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## Zero valent iron mediated degradation of the pharmaceutical diazepam

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### ABSTRACT

Parameters that influence the zero valent iron mediated degradation of the pharmaceutical diazepam (DZP) were evaluated including the iron concentration and its pre-treatment, the effect of complexation with EDTA and oxic versus anoxic condition. It was observed that acid pre-treatment of iron particles is important for degradation efficiency and that H<sub>2</sub>SO<sub>4</sub> is a better choice than HCl, resulting in higher degradation of DZP. Under oxic conditions, the degradation of DZP achieved 96% after 60 min using Fe<sup>0</sup> (25 g L<sup>-1</sup>) pre-treated with H<sub>2</sub>SO<sub>4</sub> in the presence of EDTA (119 mg L<sup>-1</sup>), while mineralization achieved around 60% after the same time. Under anoxic conditions, degradation occurred, however at lower extent, achieving 67% after 120 min. The addition of EDTA improved the treatment efficiency in 20% leading to 99% DZP degradation after 120 min. The first intermediates formed during DZP degradation were identified using LC/MS analysis and revealed the formation of mono- and di-hydroxylated products from DZP during Fe<sup>0</sup>/EDTA/O<sub>2</sub> degradation, which evidences that ·OH was the main oxidizing species formed in this process.

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### 1. Introduction

The development of sensitive analytical techniques has allowed the detection of a large number of human and veterinary drugs in the aquatic environment. The disposal of these medicines has become an environmental and health concern since it has increased as a response to population growth, longer lifetime expectancy and development of new drugs. These compounds or metabolites may remain active in the environment inducing bacterial resistance and deleterious effects on organisms. Furthermore, medicines and their metabolites are considered pseudo-persistent contaminants due to the continuous release into the environment (Kümmerer, 2004; Pérez and Barceló, 2007; Pal et al., 2010).

Due to antibiotic effect and/or to their high molecular complexity, these contaminants are not efficiently removed in conventional sewage treatment plants (STP) and as a result, a large number of pharmaceuticals have been detected in STP effluents (Hernando et al., 2006). In this context, substantial effort is carried out to evaluate the occurrence of various pharmaceuticals and to develop efficient treatment processes to remove them and decrease the environmental and health effects (Fent et al., 2006).

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The reducing power of zero valent iron (Fe<sup>0</sup>) is used for effective reduction of organochlorine compounds including trichloroethylene, perchloroethylene and DDT, as well as azo dyes besides of inorganic species such as nitrate in the aquatic environment, especially ground water (Sayles et al., 1997; Nam and Tratnyek, 2000; Sohn et al., 2006; Epolito et al., 2008). Although the reduction of these species results in significant reduction of toxicity in most cases, the overall removal of dissolved organic carbon (DOC) is low, demanding more drastic conditions to promote effective degradation of the generated intermediates.

The combination of Fe<sup>0</sup>, EDTA and oxygen (Fe<sup>0</sup>/EDTA/O<sub>2</sub>) is pointed out to promote organic pollutants degradation through an oxidative mechanism, in which Fe<sup>0</sup> is quickly oxidized to Fe(II) and Fe(III), which forms EDTA complexes reacting with oxygen through a series of one-electron transfer reactions to produce hydrogen peroxide (Laine et al., 2008). The complex Fe<sup>II</sup>EDTA reacts with H<sub>2</sub>O<sub>2</sub> through a Fenton like process resulting in the formation of hydroxyl radical, the species responsible for the pollutant oxidation. Alternatively, Fe<sup>0</sup> reacts with oxygen to produce H<sub>2</sub>O<sub>2</sub> through a two-electron transfer (Joo et al., 2004; Keenan and Sedlak, 2008a):

Diazepam (DZP) (Fig. 1) is the most common benzodiazepine drug used as hypnotic, tranquilizer and anticonvulsant and has been found at μg L<sup>-1</sup> levels in sewage treatment plant effluents and at 10 ng L<sup>-1</sup> concentrations in river and potable water (Halling-Sorensen et al., 1998). Since to our knowledge no study was carried out so far about degradation of DZP mediated by zero valent iron oxidation, the aim of the present study was to evaluate the efficiency of DZP degradation and the effect of pH, pre-treatment of iron particles, presence of O<sub>2</sub>, iron concentration and EDTA

