis.2019.04.002.
[13] X. Han, K. Xu, O. Taratula, K. Farsad, Applications of nanoparticles inbiomedical imaging, Nanoscale 11 (2019) 799–819, https://doi.org/10.1039/C9NR07616F.
[14] V.S. Saji, The Impact of Nanotechnology on Reducing Corrosion Cost, Corrosion Protection and Control Using Nanomaterials, Woodhead Publishing Series in Metals and Surface Engineering, 2012, pp. 3–15.
[15] Y.N. Slavin, J. Asnis, U.O. Häfeli, et al., Metal nanoparticles: understanding the mechanisms behind antibacterial activity, J. Nanobiotechnol. 15 (2017) 65, https://doi.org/10.1186/s12951-017-0308-z.
[16] A.P. Periyasamy, M. Venkataraman, D. Kremenakova, J. Militky, Y. Zhou, Progress in sol-gel Technology for the coatings of fabrics, Materials 13 (2020) 1838. https://doi:10.3390/ma13081838.
[17] J. Kim, S. Kwon, E. Ostler, Antimicrobial effect of silver-impregnated cellulose: potential for antimicrobial therapy, J. Biol. Eng. 3 (2009) 20, https://doi.org/10.1186/1754-1611-3-20.
[18] I. Mukha, N. Vityuk, G. Grodzyuk, S. Shcherbakov, A. Lyberopoulou, E.P. Efstathopoulos, M. Gazouli, Anticancer effect of Ag, Au, and Ag/Au bimetallic nanoparticles prepared in the presence of tryptophan, J. Nanosci. Nanotechnol. 17 (12) (2017) 8987–8994, https://doi.org/10.1166/jnn.2017.14106 (8), American Scientific Publishers.
[19] Tanushree Ghosh, Anath Bandhu Das, Bijaylaxmi Jena, Chinmay Pradhan, Antimicrobial effect of silver zinc oxide (Ag-ZnO) nanocomposite particles, Front. Life Sci. 8 (1) (2015) 47–54, https://doi.org/10.1080/21553769.2014.952048.
[20] M. Amerikova, El-Tibi I. Pencheva, V. Maslarska, S. Bozhanov, K. Tachkov, Antimicrobial activity, mechanism of action, and methods for stabilisation of defensins as new therapeutic agents, Biotechnol. Biotechnol. Equip. 33 (1) (2019) 671–682, https://doi.org/10.1080/13102818.2019.1611385.
[21] F. Mirhosseini, M. Amiri, A. Daneshkazemi, H. Zandi, Z.S. Javadi, Antimicrobial effect of different sizes of nano zinc oxide on oral microorganisms, Front Dent 16 (2) (2019) 105–112, https://doi.org/10.18502/fid.v16i2.1361.
[22] V.G. Zuin, L.Z. Ramin, M.L. Segatto, A.M. Stahl, K. Zanotti, M.R. Forim, J.B. Fernandes, To separate or not to separate: what is necessary and enough for a green and sustainable extraction of bioactive compounds from Brazilian citrus waste, Pure Appl. Chem. 1 (2020), https://doi.org/10.1186/s13065-020-00710-5 (ahead-of-print).
[23] V.G. Zuin, A.M. Stahl, K. Zanotti, M.L. Segatto, Green and Sustainable Chemistry in Latin America: which type of research is going on? And for what? Curr. Opin. Green Sustain. Chem. (2020) https://doi.org/10.1016/j.cogsc.2020.100379.
[24] P.T. Anastas, J.C. Warner, Principles of Green Chemistry. Green Chemistry: Theory and Practice, Oxford University Press, 1998, pp. 29–56. ISBN 0198502346, 9780198502340.
[25] G. Jiang, K. Ameer, H. Kim, E.J. Lee, K. Ramachandraiah, G.P. Hong, Strategies for sustainable substitution of Livestock meat, Foods 9 (9) (2020) 1227, https://doi.org/10.3390/foods9091227.
[26] R.A. Sheldon, I. Arends, U. Hanefeld, Green Chemistry and Catalysis, John Wiley & Sons, 2007, https://doi.org/10.1002/aoc.1306.
[27] V.G. Zuin, M.L. Segatto, D.P. Zandonai, G.M. Grosseli, A. Stahl, K. Zanotti, R.S. Andrade, Integrating green and sustainable chemistry into undergraduate teaching laboratories: closing and assessing the loop on the basis of a citrus biorefinery approach for the biocircular economy in Brazil, J. Chem. Educ. 96 (12) (2019) 2975–2983, https://doi.org/10.1021/acs.jchemed.9b00286.
[28] K. Kümmerer, J.H. Clark, V.G. Zuin, Rethinking chemistry for a circular economy, Science 367 (6476) (2020) 369–370, https://doi.org/10.1126/science.aba4979.
[29] V.G. Zuin, Circularity in green chemical products, processes and services: innovative routes based on integrated eco-design and solution systems, Curr. Opin. Green Sustain. Chem. 2 (2016) 40–44, https://doi.org/10.1016/j.cogsc.2016.09.008.
