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Photodegradation of lincomycin and diazepam in sewage treatment plant effluent by photo-Fenton process

Ivonete Rossi Bautitz, Raquel F. Pupo Nogueira*

UNESP – Univ Estadual Paulista, Instituto de Química de Araraquara, CP 355, 14801-970, Araraquara, SP, Brazil

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ABSTRACT

First, the effect of ferrioxalate or iron nitrate on the photo-Fenton degradation efficiency of the pharmaceuticals lincomycin (LCM) and diazepam (DZP) was evaluated. The degradation of both pharmaceuticals was improved in the presence of ferrioxalate in relation to $Fe(NO_3)$, either under black-light or solar irradiation. The degradation of the pharmaceuticals was then evaluated when present in an effluent from sewage treatment plant (STP) under black-light irradiation. Pharmaceuticals oxidation was not influenced by the matrix, since very similar results were obtained when compared to the experiments carried out in distilled water. However, DOC removal was slightly affected by the matrix, due probably to the generation of recalcitrant intermediates during effluent photodegradation and to the high content of inorganic carbon of STP effluent. Even so, high DOC removal percentages were achieved, 65% for lincomycin and 80% for diazepam after 60 min irradiation.

1. Introduction

The occurrence of pharmaceuticals in the aquatic environment is frequently reported in the literature. Synthetic hormones, antibiotics, analgesics, anti-inflammatory, lipid regulators, antiepileptics, antihypertensive, as well as some of their metabolites, have been detected around the world at low levels (ng to $\mu g\,L^{-1}$) [1]. However, despite of the low concentrations of the pharmaceutical residues detected in the environment, the lack of knowledge about the possible effects caused by these compounds is the main reason of concern. Generally, pharmaceuticals do not have acute toxic effects on aquatic organisms due to their low concentrations, but often, they may show chronic effects because of their continuous introduction in the environment acting as pseudo-persistent pollutants [2].

The major source of pharmaceuticals present in the environment is the therapeutic treatment of humans and animals. These drugs are metabolized in the body and after partial or complete absorption are excreted as metabolites or original drug. These pharmaceutical residues are directed to the sewage treatment plant (STP) or even discharged in the environment [3]. The occurrence of pharmaceutical residues in the STP effluents shows that treatment plants are not efficient to remove this type of compounds [4]. STPs are designed to treat urban and industrial wastewater and their efficiency is measured by parameters such as particulate matter, phosphate, metal ions, pathogens and nitrogen while micro-pollutants including pharmaceuticals are normally not evaluated.

Advanced oxidation processes (AOPs) have been demonstrated to be innovative and suitable technologies to remove organic compounds because they are able to produce highly oxidizing species such as hydroxyl radicals ($^{\bullet}OH$). Fenton reaction combines H_2O_2 and iron and promote the degradation of different classes of pollutants in a simple process and at mild operation conditions. The use of radiation can increase the efficiency of this process mainly due to regeneration of ferrous ions [5,6]. Besides that, the use of solar radiation decreases considerably the costs of treatment, making the solar photo-Fenton process the most economic AOP alternative [7].

The present work evaluates the photo-Fenton degradation of two pharmaceuticals: lincomycin and diazepam. Lincomycin (LCM) (Fig. 1A) is an antibiotic used in both human and veterinary medicine that inhibits mainly the growth of gram-positive bacteria. A concentration of 30.5 $ng\,L^{-1}$ of this pharmaceutical has been found in STP effluent in Italy [8]. Diazepam (DZP) (Fig. 1B) is the most common benzodiazepine drug used as hypnotic, tranquilizer, anticonvulsant and muscle relaxant and residues of this pharmaceutical were found in STP effluent at 1 $\mu g\,L^{-1}$ and in river and potable water at 10 $ng\,L^{-1}$ [1].

Considering that residues of these pharmaceuticals have been found in STP effluent, the aim of this work was to evaluate the degradation of DZP and LCM by photo-Fenton process in complex and real media such as STP effluent. The choice of iron source (ferrioxalate or $Fe(NO_3)_3$) was based on preliminary experiments carried out in distilled water.

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* Corresponding author. Tel.: +55 16 3301 6606; fax: +55 16 3301 6692.
E-mail address: nogueira@iq.unesp.br (R.F.P. Nogueira).

