Photo-Fenton Degradation Kinetics of Low Ciprofloxacin Concentration Using Different Iron Sources and pH

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Abstract

The aim of the present study was to compare the degradation kinetics of low (1 mg L^{-1}) and high (25 mg L^{-1}) concentrations of ciprofloxacin (CIP) aiming to decrease the concentration of additives and evaluate the pH limitation by the use of low iron concentrations and organic ligands. A parameterized kinetic model was satisfactorily fitted to the experimental data in order to study the performance of photo-Fenton process with specific iron sources (iron citrate, iron oxalate, iron nitrate) under different pH medium (2.5, 4.5, 6.5). The process modeling allowed selecting those process conditions (iron source, additives concentrations and pH medium) which maximize the two performance parameters related to the global equilibrium conversion and kinetic rate of the process. For the high CIP concentration, degradation was very influenced by the iron source, resulting in much lower efficiency with iron nitrate. At pH 4.5, highest TOC removal (0.87) was achieved in the presence of iron citrate, while similar CIP conversions were obtained with oxalate and citrate (0.98 after 10 min). For the low CIP concentration, much higher conversion was observed in the presence of citrate or oxalate in relation to iron nitrate up to pH 4.5.This behavior denotes the importance of complexation also at low dosages. Appropriate additives load (320 µM H_2O_2; 6 µM Fe) resulted in a CIP conversion of 0.96 after10 minutes reaction with citrate up to pH 4.5.

Keywords: antibiotic; emerging contaminants; citrate; oxalate; kinetic model; photo-Fenton

Introduction

The pharmaceuticals represent an emerging group of organic contaminants of environmental concern used in human and veterinary medicine. Their continuous use associated with the inefficiency of conventional sewage treatment systems contribute for the contamination of aquatic medium [1]. Many studies confirm the presence of these compounds in various aquatic compartments, as surface water, sewage treatment plant effluents (STP), seawater and groundwater [2-7]. Among these pharmaceuticals are the antibiotics, which are therapeutic agents used in infections by microorganisms which act on its growth inhibition or death. Beside its main application, the antibiotics have been widely used as growth promoters in animal farming [8]. Due to the poor absorption and partial metabolism by the organisms, they are excreted through the feces and urine [9].

As a consequence, the continuous exposure of aquatic organisms to low concentrations of antibiotics may lead to bacterial resistance causing the inefficiency of future application of these medicines [10, 11]. Furthermore, the antibiotics may decrease the efficiency of the wastewater treatment process and disrupt the microbial environment in water [12].

Ciprofloxacin (CIP) is a fluoroquinolone broad-spectrum antibiotic, which is active against gram-positive and gram-negative bacteria [13], interfering in the catalytic cycle of important enzymes for the nucleic acid synthesis of bacteria [14].

It has been observed that the relatively high removal efficiency of ciprofloxacin in sewage treatment plants (STP) is mainly due to sorption and photodegradation [15, 16]. Ciprofloxacin has been found in hospital effluents at concentrations varying from 11-99 $\mu g\ L^{-1}$ [17, 18], in STP influents at concentration of 0.14 $\mu g\ L^{-1}$ [19], effluents at

concentrations between 105 ng L^{-1} and 0.055 µgL^{-1} [19, 20] and raw drinking water at concentration of 0.032 µg L^{-1} [21].

The advanced oxidation processes (AOP) have already ratified their efficiency for the abatement of pharmaceuticals in water due to the non-selectivity of the hydroxyl radical, which may be effective towards different classes of pharmaceuticals which are found at low concentrations permitting its effective degradation [22-25].

In this concern, the photo-Fenton process is especially interesting for the application to the treatment of pharmaceuticals contaminated wastewater. Its high efficiency of hydroxyl radical generation by the use of iron salts and hydrogen peroxide at ambient temperature and pressure under UV or solar radiation has been already proved [26].

