Zero-valent iron mediated degradation of ciprofloxacin – Assessment of adsorption, operational parameters and degradation products

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Highlights

- Increase of ZVI concentration improved linearly the removal of ciprofloxacin up to 5 g L^{-1}.
- Adsorption increases with pH however it is not important for degradation.
- Fluoride measurements indicate partial defluorination of ciprofloxacin.
- ZVI degradation of ciprofloxacin is initiated by hydroxylation of quinolonic and benzenic ring.

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Abstract

The zero-valent iron (ZVI) mediated degradation of the antibiotic ciprofloxacin (CIP) was studied under oxic condition. Operational parameters such as ZVI concentration and initial pH value were evaluated. Increase of the ZVI concentration from 1 to 5 g L^{-1} resulted in a sharp increase of the observed pseudo-first order rate constant of CIP degradation, reaching a plateau at around 10 g L^{-1}. The contribution of adsorption to the overall removal of CIP and dissolved organic carbon (DOC) was evaluated after a procedure of acidification to pH 2.5 with sulfuric acid and sonication for 2 min. Adsorption increased as pH increased, while degradation decreased, showing that adsorption is not important for degradation. Contribution of adsorption was much more important for DOC removal than for CIP. Degradation of CIP resulted in partial defluorination since the fluoride measured corresponded to 34% of the theoretical value after 120 min of reaction. Analysis by liquid chromatography coupled to mass spectrometry showed the presence of products of hydroxylation on both piperazine and quinolonic rings generating fluorinated and defluorinated compounds as well as a product of the piperazine ring cleavage.

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1. Introduction

Zero-valent iron (ZVI) has been used for the degradation of a variety of pollutants. Under anoxic conditions, the relatively strong reducing capacity of ZVI (Fe^{2+}/Fe^{0}, E^{0} = −0.440 V) is employed for the reduction of contaminants such as nitroaromatic compounds, organochlorines and azo dyes (Satapanajaru et al., 2009). However, under anoxic conditions, ZVI cannot completely mineralize pollutants. On the other hand, under aerobic conditions, oxygen acts as an electron acceptor in a reduction involving four electrons, generating water, and a reduction involving two electrons, generating hydrogen peroxide, with ferrous ions being produced in both cases (Lee and Sedlak, 2008):

\[ 2\text{Fe}^{0} + \text{O}_2 + 4\text{H}^{+} \rightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O} \quad (1) \]

Under oxic condition, the oxidation of organic contaminants in acid medium occurs, which has been attributed to the further reaction of H$_2$O$_2$ with Fe$^{2+}$, producing hydroxyl radicals in a Fenton reaction and resulting in mineralization of pollutants (Bautitz et al., 2012). The formation of reactive oxygen species such as O$_2^-$ and OH, in addition to H$_2$O$_2$, has been discussed in the literature (Noradoun et al., 2003; Roy et al., 2003; Joo et al., 2004; Keenan and Sedlak, 2008; Laine et al., 2008).

Contamination of surface waters with pharmaceutical products is a widespread environmental problem. About three thousand different compounds, with a wide range of different chemical structures, are used as active ingredients in human and veterinary medicine (Ternes et al., 2004).

Some of the adverse environmental effects caused by drugs include resistance of pathogenic bacteria, genotoxicity, and endocrine disruption (Kümmerer, 2004). Although the drugs may
not be acutely toxic, they can have cumulative effects on the metabolism of non-target organisms (Halling-Sørensen et al., 1998) and on ecosystems (Daughton and Ternes, 1999).

Fluoroquinolone comprises an important class of non-biodegradable broad-spectrum antibiotics, used to treat diseases in both humans and animals (Bongaerts and Hoogkamp-Korstanje, 1993). A representative antibiotic of the fluoroquinolone class is ciprofloxacin (CIP) (Table 1). It has been reported that the relatively high removal efficiency of CIP in wastewater treatment plants is mainly due to sorption and not degradation (Lindberg et al., 2006). However, CIP has been detected at concentrations varying from few ng L\(^{-1}\) in aquatic environment (Locatelli et al., 2011) to mg L\(^{-1}\) in industrial effluents (Larsson et al., 2007).