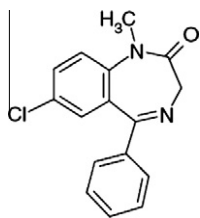


Fig. 1. Chemical structure of diazepam (DZP).

complexation using this new process. Furthermore, the chromatographic profiles of the intermediate compounds were compared to the Fenton process.

## 2. Materials and methods

### 2.1. Reagents

All the solutions were prepared using ultrapure water (Millipore Milli-Q) and analytical grade reagents. Iron powder ( $\text{Fe}^0$ ) (20 mesh 0.85 mm) was purchased from Alfa Aesar. A 0.1 M stock solution of EDTA was prepared by dissolving  $\text{Na}_2\text{H}_2\text{EDTA}$  (Mallinckrodt) in deionized water.  $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$  (Carlo Erba) was used as  $\text{Fe}^{2+}$  source.  $\text{H}_2\text{SO}_4$  and HCl (Synth) were used for  $\text{Fe}^0$  pre-treatment. High performance liquid chromatography (HPLC) grade formic acid and methanol (Tedia Brazil) were used in HPLC analysis. The pharmaceutical diazepam ( $\text{C}_{16}\text{H}_{13}\text{N}_2\text{ClO}$ ) used in the experiments was obtained from a commercial source (99% purity).

### 2.2. Degradation system

$\text{Fe}^0$  was pre-treated with 1.0 M acid solution (HCl or  $\text{H}_2\text{SO}_4$ ) in ultrasound bath for 15 s in order to dissolve surface oxides. The acid was then removed and the  $\text{Fe}^0$  was immediately added to DZP solution, resulting in a pH 2.2. Before start of the reaction, DZP solution ( $25 \text{ mg L}^{-1}$ ;  $88 \mu\text{M}$ ) was bubbled with air or  $\text{N}_2$  for 5 min. The experiments were conducted in a 400 mL glass beaker with mechanical stirring (Fisatom) for vigorous mixing of the suspension to avoid sedimentation of iron particles. The experiments started by adding  $\text{Fe}^0$  and EDTA to DZP solution (200 mL). Different concentrations of  $\text{Fe}^0$  (5, 25, 40  $\text{g L}^{-1}$ ) and EDTA (119, 223  $\text{mg L}^{-1}$ ) were evaluated. Samples were withdrawn at regular intervals, centrifuged at 2000 rpm (Centribio) for 5 min, filtered through 0.45  $\mu\text{m}$  membranes of regenerated cellulose (Sartorius) and immediately analyzed for DZP concentration and DOC.

Fenton experiments were carried out in the dark in a 400 mL glass beaker with mechanical stirring. The pH of DZP solution ( $25 \text{ mg L}^{-1}$ ) was adjusted to 2.5 with  $\text{H}_2\text{SO}_4$  and appropriate volume of  $\text{FeSO}_4$  (to result in 0.1 mM) and  $\text{H}_2\text{O}_2$  (to result in 1.0 mM) were added to start the reaction.

### 2.3. Chemical analysis

DZP concentration during the experiments was determined using reversed phase HPLC analysis in a Shimadzu (LC-20AT) equipment coupled to a photodiode array detector (SPD-M20A) with UV absorption detection at 230 nm wavelength. A C-18 column from Phenomenex, Luna 5  $\mu$  (250 mm  $\times$  4.60 mm) was used and the mobile phase was methanol:water (70:30) at a flow rate of 0.8  $\text{mL min}^{-1}$ .

For the determination of DZP intermediates the samples were extracted using C18 solid phase extraction cartridges, 360 mg from Waters. Methanol (5 mL) was used for cartridges conditioning and elution of the DZP intermediates.

