



Research article

Correlation between pH and molar iron/ligand ratio during ciprofloxacin degradation by photo-Fenton process: Identification of the main transformation products

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ABSTRACT

Ciprofloxacin has been determined with high frequency in studies involving environmental waters matrixes. However, no study evaluating the correlation between the initial pH and molar iron/organic ligand ratio has been published. This paper describes the degradation of the antibiotic ciprofloxacin by the photo-Fenton process using different sources of iron (Fe^{2+} , Fe^{3+} and Fe^{3+} -citrate and Fe^{3+} -oxalate, named FeCit and FeOx, respectively) and molar iron/organic ligand ratios at initial pH values of 2.5 and 6.5. The best results at initial pH 2.5 were achieved using FeCit and FeOx at molar iron/organic ligand ratios of 1:1 and 1:3 respectively, when the ciprofloxacin concentration reached values below the quantitation limit of the HPLC after 20 min of treatment. However, at initial pH 6.5, improvements in the results (15% for FeCit, and 46% for FeOx) were achieved by increasing the molar iron/organic ligand ratios to 1:4 (FeCit) and 1:9 (FeOx), respectively. Three transformation products, ($\text{C}_{17}\text{H}_{19}\text{FN}_3\text{O}_4$, m/z 348; $\text{C}_{17}\text{H}_{21}\text{FN}_3\text{O}_5$, m/z 366; and $\text{C}_{13}\text{H}_{12}\text{FN}_2\text{O}_3$, m/z 263) of ciprofloxacin degradation were identified, one of them not yet being reported in the literature ($\text{C}_{17}\text{H}_{21}\text{FN}_3\text{O}_5$, m/z 366). Their formation and degradation was monitored and the initial steps of their formation and degradation were proposed. The results show that the piperazine ring is more susceptible to hydroxyl radical attack than the quinolone ring, which persists in the intermediates identified. Therefore, this process can be a good alternative for the treatment of this type of pollutant at near-neutral conditions.

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1. Introduction

Pharmaceutical products have been widely used throughout the world in human and veterinary medicine. In view of this, a significant fraction of these therapeutic agents, excreted without changes through feces and urine, or to a lesser degree as metabolites, have been found in different environments (Klatte et al., 2017; Papageorgiou et al., 2016). These products are persistent in the environment, being found mainly in water, and even at trace concentrations are a risk to aquatic organisms (Ma et al., 2016; Papageorgiou et al., 2016).

Studies have shown that the main sources of contamination in water are sewage treatment plants, due the inefficient removal of these compounds and metabolites by conventional processes (Bila and Dezotti, 2003; Papageorgiou et al., 2016).

Among the contaminants, antibiotics are particularly significant, due to their persistence in the environment. This may lead to bacterial resistance, affecting not only future medical applications, but also the biological treatment of wastewaters (Alexy et al., 2004; Kümmerer, 2009).

Ciprofloxacin, CIP, a fluoroquinolone-based antibiotic, has been found at average concentrations of between 20 and 200 ng L^{-1} in surface waters in the United States of America and Brazil, respectively (Melo et al., 2009; Locatelli et al., 2011), and between 97 and 370 ng L^{-1} in sewage treatment plant effluents in France, Greece, Italy, Sweden and Switzerland (Melo et al., 2009). Concentrations of

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between 32 and 99 $\mu\text{g L}^{-1}$ have been found in hospital effluents in Brazil (Martins et al., 2008), and up to 31 mg L^{-1} in discharges from pharmaceutical industries (Larsson et al., 2007). A recent study of seasonal occurrence and removal performed in central Greece has demonstrated that among the 10 antibiotics detected in influent and effluent samples, CIP was one of the most predominant, with a maximum concentration of 591 ng L^{-1} in both influents and effluents (Papageorgiou et al., 2016). In addition, it was found that this antibiotic is harmful to the environment, possessing high acute toxicity (Papageorgiou et al., 2016). Therefore, it is imperative to evaluate and propose effective alternatives for its removal from the environment.

Studies evaluating the use of Fenton (Giri and Golder, 2014, 2015) and photo-Fenton (Bobu et al., 2008; Giri and Golder, 2015; Lima et al., 2014; Vasconcelos et al., 2009; Sun et al., 2009) processes as alternatives for wastewater treatment to degrade CIP have been assessed. The main disadvantage of the classic Fenton process is its restricted range of pH: between 2.5 and 3.0 (Pignatello, 1992, 2006). In order to overcome this limitation, and ensure its application under pH conditions close to neutrality, the use of iron complexes has been proposed (Dias et al., 2014; Nogueira et al., 2017; Perini et al., 2013, 2017). Among these studies, special attention has been focused on iron complexes formed with the ligands oxalate and citrate, due their higher quantum yield of production of Fe^{2+} ions when compared to other iron complexes (Soares et al., 2015; Clarizia et al., 2017).

Although studies on CIP degradation by photo-Fenton processes using iron complexes at near-neutral conditions have been reported (Perini et al., 2013, 2017), from what was found in a bibliographic survey, to date no study evaluating the correlation between the initial pH and molar iron/organic ligand ratio has been published.

The goal of this paper was to define the best conditions to improve the CIP degradation in a photo-Fenton process using Fe ions, organic ligands (citrate or oxalate) and control of the initial pH. At the same time, using data from UHPLC-QTOF-MS, and based on the analysis of fragmentation of the structures, the initial steps of degradation of CIP and its transformation products (TPs) were proposed. In addition, during the degradation, the evolution of the antibiotic activity (AA) of these solutions towards the bacteria *Escherichia coli* was evaluated.