The aim of this study was to investigate the ZVI/O\(_2\) mediated degradation of CIP. Firstly, iron dissolution and pH variation during reaction, as well as removal of CIP, were evaluated as a function of ZVI concentration. The contribution of adsorption on the overall removal of CIP was also assessed as a function of initial pH. Secondly, the role of Fenton reaction was discussed in view of defluorination and main degradation intermediates identified using high performance liquid chromatography (HPLC) coupled to mass spectrometry (MS) analyses.

2. Materials and methods

2.1. Reagents

CIP (98%) was obtained from Pharma Nostra (São Paulo, Brazil). ZVI iron powder (20 mesh, 840 \(\mu\)m diameter) was purchased from Alfa Aesar (Ward Hill, MA, USA). FeSO\(_4\)-7H\(_2\)O (98%) was obtained from F. Maia (São Paulo, Brazil). H\(_2\)SO\(_4\) and NaOH were purchased from Quemis (São Paulo, Brazil). EDTA was purchased from Mallinckrodt (Paris, KY, USA). 1,10-Phenanthroline was obtained from Vetec (Rio de Janeiro, Brazil). 2,2\(^{\prime}\)-Bipyridyl and peroxidase (type II-A from horseradish, 1500 units mg solid\(^{-1}\)) were purchased from Sigma–Aldrich (St. Louis, MO, USA). N,N-diethyl-1,4-phenylene-diamine (DPD) was obtained from Fluka (Steinheim, Germany). Methanol (HPLC grade) and formic acid (analytical grade) were purchased from J.T. Baker (Xalostoc, Mexico). KH\(_2\)PO\(_4\) and K\(_2\)HPO\(_4\)-7H\(_2\)O were obtained from Synth (São Paulo, Brazil). Ultrapure water (Milli-Q, Millipore, Bedford, MA, USA) was used for dilutions and for HPLC analysis.

2.2. Characterization of ZVI

Particle structure, size, and shape of ZVI used in this study were analyzed before and after the reaction using scanning electron microscopy (SEM) (Topcon SM-300, Tokyo, Japan). The crystal structure of the particles was investigated by X-ray powder diffraction (XRD) (Siemens D5000, Munich, Germany) employing Cu K\(_\alpha\) radiation. The current and accelerating voltage applied were 25 mA and 35 kV, respectively. The BET surface of the particles was determined using a Micromeritics ASAP 2010 instrument (Atlanta, GA, USA).

2.3. Procedures of degradation experiments

Firstly, the ZVI particles were washed with 1.0 M sulfuric acid solution under ultrasonication (Ultra Cleaner 1400, Unique, São Paulo, Brazil) for 30 s, followed by removal of excess acid and three subsequent washes with ultrapure water. This procedure was adopted in order to remove surface oxides from the ZVI particles, as previously described (Bautitz et al., 2012). Sufficient amount of CIP was dissolved in ultrapure water to give a concentration of 65 \(\mu\)M and used in all degradation experiments. Although this concentration is above the levels encountered in environmental samples, it was important to guarantee the analytical reliability when investigating the degradation process.

Experiments were carried out in 600 mL high form beakers under vigorous mechanical stirring (around 1500 rpm, Quimis Q235, São Paulo, Brazil) using 20 mesh ZVI, which remained fully dispersed. Under these conditions, the measured dissolved oxygen (DO) concentration (Extech Instruments 407510 DO Meter, Waltham, MA, USA) was around 8.1 mg L\(^{-1}\) throughout the experiments, and it was assumed to be the main electron acceptor in solution. The initial pH of the solution was adjusted by adding H\(_2\)SO\(_4\) (1 M) or NaOH (1 M). The experiments started with the addition of ZVI to the aqueous CIP solution. After iron addition,

<table>
<thead>
<tr>
<th>Table 1</th>
<th>LC/MS data for ZVI degradation of CIP after 30 min reaction.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Retention time (min)</td>
</tr>
<tr>
<td>CIP</td>
<td>11.9</td>
</tr>
<tr>
<td>1</td>
<td>6.4</td>
</tr>
<tr>
<td>2</td>
<td>8.3</td>
</tr>
<tr>
<td>3</td>
<td>12.9</td>
</tr>
</tbody>
</table>
the initial pH of the suspension was rechecked, and the change was less than 0.1. Most of the experiments were repeated three times, so the error bars shown in the figures represent standard deviations of triplicate experiments.