Degradation products of DZP were identified by LC/MS analysis using a nanoUPLC (nanoAcquity, Water) electrospray tandem mass spectrometry on a Q-ToF Ultima mass spectrometer (Waters) equipped with a C18 column (75  $\mu\text{m} \times 100 \text{ mm}$ ) (nanoAcquity UPLC, Waters). The mobile phase used in this case was methanol:water (60:40) containing 0.1% formic acid at a flow rate of 0.6  $\mu\text{L min}^{-1}$ . Ionization was achieved using electrospray ionization in positive mode. The optimum conditions of collision energy and cone voltage were 10 eV and 100 V, respectively. The data acquisition was controlled using MassLynx 4.0.

Mineralization of DZP was evaluated by the decay of DOC concentration, measured using a carbon analyzer (TOC 5000A – Shimadzu).

## 3. Results and discussion

### 3.1. Evaluation of operational parameters of the $\text{Fe}^0/\text{EDTA}/\text{O}_2$ system

$\text{Fe}^0$  particles are readily oxidized in the air generating oxides on the surface that may result in passivation and hinder the degradation reactions. Therefore, to renew the surface, it is necessary to dissolve the superficial oxides, usually made with HCl (Matheson and Tratnyek, 1994). In the present work, particle washing with 1 M HCl was also the first choice for the pre-treatment of iron before using it in the degradation experiments, since this acid dissolves effectively iron oxides. In the experiment carried out without iron pre-treatment ( $25 \text{ g L}^{-1}$ ), DZP oxidation achieved 60% after 60 min reaction but no removal of DOC was observed (Fig. 2). Similar DZP degradation was observed when  $\text{Fe}^0$  was pre-treated with 1 M HCl, 67%. However, mineralization was significantly improved, achieving 60% after 60 min reaction probably due to the renewal of iron surface necessary for the further oxidation of intermediates formed after DZP oxidation.

The electron transfer from  $\text{Fe}^0$  to  $\text{O}_2$  can generate  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ . Thus, the concentration of  $\text{H}_2\text{O}_2$  generated depends on  $\text{Fe}^0$

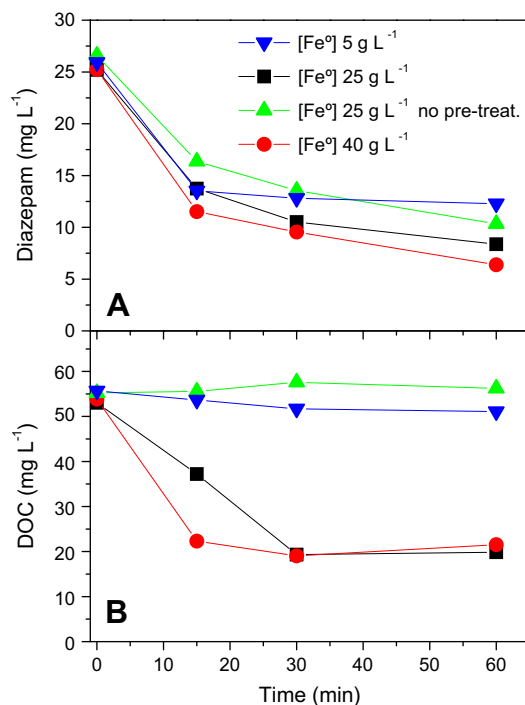
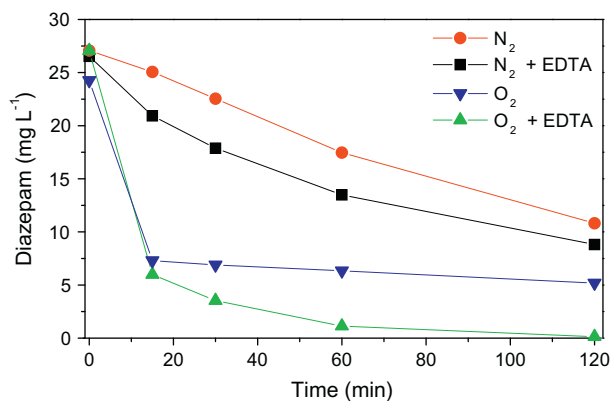


Fig. 2. Influence of the  $\text{Fe}^0$  concentration and pre-treatment on the DZP oxidation (A) and DOC removal (B). Initial concentrations:  $[\text{DZP}] = 25 \text{ mg L}^{-1}$ ;  $[\text{EDTA}] = 119 \text{ mg L}^{-1}$ ; air bubbling;  $\text{Fe}^0$  pre-treatment: HCl 1 M.