The photo-Fenton process is tightly pH dependent, with a maximum degradation efficiency of pollutants in a narrow pH range, between 2.5 to 3.0. At values above 3.0, precipitation of iron (III) hydroxides occurs reducing its interaction with H_2O_2 and consequently decreasing the production of $^{\bullet}OH$. At pH below 2.5, scavenging of $^{\bullet}OH$ by H^+ ions may also decrease the efficiency of the reaction [27]. Iron complexes have been applied in order to extend the pH range used in the photo-Fenton process, since Fe(III) complexes are soluble at neutral pH values. The application of organic ligands as oxalate and citrate in the photo-Fenton process has been shown to increase the degradation efficiency of pollutants [28-31]. Furthermore, the use of iron complexes as ferrioxalate (FeOx) is especially interesting for solar applications, since it absorbs strongly between 250-500 nm and has a high quantum efficiency of Fe^{2+} generation [32].

Considering that pharmaceutical concentrations found in different environmental samples are in the range of ng L^{-1} to µg L^{-1} it is reasonable to ponder that different

condition of Fenton reaction may be applied concerning pH, iron source and hydrogen peroxide concentration. The hypothesis is that reducing the iron concentration, precipitation is reduced permitting to apply the process at higher pH values. The question is then how much may pH be increased without decreasing the process efficiency. Another aspect refers to the iron species. In this concern the question is how important are organic ligands when low iron concentrations are applied.

Considering these two questions and that photo-Fenton degradation of emerging contaminants at low levels and pH values close to neutral was scarcely studied [24, 31, 33], the aim of the present study was to compare the degradation kinetics of high and low concentrations of ciprofloxacin aiming to decrease the concentration of additives and evaluate the pH limitation by the use of low iron concentrations and organic ligands (citrate and oxalate).

2. Material and methods

2.1 Reagents

Monohydrated ciprofloxacin hydrochloride (98%) ($C_{17}H_{18}O_3N_3F{\cdot}HCl{\cdot}H_2O$; MM=385.8 g mol^{-1}) was obtained from Pharmanostra. $Fe(NO_3)_3{\cdot}9H_2O$ (Mallinkrodt) was used to prepare aqueous 0.25 mol L^{-1} iron stock solution. Potassium oxalate (J.T. Baker) and citric acid (Synth) were used as ligands. H_2O_2 30% (w/w) (Synth) was used. Bovine liver catalase was purchased from Sigma–Aldrich. Ammonium metavanadate (Vetec) 0.06 mol L^{-1} was prepared in 0.36 mol L^{-1} H_2SO_4 (Merck) and used for hydrogen peroxide determination. Methanol (HPLC grade) and formic acid (analytical grade) were purchased from J.T. Baker. Ultrapure water (Millipore Milli Q water) was

used for dilutions and for HPLC analysis. A 0.2 mol L^{-1} H_2SO_4 and NaOH (Chemis) solution were used for pH adjustment.

2.2. Experimental degradation procedures

Experiments were carried out in an up flow reactor previously described [27]. The irradiation source was a 15 W black-light lamp with maximum emission at 365 and 410 nm. The irradiated volume of the reactor was 280 mL and a total volume of 500 mL of CIP solution was recirculated at a flow rate of 44 mL min^{-1} using a peristaltic pump (Masterflex 7518-12). The iron complexes, iron citrate (Fecit) and ferrioxalate (FeOx) were prepared *in situ* by the addition of citric acid or potassium oxalate to iron nitrate solution at the molar ratio iron to ligand 1:1 and 1:3, respectively. The pH of the solution was then adjusted to the desired value within the range 2.5-6.5 by addition of H_2SO_4 or NaOH. After pH adjustment, appropriate volume of H_2O_2 was added to the solution while magnetically stirred and it was then immediately pumped into the reactor. The lamp was only switched on once the reactor was completely filled, and at this point, the time started to be monitored. The initial concentration of ciprofloxacin was 25 mg L^{-1} or 1 mg L^{-1}, corresponding to 65 and 2.6 µmol L^{-1}, respectively.