Samples withdrawn after different reaction times (0–120 min) were centrifuged at 3000 rpm for 5 min (centrifuge Centrifio 80-2B, Curitiba, Brazil) and filtered through 0.45 μm polyvinylidene fluoride membranes (Millipore, Bedford, MA, USA) before analyses.

2.4. Chemical analyses

The concentration of CIP during the experiments was determined using reversed-phase HPLC with a diode array detector (Prominence LC 20AT, Shimadzu, Kyoto, Japan) and a C-18 column (Shim-pack CLC-ODS (M), 5 μm, 250 × 4.6 mm, Shimadzu, Kyoto, Japan) maintained at 40 °C. The mobile phase was a mixture of methanol (24%), and 0.1% (v/v) formic acid in water (76%), at a flow rate of 0.22 mL/min. The injection volume was 40 μL and the wavelength of 280 nm was used for CIP detection. Under these conditions, the CIP quantification limit was 5.5 μM. Fluoride and nitrate concentrations were determined using ion chromatography (ICS 5000 RFIC, Dionex, Sunnyvale, CA, USA). The mineralization of organic matter during CIP degradation was evaluated by measuring the decay of the dissolved organic carbon (DOC) using a total organic carbon analyzer (TOC 5000A, Shimadzu, Kyoto, Japan). The concentration of ferrous ions generated during the degradation experiments due to ZVI dissolution was measured using the spectrophotometric method employing 1,10-phenanthroline, with maximum absorption at 510 nm (UV mini-1240, Shimadzu, Kyoto, Japan) (Fortune and Mellon, 1938). Hydrogen peroxide generated in situ during the experiments was determined by measuring the absorbance at 551 nm after a peroxidase-catalyzed reaction with DPD (Bader et al., 1988). The method was modified by the addition of bipyridine and EDTA (100 mM) to minimize interference of Fe²⁺ and Fe³⁺, respectively (Balmer and Sulzberger, 1999).

LC/MS/MS was performed in a HPLC (1200 Agilent Technologies, Santa Clara, CA, USA) coupled to a 3200 QTRAP Mass Spectrometer (Linear Ion Trap Quadrupole, AB Sciex Instruments, Framingham, MA, USA) operating in a positive mode and Turbolon-Spray ionization. Fullscan and MS/MS experiments were carried out using the following parameters: curtain gas: 103 kPa, ion spray: 5500 V, gas 1: 310 kPa, gas 2: 276 kPa, temperature: 600 °C; declustering potential: 36 V, entrance potential: 4 V and interface heater: ON. The same chromatographic conditions were used as previously described.

Before LC/MS/MS analysis, 20 μL of 0.1 M EDTA and 0.1 mL of a 0.05 M bipyridine solution were added to 5.0 mL sample for complexation of ferric and ferrous ions, respectively. This procedure was important to avoid interference during MS analysis due to signal suppression. Solid phase extraction was then carried out using Sep-Pak-C18 cartridges (Waters, Milford, MA, USA). The cartridges were previously conditioned with 5 mL methanol followed by 3 mL water. Then 5 mL of sample was percolated through the cartridge and recovered with 5 mL of 50:50 (v/v) methanol and formic acid 0.1% (v/v) aqueous solution, followed by filtration through 0.22 μm filter (Millipore, Bedford, MA, USA). The recovery of CIP (65 μM) varied in the range of 95–105%.

3. Results and discussion

3.1. Surface analysis of ZVI particles

The 20 mesh ZVI particles were characterized by SEM and XRD before and after CIP degradation (Fig. 1). The SEM images showed that the unreacted particles were not uniform in shape and size, and had a relatively smooth surface (Fig. 1a). The residual ZVI particles collected after 120 min of reaction were more porous and rougher than the unreacted particles, which was indicative of iron dissolution.