[30] Lei Li, Xiaolian Liu, Gang Wang, Yalin Liu, Weimin Kang, Nanping Deng, XupinZhuang, Xinghai Zhou, Research progress of ultrafine alumina fiber prepared by sol-gel method: a review, Chem. Eng. J. 421 (2) (2021) 127744, https://doi.org/10.1016/j.cej.2020.127744. ISSN 1385-8947.
[31] C.J. Brinker, G.W. Scherer, Sol-gel Science: the Physics and Chemistry of Sol-Gel Processing, Academic Press, 2013.
[32] M. Parashar, V.K. Shukla, R. Singh, Metal oxides nanoparticles via sol–gel method: a review on synthesis, characterization and applications, J. Mater. Sci. Mater. Electron. 31 (2020) 3729–3749, https://doi.org/10.1007/s10854-020-02994-8.

[33] R. Arreche, M. Blanco, P. Vázquez, Síntesis de sílice mediante el método sol-gel y su aplicación como aditivos antimicrobianos en pinturas higiénicas, Rev. Rev. Interam.: Revista Tecnología y Ciencia 28 (2016) 46–52, 1666-6933.
[34] R.K. Iler, The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry, John Wiley and Sons Ltd., New York, 1979.
[35] M.V. Gallegos, Estudio del uso de óxidos de metales de transición obtenidos a partir del reciclado de pilas como fases activas y soportes en la remoción de compuestos orgánicos volátiles y otras aplicaciones (Doctoral Thesis), La Plata National University, 2017.
[36] M.L.R. Falco, Optimización de un proceso biohidrometalúrgico de recuperación de metales de pilas alcalinas y de cinc-carbón agotadas (Doctoral Thesis), La Plata National University, 2013.
[37] G. Curutchet, E. Donati, C. Oliver, C. Pogliani, M.R. Viera, Development of Thiobacillus biofilms for metal recovery, Methods Enzymol. 337 (2001) 171–186, https://doi.org/10.1016/S0076-6879(01)37013-1.
[38] B. Tomšič, B. Simončič, B. Orel, M. Žerjav, H. Schroers, A. Simončič, Z. Samardžija, Antimicrobial activity of AgCl embedded in a silica matrix on cotton fabric, Carbohydr. Polym. 75 (4) (2009) 618–626, https://doi.org/10.1016/j.carbpol.2008.09.013.
[39] M.D. Balakumaran, R. Ramachandran, S. Jagadeeswari, P.T. Kalaichelvan, In vitro biological properties and characterization of nanosilver coated cotton fabrics – an application for antimicrobial textile finishing Inter, Biodeterioration and Biodegradation 107 (2016) 48–55, https://doi.org/10.1016/j.ibiod.2015.11.011.
[40] L. Budama, B.A. Çakır, Ö. Topel, N. Hoda, A new strategy for producing antibacterial textile surfaces using silver nanoparticles, Chem. Eng. J. 228 (2013) 489–495, https://doi.org/10.1016/j.cej.2013.05.018.
[41] Zapata, A., Ramirez-Arcos, S. A comparative 2015 study of McFarland turbidity standards and the Densimat photometer to determine bacterial cell Density. Curr. Microbiol. 70, 907–909 https://doi.org/10.1007/s00284-015-0801-2.
[42] L. Barker, B. Lien, O. Brun, D. Schaak, McDonough, L. Chee Chan, A Mycobacterium marinum zone of inhibition assay as a method for screening potential antimycobacterial compounds from marine extracts, Planta Med. 73 (6) (2007) 559–563, https://doi.org/10.1055/s-2007-981522.
[43] Surendra Sarsaiya, Sanjeev Kumar Awasthi, Mukesh Kumar Awasthi, Abhishek Kumar Awasthi, Saket Mishra, Jishuang Chen, The dynamic of cellulase activity of fungi inhabiting organic municipal solid waste, Bioresour. Technol. 251 (2018) 411–415, https://doi.org/10.1016/j.biortech.2017.12.011.
[44] Amira M. G. Darwish and Ahmed M. Abdel-Azeem , Chapter 9: Chaetomium enzymes and their applications, A. M. Abdel-Azeem (ed.), Recent Developments on Genus Chaetomium, Fungal Biology. https://doi.org/10.1007/978-3-030-31612-9_9.
[45] O. Batuman, M. Ritenour, A. Vicent, H. Li, J.-W. Hyun, V. Catara, H. Ma, L.M. Cano, Diseases caused by fungi and oomycetes, in: The Genus Citrus, Woodhead Publishing, 2020, pp. 349–369, https://doi.org/10.1016/C2016-0-02375-6 (Chapter 17).
[46] M.A. Haque, Y. Wang, Z. Shen, X. Li, M.K. Saleemi, C. He, Mycotoxin contamination and control strategy in human, domestic animal and poultry: a review, Microb. Pathog. 142 (2020) 104095, https://doi.org/10.1016/j.micpath.2020.104095.
[47] A. Rokas, M.E. Mead, J.L. Steenwyk, N.L. Oberlies, G.H. Goldman, Evolving moldy murderers: Aspergillus section Fumigati as a model for studying the repeated evolution of fungal pathogenicity, PLoS Pathog. 16 (2) (2020), e1008315, https://doi.org/10.1371/journal.ppat.1008315.