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Paracetamol degradation intermediates and toxicity during photo-Fenton treatment using different iron species

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ABSTRACT

The photo-Fenton degradation of paracetamol (PCT) was evaluated using $FeSO_4$ and the iron complex potassium ferrioxalate (FeOx) as iron source under simulated solar light. The efficiency of the degradation process was evaluated considering the decay of PCT and total organic carbon concentration and the generation of carboxylic acids, ammonium and nitrate, expressed as total nitrogen. The results showed that the degradation was favored in the presence of $FeSO_4$ in relation to FeOx. The higher concentration of hydroxylated intermediates generated in the presence of $FeSO_4$ in relation to FeOx probably enhanced the reduction of Fe(III) to Fe(II) improving the degradation efficiency. The degradation products were determined using liquid chromatography electrospray time-of-flight mass spectrometry. Although at different concentrations, the same intermediates were generated using either $FeSO_4$ or FeOx, which were mainly products of hydroxylation reactions and acetamide. The toxicity of the sample for *Vibrio fischeri* and *Daphnia magna* decreased from 100% to less than 40% during photo-Fenton treatment in the presence of both iron species, except for *D. magna* in the presence of FeOx due to the toxicity of oxalate to this organism. The considerable decrease of the sample toxicity during photo-Fenton treatment using $FeSO_4$ indicates a safe application of the process for the removal of this pharmaceutical.

1. Introduction

Pharmaceuticals have received increased attention as aquatic contaminants due to the occurrence of a large number of anti-inflammatories, analgesics, betablockers, lipid regulators, antibiotics, anti-epileptics and estrogens at concentration levels of ng L^{-1} to μg L^{-1} in sewage treatment plant effluents (STP), surface and groundwater and even in drinking water (Bartelt-Hunt et al., 2011; Huang et al., 2011; Li and Zhang, 2011; Ziylan et al., 2011; Yu et al., 2011). The occurrence of pharmaceuticals in these matrices indicates their poor degradability in municipal STP (Stumpf et al., 1999; Heberer, 2002; Andreozzi et al., 2003a; Lindqvist et al., 2005; Quinn et al., 2008; Santos et al., 2009). Considering that thousands of tons of pharmaceutical substances are produced and used yearly in human and veterinary medicine and animal production, considerable amounts of these substances can reach the aquatic environment, mainly by receiving wastewater from STP as a result of their incomplete removal. Among the pharmaceuticals, the analgesic and antipyretic

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paracetamol (PCT) has been found at concentrations of 0.22 and 6.8 μg L^{-1} in STP effluents in Spain and Korea, respectively, at concentrations of 0.033 and 0.071 μg L^{-1} in surface waters in South Korea and France, respectively, and at concentrations in the range of μg L^{-1} in hospital effluents (Gómez et al., 2007; Kim et al., 2007; Vulliet et al., 2011).

Therefore, it is of high interest to develop efficient treatment processes for limiting the presence of pharmaceutical contaminants in aquatic environments. Furthermore, identification of intermediate products and evaluation of the sample toxicity after treatment are essential to guarantee the safe application of the treatment process.

The literature reports degradation of PCT using various treatments, including ozonation, H_2O_2/UV, TiO_2/UV, electrochemical and photo-Fenton (Vogna et al., 2002; Andreozzi et al., 2003b; Skoumal et al., 2006; Sirés et al., 2006; Yang et al., 2008; Dalmázio et al., 2008; Zhang et al., 2008; Durán et al., 2011; Jordá et al., 2011; Almeida et al., 2011). Although the photo-Fenton degradation of PCT has been evaluated, a study about the intermediates generated and sample toxicity after the treatment using different iron species has not been reported. The effect of iron species is very important, since it can be determinant for an efficient degradation as previously observed for the herbicide tebuthiuron, the degradation of which was drastically improved in the presence of ferrioxalate, while the degradation 4-chlorophenol was favored by the use of $Fe(NO_3)_3$ (Nogueira et al., 2005a; Silva et al., 2010). PCT intermediates described in the literature have been determined using GC–MS techniques, which do not allow a direct injection of the aqueous sample (Chiron et al., 1997; Aguera and Fernández-Alba, 1998). On the other hand, mass spectrometry combined with liquid chromatography (LC-MS) is a simple, robust and effective technique, suitable for species having a wide range of polarity, and was shown to be a powerful tool for the identification of intermediates and unknown compounds in environmental samples.