XRD analysis of the unreacted ZVI particles showed peaks at 2θ of 44.94° and 65.16° that could be attributed to the (110) and (200) planes of Fe⁰, respectively (Fang et al., 2010). XRD analysis of residual ZVI particles after the degradation reaction showed a decrease in the intensity of the Fe⁰ peaks and the appearance of a peak at 2θ of 35.43°, attributed to Fe₂O₃ formation during the reaction (Chen et al., 2007) (Fig. 1b). The measured BET surface area of the iron powder was 0.008 m² g⁻¹.

3.2. Effect of ZVI concentration

The effect of ZVI concentration on CIP degradation was investigated in the concentration range of 1–15 g L⁻¹ at the initial pH 2.5. It is important to mention that no significant decrease of CIP concentration (<5%) was observed after 120 min reaction in the absence of ZVI at pH 2.5, indicating its stability under these conditions. The initial degradation rate of CIP increased with increasing ZVI concentrations (Fig. 2a). A sharp and linear increase of pseudo-first order rate constants (kₘₚ) was observed as ZVI concentration increased from 1 to 5 g L⁻¹, tending to a plateau above 10 g L⁻¹ as can be seen in the insert of Fig. 2a. This plateau was probably related to the fast dissolution of ZVI at the elevated concentration, achieving 1.79 mM Fe²⁺ after 15 min reaction using 15 g L⁻¹ ZVI, while between 0.46 and 1.05 mM were generated when using 1.0 and 10 g L⁻¹ ZVI, respectively. The high Fe²⁺ concentration may hinder the degradation by scavenging of the hydroxyl radicals generated in the Fenton reaction:

\[
\text{Fe}^{2+} + \text{OH} \rightarrow \text{Fe}^{3+} + \text{OH}^\cdot
\]

However, Fe²⁺ concentration decreased gradually after the maximum value due to iron precipitation when ZVI of high concentrations were applied (10 and 15 g L⁻¹) (Fig. 2b). Furthermore, it was observed that the pH increased rapidly at the beginning of each experiment, especially when high ZVI concentrations were used, and stabilized near pH 5.5 (Fig. 2c). The increase of pH may also have limited higher degradation of CIP due to iron precipitation and passivation of the ZVI surface by the deposition of iron oxides such as the Fe₂O₃ which was identified in the XRD diffractogram of the residual iron (Fig. 1b).

After 120 min of reaction, the two lowest ZVI concentrations (1 and 2.5 g L⁻¹) resulted in 80% CIP degradation, while ZVI of 5, 10, and 15 g L⁻¹ resulted in approximately 92% CIP degradation. The concentration of 2.5 g L⁻¹ was therefore considered to be satisfactory and was employed in subsequent experiments, since efficient degradation was obtained with less iron dissolution (1.35 mM) and pH variation than those observed when higher concentrations of ZVI were used.

3.3. Effects of initial pH on adsorption

Firstly, experiments were carried out to estimate the contribution of adsorption and/or co-precipitation processes to the overall removal of CIP. Adsorption/co-precipitation of CIP was evaluated in experiments performed using different initial pH values, in which the entire suspension remaining at the end of the experiment (after 120 min of reaction) was acidified to pH 2.5 by adding 3 M sulfuric acid. Sonication was performed for 2 min to promote CIP desorption, followed by centrifugation and filtration. The percentage of CIP removed by adsorption was calculated according to:

\[
\%\text{CIP}_{\text{ads}} = \frac{[\text{CIP}]_{\text{final}} - [\text{CIP}]_{\text{initial}}}{[\text{CIP}]_{\text{initial}}} \times 100
\]
where $[\text{CIP}]_{\text{final 1}}$ is the concentration of CIP at the end of the experiment, $[\text{CIP}]_{\text{final 2}}$ is the concentration of CIP at the end of the experiment after desorption, and $[\text{CIP}]_{\text{initial}}$ is the initial CIP concentration. An analogous calculation was performed for DOC.