Theoretical stoichiometric H_2O_2 dose for totally degrading 65 µmol L^{-1} CIP (high ciprofloxacin concentration) into CO_2, H_2O and inorganic acids is 3 mmol L^{-1}. In these experiments hydrogen peroxide dose was fixed as 2 times the stoichiometric amount, 6 mmol L^{-1} (204 mg L^{-1}), for the three pH values and three iron sources. Experiments with 8 mmol L^{-1} hydrogen peroxide dose were also carried out at pH 2.5. Over stoichiometric hydrogen peroxide concentrations are desirable in order to ensure enough amount for the Fenton reaction whatever iron source is tested. For the low ciprofloxacin concentration (2.6 µmol L^{-1}), the concentration of hydrogen peroxide was

153 fixed ensuring a H_2O_2/Fe ratio of 50 with 2.6, 6.4, 16 µmol L^{-1} iron (0.14, 0.36, 0.90 mg
154 L^{-1}). The lowest iron concentration was equal to the CIP concentration and then
155 increased 2.5 times. Thus the hydrogen peroxide concentrations applied were 0.13, 0.32
156 and 0.80 mmol L^{-1} (4.4, 11 and 27 mg L^{-1}), which correspond to approximately 1, 2.5
157 and 6.5 times the stoichiometric amount, respectively.

158 Table 1 summarizes the operating conditions of every experiment carried out
159 under high (H) and low (L) concentrations of ciprofloxacin and additives. Molar
160 H_2O_2/Fe and H_2O_2/CIP ratios are also indicated.

161

162 *2.3. Chemical analysis*

163 The concentration of ciprofloxacin during the experiments at high concentrations
164 was determined using reversed-phase high performance liquid chromatography (HPLC),
165 coupled to a diode array detector (DAD) (SPD-M20A). At low concentrations, a
166 fluorescence detector (FL) (RF-20A) from Shimadzu (LC 20AT Prominense) was used.
167 A C-18 column (Shim-pack CLC (M) 5 µ x 250 x 4.6 mm Shimadzu) was used in both
168 cases and the mobile phase was a mixture of methanol:formic acid 0.1% (24:76) at a
169 flow rate of 1.0 mL min^{-1}. The injection volume was 40 µL. Under these conditions,
170 retention time of ciprofloxacin was 9.6 min. The wavelength of 280 nm was used for
171 detection in HPLC-DAD system and the quantification limit was 0.325 mg L^{-1}. In the
172 HPLC-FL system, the chromatographic conditions were the same as for DAD, using the
173 wavelength of 278 nm for excitation and 445 nm for emission. The quantification limit
174 in this case was 0.0137 mg L^{-1}. The enzyme catalase was used to interrupt the Fenton
175 reaction by the decomposition of residual H_2O_2, after pH adjustment to 6-7 for iron
176 precipitation. The samples were filtered through 0.45 µm polyvinylidene fluoride
177 (PVDF) membrane (Millipore) before HPLC analysis.

178 The mineralization of organic matter during ciprofloxacin degradation was
179 evaluated by measuring the decay of the total organic carbon concentration (TOC) using
180 a TOC analyzer (Shimadzu TOC 5000A). TOC was measured immediately after the
181 sample withdrawal and without previous treatment. The TOC content includes the
182 carbon from the target compound, from the degradation products generated during
183 irradiation and from oxalate or citrate when these ligands were used. It is important to
184 mention that the proportion of oxalate to iron was 3:1 while of citrate was 1:1, resulting
185 in the same initial carbon amount since citrate has 6 carbon atoms and oxalate 2. So the
186 initial TOC concentration when oxalate or citrate was used was 24.8 mg L^{-1} and 13.3
187 mg L^{-1} in the case of iron nitrate for high CIP concentration, which refers only to CIP
188 content.
189 When performing the degradation experiments of ciprofloxacin at 25 mg L^{-1}
190 both mineralization and the decay of ciprofloxacin concentration were measured. When
191 performing the degradation experiments of ciprofloxacin at 1 mg L^{-1}, mineralization
192 was not evaluated since the quantification limit of this technique (1 mg L^{-1}) was not
193 sufficiently low, since TOC theoretical values varied from 0.72 to 1.7 mg L^{-1} for the
194 different oxalate or citrate concentrations.
195 The residual hydrogen peroxide concentration was determined
196 spectrophotometrically (Shimadzu UV mini-1240) by measuring the absorption at 450
197 nm after reaction with ammonium metavanadate [34].
198
199 *2.4. Kinetic parameters analysis*
200 A semi-empirical model already evaluated in previous works was proposed for
201 characterizing the performance of the process under study [35]. The simplifying
202 approaches to describe the TOC evolution are:

- ✓ 1st order kinetics, for which the rate is a function of the initial values of these factors.
- ✓ Equilibrium state (*plateau*) is achieved under specific conditions, so, a limit concentration exists, $[TOC]^{\infty}$.

A driving force leading to the equilibrium may be proposed, which is proportional to the gap to the equilibrium, $[TOC]-[TOC]^{\infty}$. The degradation rate may be formulated as:

$$\frac{d[TOC]}{dt} = -k_{TOC}([TOC] - [TOC])^{\infty}) \quad (1)$$

The integration of this rate law leads to the analytical expression for the TOC evolution under given initial conditions:

$$[TOC] = [TOC]^{\infty} + ([TOC]^{0} - TOC^{\infty}).e^{-k_{TOC}\,t} \quad (2)$$

which can be expressed in terms of maximum TOC removal (ξ, degradation attained) by the following equation:

$$\xi = \xi^{max}(1 - e^{-k_{TOC}\,t}) \text{ being } \xi^{max} = \frac{[TOC]^{0} - [TOC]^{\infty}}{[TOC]^{0}} \quad (3)$$

Hence, the performance of the degradation process may be characterized by determining the two parameters of the model, ξ^{max} and k_{TOC}, which were obtained by fitting the model to the experimental data under the least squares criterion.

In the case of the decay of ciprofloxacin concentration, since total conversion occurs in most of the cases, the conversion after 10 min ($\xi^{10\ min}$) was used for characterizing the degradation process besides of *k*, first order kinetic, represented in this case as k_{CIP}.

3. Results and discussion

A set of experiments varying iron species, pH and concentrations of ciprofloxacin and additives under blacklight radiation were carried out. Firstly the degradation of ciprofloxacin (CIP) was studied at the initial concentration of 25 mg L^{-1} (65 µmol L^{-1}) using fixed concentrations of iron (0.16 mmol L^{-1}; 9 mg L^{-1}) and hydrogen peroxide (6 mmol L^{-1}; 204 mg L^{-1}), however at different pH values (2.5, 4.5 and 6.5) and complexing agents (oxalate and citrate) in order to evaluate the photo-Fenton degradation kinetics of the antibiotic. Experiments with 8 mmol L^{-1} H_2O_2 (292 mg L^{-1}) and 0.16 mmol L^{-1} iron were also carried out at pH 2.5 with the aim of comparing the degradation of high and low CIP concentrations with the same H_2O_2/Fe ratio..

Subsequently, considering the lack of studies on photo-Fenton degradation of emerging contaminants at low concentrations at pH values close to neutral and reduced additives concentrations, the initial concentration of ciprofloxacin was reduced to 1 mg L^{-1} (2.6 µmol L^{-1}). Iron and hydrogen peroxide concentrations were also reduced aiming to evaluate the pH limitation and to study its degradation kinetics under these low level concentrations. It is important to mention that no significant change in the pH (±0.2) was observed until the end of experiment for initial pH values of 2.5 and 4.5 for both high and low concentrations. Only for the initial pH 6.5 a slight increase to 7.1 was observed.