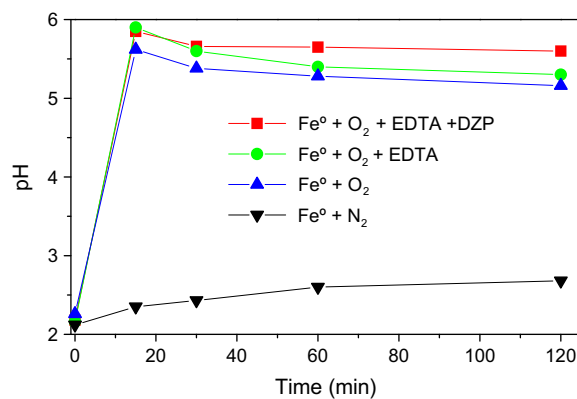


**Fig. 3.** Influence of air or N<sub>2</sub> bubbling on DZP degradation. Initial concentrations: [DZP] = 25 mg L<sup>-1</sup>; [Fe<sup>0</sup>] = 25 g L<sup>-1</sup>; [EDTA] = 119 mg L<sup>-1</sup>. Fe<sup>0</sup> pre-treatment: H<sub>2</sub>SO<sub>4</sub> 1 M.

concentration influencing the rate of Fenton reaction, reason why Fe<sup>0</sup> concentration in the presence of EDTA was evaluated in this work. The lowest Fe<sup>0</sup> concentration evaluated (5 g L<sup>-1</sup>) promoted 50% DZP oxidation while increasing the concentration to 25 and 40 g L<sup>-1</sup> increased slightly DZP oxidation to 67 and 75% after 60 min reaction, respectively (Fig. 2). Although some improvement of DZP oxidation was observed, total oxidation was not achieved even increasing eight times the Fe<sup>0</sup> concentration (5–40 g L<sup>-1</sup>). On the other hand, removal of DOC was considerably improved with increasing Fe<sup>0</sup> concentrations, achieving 60% removal after 30 min using either 25 or 40 g L<sup>-1</sup>, while no removal was observed with 5 g L<sup>-1</sup>. This improvement on DOC removal may be partially due to EDTA adsorption or degradation, since DZP degradation was not significantly improved. The experimental difficulty in evaluating adsorption *versus* oxidation on Fe<sup>0</sup> particles did not allow any conclusion about this effect.

Considering that total oxidation of DZP was not achieved even after increasing the Fe<sup>0</sup> concentration and applying HCl pre-treatment, the substitution of HCl with H<sub>2</sub>SO<sub>4</sub> in the pre-treatment procedure was also evaluated. When H<sub>2</sub>SO<sub>4</sub> was used for the pre-treatment of Fe<sup>0</sup> particles, degradation of DZP was significantly improved compared to HCl treated Fe particles, achieving 96% after 60 min reaction (Fig. 3, green line).<sup>3</sup> Considering that oxygenated Fe<sup>0</sup> reactions may lead to a Fenton process in which ·OH is the oxidizing species and that chloride ions are known to be ·OH scavengers (Kiwu et al., 2000), the H<sub>2</sub>SO<sub>4</sub> appeared to be a better choice for the pre-treatment of Fe<sup>0</sup> particles than HCl and it was used in further experiments. Although sulfate may also interfere in the Fenton process due to coordination of iron(III) (De Laat and Le, 2005) it is not a ·OH scavenger and at low concentrations has little effect on Fenton reaction (Pignatello et al., 2006).