Based on this procedure, it was possible to calculate that only 6.5% of the 80% CIP removed after 120 min was due to adsorption/co-precipitation, for an initial pH of 2.5 (Fig. 3a). At initial pHs of 4.5 and 6.5, total CIP removal (adsorption/co-precipitation and degradation) was 79% and 88%, respectively, similar to that observed at pH 2.5 (80%). However, adsorption/co-precipitation played a more important role, reaching 26% and 37% at initial pHs of 4.5 and 6.5, respectively, due to the greater formation of corrosion products on ZVI particles at higher pH. The lower adsorption/co-precipitation of CIP at an initial pH of 2.5, compared to higher pH values, was due to the slow increase of pH during the reaction, reaching a maximum value at 60 min (pH = 5.5). In the case of initial pHs 4.5 and 6.5, pH values of 6.8 and 7.2, respectively, were measured in the first 15 min, and then remained constant until the end of the experiment (120 min).

This strong interaction of CIP molecules with the iron oxides formed during the CIP degradation process at pH values close to neutral is due to the predominance of the zwitterionic form, which is the major contributor to the sorption process (Gu and Karthikeyan, 2005). The sorption occurs due to the formation of a bidentate complex between the metal and oxygen atoms of the keto and carboxylic groups of the CIP molecule (Nowara et al., 1997; Gu and Karthikeyan, 2005). On the other hand, the piperazine group, which has two nitrogen atoms, plays a negligible role in the sorption of CIP (Zhang and Huang, 2007).

Removal of DOC increased as pH increased, due to the dominant contribution of adsorption/co-precipitation, with a maximum of 78% which was achieved at pH 6.5 through adsorption/co-precipitation (Fig. 3b). At pH 2.5, 14% DOC removed could be attributed to
adsorption/co-precipitation while at pH 4.5 DOC removal due to adsorption/co-precipitation increased to 41%, showing that its contribution increased as the pH increased. Increase of DOC adsorption with pH was also previously observed during ZVI mediated degradation of 2,4-dichlorophenoxy acetic acid (Velosa and Nogueira, 2013).

These results demonstrate that adsorption/co-precipitation was the main process responsible for the removal of DOC at pHs 4.5 and 6.5. Considering that the adsorption of CIP to the iron oxides is favored due to the presence of keto and carboxylic groups in the molecule (Gu and Karthikeyan, 2005), it appears that these groups were still present in the structure of the degradation products, which will be discussed in Section 3.5.

In addition to the effect on adsorption/co-precipitation, the initial pH had also a substantial influence on the ZVI dissolution. Low Fe$^{2+}$ concentrations were detected at pH 4.5 (66 μM) and 6.5 (20 μM) (Fig. 4a), due to the unfavorable dissolution of ZVI according to Eqs. (1) and (2), and the hydrolysis and precipitation of iron ions at pH above 4, while 1.35 mM Fe$^{2+}$ was generated at pH 2.5 after 120 min reaction using ZVI of 2.5 g L$^{-1}$ as already shown (Fig. 2b).

The maximum concentrations of H$_2$O$_2$ generated during CIP degradation at pHs 4.5 and 6.5 were 11 μM and 4.1 μM, respectively, after 15 min of reaction, followed by a gradual decrease (Fig. 4a). Quantification of H$_2$O$_2$ was not possible at pH 2.5, due to the high concentrations of Fe$^{2+}$ generated at this pH, favoring the formation of a colored complex with the bipyridine used in the method, which interfered with the quantification of H$_2$O$_2$. Furthermore, the high concentration of Fe$^{2+}$ present in the solution (0.75 mM after 15 min) at pH 2.5 resulted in the immediate consumption of in situ generated H$_2$O$_2$ through the Fenton reaction producing OH$,^\cdot$ which occurs to a lesser extent at pH above 4.

