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Degradation of the emerging contaminant Atenolol by $K_2Fe^{VI}O_4$: assessment of biodegradability and degradation products

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Pharmaceuticals and their metabolites are an emerging class of contaminants of concern due to their persistence in the environment[1]; among them, β-blockers constitute an important group of prescription drugs on the therapy of cardiovascular diseases.

Potassium ferrate ($K_2Fe^{VI}O_4$), a strong oxidant (2.2 V, very acidic pH), can be considered as an option for the treatment of (bio)recalcitrant contaminants; moreover, its dual character oxidant/coagulant makes it useful for water and wastewater treatment strategies[2].

The degradation of Atenolol (Ate) by Fe^{VI} was simulated in aqueous solution using the molar ratios 1:1 and 1:10 Atenolol:Fe^{VI}, respectively. The experiments were performed in a 1000 mL stirred tank reactor at pH 7 and temperature of 20±1 ºC for 120 min. After the treatment the samples were adjusted to pH 8, centrifuged (4000 rpm) and filtered through 0.45 µm filters.

In order to identify the degradation products of Ate, LC–ESI-MS^n was used (Agilent Series 1100 LC tandem MS analyzer Bruker Esquire 6000 Ion Trap). A C18 ec column (RP18 CC 125-4 mm Nucleodur 100-5) and a pre-column (RP18 CC 8-4 mm Nucleodur 100-5) were uses.

Gradient elution was used for the mobile phase (A: formic acid 0.1% v/v and B: acetonitrile) as follows: 0-3 min isocratic with 1% of B (delayed to waste in order to minimize the introduction of Fe ions into the ESI), 3-5 min linear gradient (lg) of 1-5% B; 5-10 min lg of 5-20% B; 10-13 min isocratic of 20% B; 13-23 min lg of 20-50% B, 23-28 min isocratic flow of 50% B; 28-29 min lg 50-1% B keeping from 29-35 min 1% B to equilibrate the column; flow rate 0.5 mL min^{-1}, injection volume 20 µL, and column temperature 30 ºC.

The Dissolved Organic Carbon (DOC) was monitored by a total organic carbon analyzer (Shimadzu 5050A TOC Analyzer) and the biodegradability was tested by 28-day Closed Bottle Test (CBT) according to OECD 301 D.

The reduction of DOC showed no mineralization of Ate at the both ratios studied; but the LC-MS^n analysis of Ate showed reduction of 5.20% and 71.5% for Ate:Fe^{VI} at 1:1 and 1:10, respectively. Accordingly, Ate was converted to intermediaries. Moreover, it can be inferred that the coagulation wasn't an effective process in this case.

The identification of the degradation products was done by Scan Mode (SM); the intermediaries were extracted, identified and the posterior confirmation was performed fragmenting by MS^2 using Multi Reaction Mode (MRM). It was identified 10 degradation products with the following m/z ratio: 419.0, 387.0, 327.2, 283.2, 225.2, 210.0, 208.0, 194.0, 182.1 and 131.0. The mechanism of the degradation process is proposed.

In order to assess the biodegradability, an aliquot of treated Ate aqueous solution (120 min,1:10 Ate:Fe^{VI}) was taken for the CBT test, and it was observed an increase of biodegradability up to 72.7%. Thus, it is concluded that the degradation products can be considered as ready biodegradable (> 60%).

Therefore, despite no mineralization, it was observed that the use of potassium ferrate constitutes an interesting option for the treatment of emerging contaminants in aquatic systems.

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