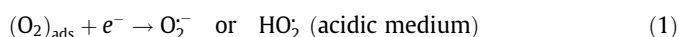
Moreover, it has been observed before that EDTA plays a key role in the Fe<sup>0</sup>/EDTA/O<sub>2</sub> system, by increasing H<sub>2</sub>O<sub>2</sub> generation and consequently improving pollutant degradation (Keenan and Sedlak, 2008b). The presence of O<sub>2</sub> was determinant for DZP degradation since in the presence of O<sub>2</sub> 73% DZP were removed after 15 min, while only 7% removal was observed under N<sub>2</sub> flow after the same time (Fig. 3). These results reinforce that the reductive mechanism in the presence of N<sub>2</sub> leads to a poor degradation in comparison to the oxidative mechanism. The effect of EDTA was more important in the presence of O<sub>2</sub> improving DZP degradation, achieving 99% after 120 min reaction while in the absence of EDTA, DZP degradation was 79% after the same time (Fig. 3). Under N<sub>2</sub>



**Fig. 4.** pH profile during DZP degradation. Initial conditions: [DZP] = 25 mg L<sup>-1</sup>; [Fe<sup>0</sup>] = 25 g L<sup>-1</sup>; [EDTA] = 119 mg L<sup>-1</sup>; Fe<sup>0</sup> pre-treatment: H<sub>2</sub>SO<sub>4</sub> 1 M.

flow, a slight effect of EDTA on DZP degradation rate was observed, achieving 67% removal, similar to the obtained in the absence of EDTA (60%) after 120 min reaction (Fig. 3). These results suggest that the reduction of the target compound may occur on Fe<sup>0</sup> surface without H<sub>2</sub>O<sub>2</sub> formation, leading to no DOC removal.

The role of EDTA in the oxygenated system is related to the formation of Fe<sup>II</sup>EDTA complex after fast oxidation of Fe<sup>0</sup> to Fe(II) and Fe(III). Fe<sup>II</sup>EDTA complex is capable of activating dissolved oxygen, generating reactive oxygen species as O<sub>2</sub><sup>-</sup> or HO<sub>2</sub>, which are postulated to be responsible for H<sub>2</sub>O<sub>2</sub> formation:



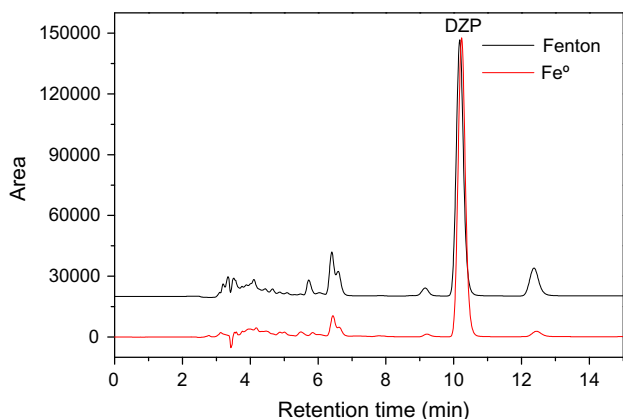
Fe<sup>II</sup>EDTA reacts with H<sub>2</sub>O<sub>2</sub> through a Fenton-like process and promotes a continuous production of H<sub>2</sub>O<sub>2</sub>, leading to fast oxidative degradation of the pollutants. Furthermore, the complexation of Fe(III) with EDTA may enhance Fe(III) solubility preventing coprecipitation of Fe(II) and passivation of Fe<sup>0</sup> surface (Keenan and Sedlak, 2008b; Zhou et al., 2009a). An experiment carried out in the same conditions but with higher EDTA concentration (223 mg L<sup>-1</sup>) resulted in a very similar DZP degradation, indicating that EDTA was not limiting the reaction under these conditions (data not shown).