It is interesting to note that the profiles of Fe$^{2+}$ and H$_2$O$_2$ generation were very similar, with maxima achieved at 15 min followed by a slow decrease for both pH values (4.5 and 6.5). The decreases in the Fe$^{2+}$ and H$_2$O$_2$ concentrations were probably due to iron precipitation, which prevented ZVI dissolution and consequently also inhibited H$_2$O$_2$ generation. However, during the course of the reaction the Fe$^{2+}$/H$_2$O$_2$ molar ratio increased from 6 to 8.4 between 15 and 120 min, when an initial pH of 4.5 was used, indicating a tendency for accumulation of Fe$^{2+}$ in the solution. Although the absolute concentrations were much lower, this tendency for Fe$^{2+}$ accumulation was also observed in the case of an initial pH of 6.5, as the Fe$^{2+}$/H$_2$O$_2$ molar ratio also increased from 4.2 to 10.5, indicating the much lower generation of H$_2$O$_2$, and consequently also hydroxyl radicals at this pH. Comparison of the Fe$^{2+}$/H$_2$O$_2$ ratios obtained during CIP degradation at initial pHs 4.5 and 6.5 also revealed that an increase in pH had a greater influence on H$_2$O$_2$ generation than on ZVI dissolution.

To further investigate the role of H$_2$O$_2$ and other oxidizing species, and to assess their contribution to CIP degradation at each pH studied, methanol (100 mM) was added at the beginning of the reaction in order to scavenge OH$^\cdot$ formed in the solution. The degradation of CIP greatly decreased in the presence of methanol at pH 2.5, achieving only 7% after 30 min while 76% was achieved in the absence of methanol, indicating that the OH$^\cdot$ produced in Fenton reaction was the major species responsible for the CIP degradation at this pH. However, at pHs 4.5 and 6.5, lower effect of methanol was observed indicating a lower contribution of hydroxyl radical than that at pH 2.5, achieving about 47% removal after 120 min at both pH values, slightly higher than the contributions of adsorption/co-precipitation (26% and 37% at pHs 4.5 and 6.5, respectively) (Fig. 4b).

### 3.4. Generation of fluoride and nitrate

Removal of fluoride from fluorinated compounds is important in a treatment process since it may result in a decrease of toxicity (Purser et al., 2008). Low fluoride removal was previously reported...
for the photocatalytic degradation of CIP (Paul et al., 2010). The concentration of fluoride during CIP degradation using 2.5 g L\(^{-1}\) ZVI increased almost linearly up to 90 min, reaching approximately 22 \(\mu\)M, after which there was no further increase up to 120 min. This fluoride concentration corresponded to only 34% of the theoretical concentration (65 \(\mu\)M), indicating that there was still a considerable concentration of fluorinated intermediates, since 80% of the initial concentration of CIP had been degraded and only 30% were mineralized (Fig. 5).

A sharp increase in the concentration of nitrate to 72 \(\mu\)M was observed in the first 15 min of reaction. This concentration reflected the generation of 46 \(\mu\)M nitrate, corresponding to 24% of the theoretical amount of N in the CIP molecule (195 \(\mu\)M). However, the NO\(_3\) concentration subsequently decreased sharply to levels similar to those measured initially. This decrease in the nitrate concentration could be due to adsorption on iron/iron oxides particles (Westerhoff and James, 2003) since a reduction process to ammonium ion is improbable at the oxidizing conditions used in this work (Yang and Lee, 2005). Therefore nitrate concentration does not enable conclusions to be drawn concerning the release of the nitrogen content of the organic intermediates after 15 min of reaction.

3.5. Main degradation products

LC/MS/MS analyses of the sample containing CIP before degradation detected the ion \([\text{M}+\text{H}]^+\) = 332, which corresponds to the pseudo-molecular ion of CIP. MS/MS experiment of \([\text{M}+\text{H}]^+\) = 332 was performed to assess the fragmentation profile of the parent compound and the main fragment ions detected were \([\text{M}+\text{H}]^+\) = 314, which corresponds to water loss, \([\text{M}+\text{H}]^+\) = 288, due to carboxyl group loss (COO\(^-\)), \([\text{M}+\text{H}]^+\) = 245 due to piperazine cleavage and \([\text{M}+\text{H}]^+\) = 231 due to cyclopropyl ring elimination (Fig. SM1).