2. Materials and methods

2.1. Reagents

All solutions were prepared using distilled water. CIP standard was purchased from Sigma-Aldrich (98% certified purity). HPLC-UV-grade methanol (J.T. Baker) was used in HPLC-DAD analyses. Acetonitrile LC-MS-grade was supplied by Fluka Chromasolv, and used for UPLC-QTOF-MS analysis. Milli-Q ultra-pure water from Millipore, and formic acid (98%) from Sigma-Aldrich were also used. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, both from Vetec, were used to prepare aqueous stock solutions containing 2 g L^{-1} in terms of iron, the Fe^{2+} solution being prepared in 0.5 mol L^{-1} H_2SO_4 (Synth), in order to minimize its oxidation. Other reagents employed in this study were: bovine catalase (Sigma-Aldrich), sodium citrate dihydrate (Anidrol), hydroxylamine hydrochloride (Vetec), and sodium acetate (Panreac). The following reagents were all from Synth: H_3PO_4 , Na_2SO_3 , NaOH, 1,10-phenanthroline, potassium oxalate, potassium titanium oxide oxalate dihydrate, and H_2O_2 (30% w/w). All reagents were used without further purification.

2.2. Degradation

The photo-Fenton experiments were performed at lab-scale by exposing 500 mL of 10 $\mu\text{mol L}^{-1}$ (equivalent to 3.3 mg L^{-1}) CIP solutions to the radiation furnished by two 10 W dark light lamps (Fig. 1-SM). These lamps were positioned in parallel (separated by a distance of 3.5 cm) and at 1 cm from the top of a dark-glass vessel of 4.3 cm depth and 15.5 cm diameter. This container was filled with the CIP solution to a depth of 3.8 cm. The UVA irradiance was measured using a radiometer (PMA 2100 Solar Light, Co.) with the UVA (320–400 nm) sensor positioned at the same angle of incidence to the reaction vessel as the radiation, and at 1 cm from the lamps. The average irradiance obtained was 30 W m^{-2} .

The concentrations of iron and H_2O_2 used were 10 $\mu\text{mol L}^{-1}$ (equivalent to 0.56 mg L^{-1}) and 940 $\mu\text{mol L}^{-1}$ (equivalent to 32 mg L^{-1}), respectively. The concentration of H_2O_2 used in all experiments was twice the theoretical value, to ensure an excess of this reagent in the reaction medium. The choice of iron concentration was based on a previous work that suggested the use of an $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio close to 0.01:1 to improve the photo-Fenton process during CIP degradation (Sun et al., 2009).

For the photo-Fenton reactions mediated by iron complexes, sodium citrate and potassium oxalate were used as sources of citrate and oxalate. The solutions containing the iron complexes were prepared by direct mixture of aqueous solutions of $\text{Fe}(\text{NO}_3)_3$ and sodium citrate or potassium oxalate, at different molar iron-to-ligand ratios, in separate containers, and transferred in sequence to the solutions containing CIP. The formation of color after mixing the iron and complexing agent solutions (citrate and oxalate) confirmed the presence of the iron complexes.

Two set of assays were performed to optimize the CIP degradation: (1) Influence of iron species (ferrous sulfate, ferric nitrate, FeCit and FeOx) at initial pHs 2.5 and 6.5; (2) Influence of molar iron/organic ligand ratios (1:1, 1:1.5, 1:3 and 1:4 for Fe/Cit and 1:3, 1:4.5, 1:9 and 1:12 for Fe/Ox).

Control experiments (photolysis, Fenton and Fenton-like) using the same experimental conditions (10 $\mu\text{mol L}^{-1}$ Fe^{2+} or Fe^{3+} , 940 $\mu\text{mol L}^{-1}$ H_2O_2 and pH 2.5) were also carried using the same initial concentration of CIP (10 $\mu\text{mol L}^{-1}$).

To avoid perturbation, aliquots of just 5 mL were withdrawn at 0, 2, 5, 10, 15, 20, 25 and 30 min of reaction, to avoid removal of more than 10% of the total volume of the solution. After sampling, an excess of 1.0 mol L^{-1} Na_2SO_3 was added to the samples (except in the analyses of AA, H_2O_2 and iron content), considering the stoichiometry between H_2O_2 and Na_2SO_3 and the initial number of moles of H_2O_2 , to ensure the removal of the remaining H_2O_2 , stopping the Fenton reactions. Before analyses, the samples were also filtered using membranes of 0.45 μm mean pore size. For evaluation of the AA towards *E. coli*, the pH of the samples were firstly adjusted to between 6 and 8, followed by addition, under stirring for 30 s, of 200 μL of an aqueous solution containing 0.4 g L^{-1} of bovine catalase, to ensure the removal of the residual H_2O_2 .

2.3. Chemical analyses and bioassays

A high-performance liquid chromatograph (LC-6AD, Shimadzu), equipped with a UV-DAD detector (SPD-M20A, Shimadzu) and a Phenomenex C-18 column (5 μm , 250 \times 4.6 mm) as stationary phase was used to monitor CIP concentration during the photocatalytic experiments. The mobile phase consisted of an isocratic 70:30 (vol %) mixture of methanol and an aqueous solution containing 0.017 mol L^{-1} of H_3PO_4 , at a flow rate of 1.0 mL min^{-1} . The detection was at 278 nm. Under these conditions, a retention time of 7.3 ± 0.1 min and a limit of quantification (LQ) of the equipment

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