The efficiency of the contaminant degradation in iron mediated processes is generally strongly affected by pH, as in the case of Fenton reaction in which optimum efficiency is obtained at pH around 3. In the present work, in the beginning of the degradation experiments in both Fe<sup>0</sup> system (presence or absence of O<sub>2</sub>) the pH was 2.2 due to the residual acid used in the Fe<sup>0</sup> pre-treatment. The presence or absence of O<sub>2</sub> directly affected the pH profile during degradation experiments (Fig. 4). In the absence of O<sub>2</sub>, the pH increased slightly from 2.2 to 2.7 as reaction proceeds. Differently, in the presence of O<sub>2</sub> (Fe<sup>0</sup>/EDTA/O<sub>2</sub> system) the pH increased rapidly achieving values close to 6 after the first 10 min reaction, stabilizing at between 5.3 and 5.6 until the end of experiment (120 min) (Fig. 4).

According to previous studies (Matheson and Tratnyek, 1994), in the absence of O<sub>2</sub>, Fe<sup>0</sup> is oxidized to Fe<sup>2+</sup> while H<sup>+</sup> is reduced to H<sub>2</sub> (Eq. (3)). The reduction of H<sub>2</sub>O generates OH<sup>-</sup> according to Eq. (4) contributing to a significant increase of pH to values close to 6, not observed in this work in the absence of O<sub>2</sub>.



<sup>3</sup> For interpretation of color in Fig. 3, the reader is referred to the web version of this article.



**Fig. 5.** HPLC–UV chromatogram of samples obtained in the Fenton process after 2 min of treatment and  $\text{Fe}^0/\text{EDTA}/\text{O}_2$  system after 120 min of treatment. Initial conditions: Fenton -  $[\text{DZP}] = 25 \text{ mg L}^{-1}$ ;  $[\text{FeSO}_4] = 0.10 \text{ mM}$ ;  $[\text{H}_2\text{O}_2] = 1.0 \text{ mM}$ ; pH 2.5.  $\text{Fe}^0/\text{EDTA}/\text{O}_2$  -  $[\text{DZP}] = 25 \text{ mg L}^{-1}$ ;  $[\text{Fe}^0] = 25 \text{ g L}^{-1}$ ;  $[\text{EDTA}] = 119 \text{ mg L}^{-1}$ , air bubbling.

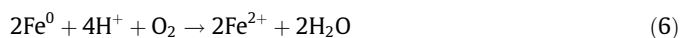
According to Eq. (5),  $\text{Fe}^0$  is also oxidized to  $\text{Fe}^{2+}$  in the presence of  $\text{O}_2$  generating  $\text{OH}^-$  with the same stoichiometry in relation to  $\text{Fe}^0$ .



Considering that in oxic and anoxic medium  $\text{OH}^-$  is generated in the same stoichiometry in relation to  $\text{Fe}^0$ , the lower pH increase in anoxic medium is related to the lower dissolution of iron. The pH stabilization after a sharp initial increase has been attributed by many authors to the formation of organic acids during the degradation of