3.1. Degradation of ciprofloxacin (CIP) at high dosages

When comparing the conversion of 25 mg L^{-1} (65 µmol L^{-1}) ciprofloxacin using the three iron species at pH 4.5, the benefit of using the iron complexes FeOx and Fecit for the pharmaceutical conversion was clear, reaching almost total conversion after 10 minutes with both complexes, while in the presence of iron nitrate, only about 0.20 of

CIP was converted after the same time (Figure 1A). Although the conversion of ciprofloxacin with either oxalate or citrate was very similar, citrate achieved higher maximum TOC removal, 0.699, and with oxalate the maximum conversion achieved was 0.411, while insignificant TOC removal (below 0.05) was observed when using iron nitrate (Fig. 1B). The higher CIP conversion in the presence of iron citrate and oxalate in relation to iron aqueous-complexes can be attributed to the higher quantum yield for Fe(II) generation (Φ_{FeII}) [36, 37]. Furthermore, the quantum yield of either iron aqueous-complexes as well as organic complexes depends on the solution pH. According to previous works, increasing pH from 2.7 to 4.0 increases the Φ_{FeII} in approximately 50% in the presence of citrate. However, in the presence of oxalate, the same increase in pH causes a decrease in the Φ_{FeII} of about 50% [38].

It was also observed a very different H_2O_2 consumption for the three iron sources as pH increases. No significant difference on H_2O_2 consumption was observed at pH 2.5, while at pH 4.5, 80% were consumed after 90 min in the presence of Fecit and FeOx and only 30% were consumed in the presence of iron nitrate (data not shown). These results indicate the low reactivity of $Fe(NO_3)_3$ with H_2O_2 at this pH condition leading to low degradation efficiency. The higher H_2O_2 consumption in the presence of organic complexes is also related to the higher quantum yield of Fe(II) generation when compared to iron nitrate, as previously reported [25, 39, 40].

The system performance can be well visualized by the rate constant of CIP conversion (k_{CIP}) *vs*. CIP conversion after 10 min ($\xi^{10\ min}$) and compared to rate constant of mineralization (k_{TOC}) *vs*. maximum TOC removal (ξ^{max}) chart (Fig. 2), allowing the parametrical characterization of the influences of iron source and pH on the system behaviour. In relation to CIP conversion after 10 min, the parameters of the model move within the range $\xi^{10\ min}$ = [0.194, 0.991] and k_{CIP} = [0.002, 0.065], with highest rate

constant observed with Fecit at pH 2.5, while very similar CIP conversions were obtained with FeOx (pH 2.5 and 4.5), Fecit at pH 4.5 and nitrate at pH 2.5, however in all cases with much lower rate constants than with Fecit at pH 2.5. Further increase of pH to 6.5 decreased significantly both the CIP conversion after 10 min and rate constant for all iron species, showing clearly the pH limitation for CIP degradation under these conditions even with FeOx or Fecit complexes (Fig. 2A).

In relation to mineralization, the parameters of the model move within the following range: ξ^{max} = [0.070, 0.878] and k_{TOC} = [0.011, 0.050], with minimum values corresponding to iron nitrate at pH 6.5 and maximum values to iron oxalate at pH 2.5 (Fig. 2B). Similar maximum TOC removal at pH 2.5 were obtained with FeOx and Fecit. Iron nitrate resulted also in relatively high TOC removal at pH 2.5, however at much lower rate constant. It is important to mention that in the case of iron nitrate at both pH 4.5 and 6.5, the results did not fit the semi-empirical kinetic model proposed, since the ξ^{max} attained in both cases was insignificant (below 0.05).

Given the good results of iron citrate, the study of ciprofloxacin degradation at low concentrations was focused on this complex, while for comparison some experiments were also carried out with other iron sources.

3.2. Degradation of ciprofloxacin at low dosages

For the degradation of 1 mg L^{-1} (2.6 µmol L^{-1}) ciprofloxacin, the iron concentration was varied from 2.6 to 16 µmol L^{-1}. An experiment carried out in the absence of hydrogen peroxide with 16 µmol L^{-1} Fecit (experiment L0, Table 1) resulted in a very low CIP conversion ($\xi^{10\ min}$) of 0.142 and rate constant (k_{CIP}) of 0.002, indicating that the contribution of iron citrate photolysis for the degradation of the target compound is not substantial. In the experiments in the presence of hydrogen peroxide,

298 although the much lower iron concentration would reduce the tendency of iron
299 precipitation during the degradation process, it is possible to observe that iron
300 complexation is still very important for an efficient degradation of CIP. When
301 comparing the CIP conversion using iron citrate with iron nitrate at 6.4 μmol L^{-1} iron
302 concentration, both at pH 2.5, much higher CIP conversion was observed with iron
303 citrate achieving 0.94 after 10 min, while with iron nitrate only 0.54 were achieved,
304 similar to the results obtained at pH 6.5 with iron citrate (Fig. 3). Despite the low iron
305 concentrations, iron nitrate promoted also low CIP conversions at pH 4.5 and 6.5,
306 achieving 0.31 and 0.20, respectively.