The sample taken after 30 min reaction was chosen for LC/MS/MS investigation since it showed the highest number and concentration of the intermediates generated during the ZVI mediated degradation of CIP. LC/MS/MS analysis of the 30 min reaction sample (initial pH 2.5) showed the presence of three main intermediate compounds (Table 1). Intermediate 1 with \([\text{M}+\text{H}]^+\) = 330 presented the lowest retention time (\(t_r = 6.4\) min), indicating the highest polarity among the detected products. This high polarity is justified by the attack of hydroxyl radical on benzene ring and consequent substitution of the fluorine atom, released as fluoride (Fig. 5). The substitution of fluorine atom by a hydroxyl group was previously observed in photo-Fenton degradation of ofloxacin, antibiotic of the fluoroquinolone class (Michael et al., 2013). The MS/MS experiments of \([\text{M}+\text{H}]^+\) = 330 showed the main fragments \([\text{M}+\text{H}]^+\) = 312 (loss of water) and \([\text{M}+\text{H}]^+\) = 286 (loss of COO\(^-\)) (Fig. SM2a).

The intermediate 2 showed \([\text{M}+\text{H}]^+\) = 334 which is in accordance with a product of piperazine ring cleavage. The fragments...
detected (m/z 316 and 290) are due to the losses of water and COO⁻, respectively (Fig. SM2b). The cleavage of piperazine ring was also previously observed during the degradation of CIP by UV/H₂O₂ (Guo et al., 2013) and photo-Fenton degradation of ofloxacin (Michael et al., 2013). It is interesting to note that despite the cleavage of the piperazine ring no nitrogen loss was observed.

The intermediate 3 showed m/z 348 ([M+H⁺]) , which also indicates the hydroxyl radical attack. However, in this case no fluoride was released since the attack of hydroxyl radical occurred in the quinolinic ring of CIP. Despite the presence of the hydroxyl group in quinolinic ring, a lower polarity in relation to CIP is expected, due to the formation of hydrogen bond between carbonyl from carboxylic group and OH group attached to the quinolinic ring, which is in accordance with the longer retention time observed in chromatographic analysis (tᵣ = 12.9 min). The fragments detected (m/z 330 and 304) correspond to the losses of water and COO⁻. Another fragment detected was m/z 261, which corresponds to the cleavage of piperazine ring, confirms the same fragmentation pattern than that of CIP (Fig. SM2c).

The degradation products of CIP indicated that hydroxyl radicals, generated in the Fenton reaction that occurs as a consequence of iron dissolution and hydrogen peroxide formation, play an important role in the ZVI mediated degradation under oxygenated conditions, initiating three main degradation routes (Fig. 6).

4. Conclusions

Increase in the concentration of ZVI improved removal of the antibiotic CIP, with a plateau reached above 10 g L⁻¹. A fast generation of Fe²⁺ due to iron dissolution and fast increase of pH showed that high ZVI concentrations were detrimental to the efficient degradation of CIP. The contribution of CIP adsorption onto iron particles was shown to be negligible at pH 2.5 and increased with pH, while degradation decreased, demonstrating the importance of the homogeneous process. However, higher adsorption of DOC, was observed due to the formation of iron oxide (Fe₂O₃) as reaction proceeded demonstrated by XRD analyses of the residual iron.

Increase of pH also influenced the generation of H₂O₂, which was about three times lower for an initial pH of 6.5, compared to pH 4.5. The contribution of the hydroxyl radical to the degradation process was confirmed by a drastic decrease in CIP degradation at pH 2.5 when methanol was added to the reaction medium in order to scavenge the hydroxyl radicals.

Three CIP degradation products were identified and confirmed that reaction was initiated by hydroxyl radical attack both to the benzene ring, resulting in substitution of fluorine atom (defluorination), as well as to the quinolinic ring, that is in accordance with partial defluorination observed in fluoride measurements. Reaction at piperazine ring was also observed leading to ring cleavage. These results also confirmed the role of the Fenton reaction in homogeneous medium for the ZVI degradation under oxygenated conditions.

Considering the higher degradation and lower adsorption of CIP and its degradation products on ZVI, the degradation process at pH 2.5 showed to be more advantageous than at pHs 4.5 or 6.5, reaching 80% removal. However, for a practical application, the toxicity evaluation for the degradation products is necessary to guarantee the safe application of the process.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.07.071.

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