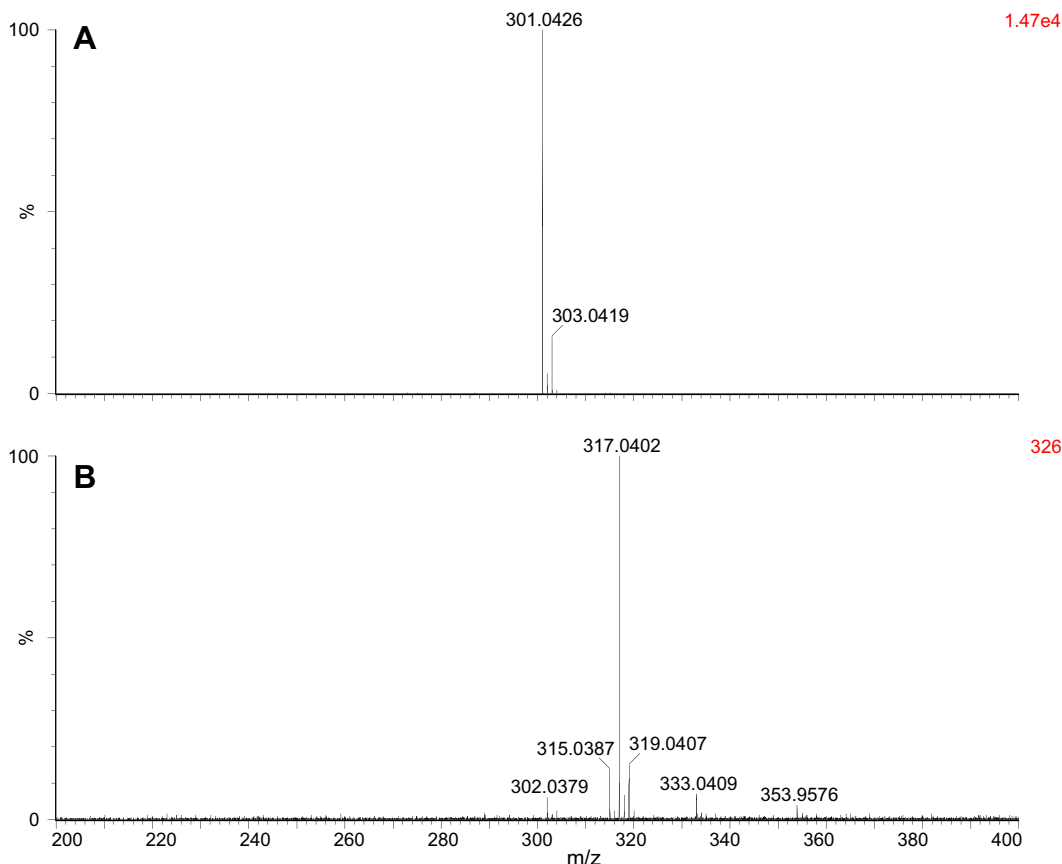
the target compound and EDTA, which prevent the further increase of pH as expected according to reaction 4 (Noradoun et al., 2003; Zhou et al., 2009a). However, the pH profile during  $\text{Fe}^0$  dissolution in the absence of organic compounds was very similar, stabilizing at pH 5.2 (Fig. 4). Therefore, the reason for pH stabilization at 5–6 is a consequence of a balance between  $\text{OH}^-$  generation during  $\text{Fe}^0$  corrosion by water and oxygen (Eq. (5)) and the hydrolysis of ferrous and ferric ions produced by the same process.

To investigate the influence of pH on DZP degradation in the  $\text{Fe}^0/\text{EDTA}/\text{O}_2$  system, an experiment was carried out maintaining the pH  $3.0 \pm 0.5$  with addition of  $\text{H}_2\text{SO}_4$ . DZP oxidation achieved 93% after 60 min treatment, similar to the obtained without pH control, but on the other hand, only 3% DOC was removed after the same time (data not shown). Although  $\text{Fe}^{\text{II}}/\text{EDTA}$  oxidation by molecular oxygen was previously reported to be maximum at pH 2.5–3.0 (Seibig and van Eldik, 1997), the low mineralization obtained in the present work at pH 3 suggests that  $\text{H}_2\text{O}_2$  generated was sufficient for DZP oxidation, but not for DOC removal which was inhibited at pH 3. This occurred probably due to the competition between  $\text{O}_2$  reduction by electron transfer and  $\text{Fe}^0$  corrosion by  $\text{H}^+$  (Eq. (6)), that consumes the iron with no  $\text{H}_2\text{O}_2$  generation.



### 3.2. $\text{Fe}^0$ versus $\text{Fe}^{2+}$ mediated degradation of DZP

Direct generation of  $\text{H}_2\text{O}_2$  may occur as a result of reduction of adsorbed  $\text{O}_2$  on  $\text{Fe}^0$  surface, which is reduced to  $\text{O}_2^-$  or hydroperoxyl radical ( $\text{HO}_2^-$ ) (Eq. (1)). These radicals can recombine and rapidly generate  $\text{H}_2\text{O}_2$  (Joo et al., 2004), leading to a further



**Fig. 6.** Mass spectra of DZP intermediate with  $m/z$  301 (A) and  $m/z$  317 (B) formed during  $\text{Fe}^0/\text{EDTA}/\text{O}_2$  system.