The aim of the present work was to compare the degradation efficiency, intermediates generated and toxicity evolution during photo-Fenton degradation of PCT using two iron species, $FeSO_4$ and FeOx.

2. Materials and methods

2.1. *Reagents*

All PCT solutions were prepared in distilled water. PCT was purchased from Sigma–Aldrich and used as received. H_2O_2 30% (w/w) (POCH, SA), $FeSO_4.7H_2O$ and sulfuric acid (POCH SA), NaOH and bovine liver catalase (Sigma–Aldrich) were also used as received. Potassium ferrioxalate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$), named as FeOx, was prepared and purified as described previously (Hatchard and Parker, 1956) using iron nitrate and potassium oxalate (Mallinkrodt). An aqueous FeOx stock solution was prepared at a concentration of 0.25 M and stored in the dark at room temperature. Ammonium metavanadate (Sigma–Aldrich) solution was prepared at a concentration of 0.060 M in 0.36 M H_2SO_4. All reagents were analytical grade. HPLC-grade acetonitrile and methanol (Merck), and formic acid (Fluka) were used for HPLC analysis.

2.2. *Hydrolysis, photolysis and photo-Fenton experiments*

To evaluate the hydrolysis and photolysis of PCT, the solutions were prepared by dissolving PCT in distilled water at an initial concentration of 15 mg L^{-1} (TOC = 9.6 mg C L^{-1}). The contribution of hydrolysis was evaluated using 250 mL beakers at two different pH values (2.5 – adjusted by addition of H_2SO_4 and 4.2 – natural pH of PCT solution). The beakers were kept in the dark at room temperature for 48 h. The photolysis and photo-Fenton experiments were conducted in a solar simulator (Suntest CPS+ from Heraeus, Germany) equipped with a 1100 W xenon arc lamp and special filters restricting transmission of light below 290 nm. The lamp was set to minimum intensity (250 W m^{-2}), since under high intensity the intermediates generated could be quickly degraded making their detection difficult. Photodegradation experiments were performed exposing 2 L of PCT solution in open pyrex glass vessels (Schott Durand, Germany), 14 cm deep and with 14 cm diameter, provided with an internal recirculating water system to maintain the internal temperature at 25 ± 2 °C.

The PCT concentration in the photo-Fenton experiments was 50 mg L^{-1} (TOC = 31.8 mg C L^{-1}). Although this concentration is higher than that found in aqueous environment, it was chosen to permit an adequate detection of intermediates. The initial concentration of $FeSO_4 \cdot 7H_2O$ or FeOx was 0.05 mM, which is below the maximum concentration of iron allowed in wastewater according to Brazilian legislation. Based on previous work of Trovó et al. (2011), the initial H_2O_2 concentration was 120 mg L^{-1} and a new addition of H_2O_2 (after 180 min) was made during the experiment using $FeSO_4$ as iron source. The initial pH was adjusted to between 2.5 and 2.8, the optimum pH range for the photo-Fenton process.

2.3. *Chemical analysis*

Before LC-MS analysis, the solution pH was adjusted to between 6 and 8, and 0.5 mL catalase solution (0.1 g L^{-1}) was added to 25 mL of sample to quench the reaction and guarantee the absence of hydrogen peroxide before the bioassays. The samples were then filtered through 0.45 μm membranes. The PCT concentrations and intermediates were determined using liquid chromatography electrospray time-of-flight mass spectrometry (LC-ESI-TOF-MS), in positive ionization mode, using an Agilent equipment (Series 1100) equipped with a 3 mm × 250 mm reverse-phase C_{18} analytical column, 5 μm particle size (Zorbax SB-C18, Agilent Technologies). Mobile phases were acetonitrile and water with 0.1% formic acid, at a flow rate of 0.4 mL min^{-1}. A linear gradient progressed from 10% acetonitrile (initial conditions) to 100% in 50 min, and was maintained at 100% for 3 min. A 15 min post-run time back to the initial mobile-phase composition was allowed after each analysis. The injection volume was 20 μL. Under these conditions, PCT retention time was 9.5 min. This chromatographic system was connected to an Agilent MSD time-of-flight mass spectrometer with an electrospray interface operating under the following conditions: capillary, 4000 V; nebulizer, 40 psi; drying gas, 7.0 L min^{-1}; gas temperature, 300 °C; skimmer voltage, 60 V; octapole dc1, 36.5 V; octapole rf, 250 V; fragmentor, 190 V.