307 An interesting aspect is that at this iron concentration range, the efficiency of
308 CIP conversion with the use of citrate is independent of pH until pH 4.5, declining
309 considerably at pH 6.5. Similar behavior was observed with FeOx, although a slight
310 decrease of CIP conversion was observed when increasing the pH from 2.5 to 4.5 (Fig.
311 3C). This may be related to the higher Φ_{FeII} of iron citrate at pH around 4 in comparison
312 to FeOx, as previously discussed [38].

313 As already shown for high dosages (section 3.1), the system performance can be
314 well visualized in the conversion rate constant (k_{CIP}) *vs*. CIP conversion after 10 min
315 ($\xi^{10\ min}$), allowing the parametrical characterization of the influences of iron source and
316 pH on the system behavior (Fig. 4). The parameters of the model move within the
317 following range: $\xi^{10\ min}$ = [0.309, 0.989] and k_{CIP} = [0.004, 0.068] with a satisfactory
318 model adjustment, with only one value with correlation coefficient R^2 below 0.950
319 (0.899).

320 For a low ciprofloxacin concentration (2.6 μmol L^{-1}) it is also interesting to
321 discuss the effect of the reagent amounts related to the CIP concentration, remembering
322 that in all cases H_2O_2/Fe ratio was fixed at 50. A similar behavior was observed with

Fecit and FeOx at pH 2.5 and pH 4.5 when hydrogen peroxide concentration was 2.5 times the stoichiometric amount. However, using stoichiometric H_2O_2 concentration (H_2O_2/CIP = 50), only Fecit resulted in significant CIP conversions after 10 min (0.75) at pH 2.5 and 4.5, indicating that Fecit is the iron species least affected by the pH.

Higher H_2O_2/CIP ratio (H_2O_2/CIP = 308) resulted in an important effect on the rate constant, achieving k_{CIP} = 0.07, but a lower effect on CIP conversion after 10 min. On the other hand, these results suggest that at intermediate concentrations, as H_2O_2/CIP ratio = 123, almost total conversions (higher than 0.90) are observed after 10 min with rate constants between 0.02 and 0.03 with Fecit up to pH 4.5. In relation to oxalate, similar results are obtained only at pH 2.5.

The degradation of low and high CIP dosages under the same H_2O_2/CIP ratio (123) and H_2O_2/Fe ratio (50) at pH 2.5 (experiments H10 and L4; H11 and L10; H12 and L13) resulted in very similar degradation behavior (data not shown), demanding however, lower concentrations of iron and hydrogen peroxide at low CIP dosages.

Conclusions

The kinetic model applied was satisfactorily fitted to the experimental data. The degradation performance of high and low concentration of ciprofloxacin was characterized by TOC removal (ξ^{max}, k_{TOC}) and CIP conversion ($\xi^{10\ min}$, k_{CIP}). The system performance was evaluated at different Fenton additives (concentration, iron source) and pH values showing that:

- The system behaved similarly under high and low concentration.

- The pH limitation showed to be critical in the absence of organic ligands, resulting in low CIP conversions with iron nitrate at both high and low dosages, except at pH 2.5.
- Iron citrate permitted to achieve significant CIP conversions at pH 2.5 and 4.5, being the best choice up to pH 4.5 with a H_2O_2/CIP ratio between 50 and 123.
- Iron citrate was the iron species least affected by the pH.
- Similar behavior was observed with oxalate, however only at 123 H_2O_2/CIP ratio.

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