degradation through homogeneous Fenton reaction. Therefore, in order to evaluate if the main role of Fe<sup>0</sup> in the Fe<sup>0</sup>/EDTA/O<sub>2</sub> system was the electron transfer to O<sub>2</sub> and consequently H<sub>2</sub>O<sub>2</sub> generation or only a source of Fe(II) for Fenton like reaction, an experiment was carried out substituting Fe<sup>0</sup> with Fe(II) (FeSO<sub>4</sub>). No degradation of DZP was observed in the presence of FeSO<sub>4</sub>, EDTA and O<sub>2</sub> (data not shown), while in the presence of Fe<sup>0</sup> even at a low concentration (5 g L<sup>-1</sup>) 50% degradation was achieved after 60 min indicating that probably the H<sub>2</sub>O<sub>2</sub> formation through electron transfer from Fe<sup>0</sup> was the main responsible for the degradation process.

The postulated degradation mechanism in Fe<sup>0</sup>/EDTA/O<sub>2</sub> system involves the generation of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> leading to the Fenton process (Keenan and Sedlak, 2008b). Fenton DZP degradation was also carried out in this work in order to compare to Fe<sup>0</sup>/EDTA/O<sub>2</sub> system. The HPLC–UV chromatograms of DZP degradation using both processes showed a very similar pattern, with the generation of a less polar compound with retention time 12.4 min, and at least three other intermediates more polar than DZP (Fig. 5). The DZP degradation by Fenton process was previously evaluated and total oxidation was observed after 30 min treatment (Bautitz and Nogueira, 2010). The Fenton DZP degradation was much faster compared to Fe<sup>0</sup>/EDTA/O<sub>2</sub> system, since after 120 min a significant residual concentration of DZP was detected as shown in HPLC chromatograms (Fig. 5).

Using LC/MS analysis, at least eight DZP intermediates were detected in the Fe<sup>0</sup>/EDTA/O<sub>2</sub> process which corresponded to four structural isomers with a mass to charge ratio (*m/z*) 301 and four structural isomers with *m/z* 317 (Fig. 6). Considering that the pseudo-molecular ion of DZP [M + H]<sup>+</sup> is *m/z* 285, the isomers with *m/z* 301 may correspond to the molecular formula C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>ClO<sub>2</sub> which is consistent with the addition of one hydroxyl radical to different positions in the DZP structure generating monohydroxylated isomers. The isomers with *m/z* 317 may correspond to the molecular formula C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>ClO<sub>3</sub>, consistent with the addition of two hydroxyl radicals to different positions in the DZP structure.

The Fenton like mechanism in Fe<sup>0</sup>/EDTA/O<sub>2</sub> system was also proposed by other authors (Laine et al., 2008; Zhou et al., 2008, 2009b). The results of the present work demonstrated that the oxidizing species formed either in Fenton process or mediated by Fe<sup>0</sup> was the same, once similar intermediates were formed. Besides that, the hydroxylated intermediates indicate that ·OH was the oxidizing specie formed in both processes.

#### 4. Conclusions

The Fe<sup>0</sup>/EDTA/O<sub>2</sub> system promoted significant degradation of DZP (96%) and mineralization (60%) after 60 min when using H<sub>2</sub>SO<sub>4</sub> treated iron particles, denoting the process efficiency for degradation of complex molecules as pharmaceuticals. Degradation process was improved by the increase of iron concentration and the presence of EDTA. Degradation under N<sub>2</sub> flux was also observed, however, at lower extent and without mineralization. According to the results obtained in LC–MS analysis, the degradation of DZP using Fe<sup>0</sup>/EDTA/O<sub>2</sub> system appears to be a Fenton like process since it generated hydroxylated intermediates as a result of ·OH attack to DZP rings. The results shown in this work indicate that the Fe<sup>0</sup>/EDTA/O<sub>2</sub> system may be applied for the degradation of complex molecules as pharmaceutical DZP. However, toxicity evaluation will determine its safe application since total mineralization was not observed.

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