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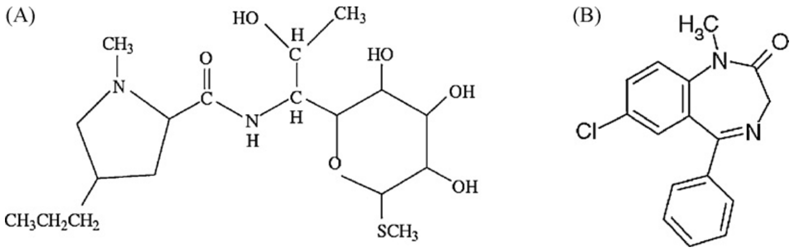

Fig. 1. Chemical structure of lincomycin (A) and diazepam (B).

2. Materials and methods

2.1. Reagents

Unless specified, all the solutions were prepared using ultrapure water (Millipore Milli-Q) and analytical grade reagents. H_2O_2 30% (w/w) (Synth) was used. Potassium ferrioxalate ($K_3Fe(C_2O_4)_3{\cdot}3H_2O$) was prepared and purified as described previously [9] using iron nitrate and potassium oxalate (Mallinkrodt). An aqueous potassium ferrioxalate stock solution was prepared at a concentration of 0.25 M and stored in the dark at room temperature for a maximum of 1 week. Methanol and acetonitrile HPLC grade (Tedia Brazil), and potassium dihydrogenphosphate (KH_2PO_4) were used in HPLC analysis. Lincomycin chloridrate was purchased from Sigma–Aldrich and diazepam was obtained from a commercial source.

2.2. Effluent from sewage treatment plant (STP)

In order to evaluate the pharmaceutical degradation when present in a sewage treatment plant effluent (STP), a sample of STP was collected after complete treatment and kept refrigerated for a maximum of 10 days until the experiments were performed, period that resulted in no significant changes in the sample characteristics in relation to total and inorganic carbon. This STP is based on activated sludge treatment and services a population of approximately 200,000 inhabitants of the city of Araraquara. The main parameters determined for this sample are shown in Table 1.

2.3. Degradation procedures

Experiments were carried out using either black-light or solar radiation. Under black-light, an upflow reactor previously described by Nogueira and Guimarães [10] equipped with a 15 W black-light fluorescent lamp with a maximum emission at 365 nm was used. The irradiated volume of the reactor was 280 mL and a total volume of 500–800 mL of pharmaceutical solution was recirculated at a flow rate of 80 mL min^{-1} using a peristaltic pump (Masterflex 7518-12).

Table 1
Main parameters determined for the sample of sewage treatment plant effluent.

Total carbon (mg L^{-1})[a]	99.6
Inorganic carbon (mg L^{-1})[a]	55.5
Total organic carbon (mg L^{-1})[a]	44.1
pH[a]	6.9
BOD (mg O_2 L^{-1})[b]	64.0
COD (mg O_2 L^{-1})[b]	378
Turbidity (nephelometric units)[b]	385
Dissolved O_2 (mg L^{-1})[b]	0.7
Total chloride (mg L^{-1})[b]	53.0
Nitrate (mg L^{-1})[b]	1.20

[a] Determined in our laboratory.
[b] Obtained from the STP facility.

The reactor used under solar radiation, was composed of a glass tube, placed over a reflective surface fitted at an angle of 22° and at a distance of 3 cm from it, which was previously described by Trovó et al. [11]. The solar energy dose accumulated during the exposure time and the average irradiance were measured using a radiometer (PMA 2100 Solar Light Co.) in the UVA region (320–400 nm) with the sensor placed at the same angle as that of the system.

In both systems, the concentration of the pharmaceuticals LCM and DZP was 25 mg L^{-1} and the sample was recirculated after pH adjustment with H_2SO_4 to 2.5 and addition of appropriate volume of iron and H_2O_2 stock solutions. Given that Brazilian legislation limits the iron concentration for discharge of effluents in 15 mg L^{-1} (0.27 mM), the iron concentration used in all experiments was 0.20 mM (ferrioxalate, $FeSO_4$ or $Fe(NO_3)_3$).

In the experiments carried out to evaluate the influence of iron source and hydrogen peroxide concentration, the pharmaceuticals were dissolved in distilled water. To evaluate matrix effects, the pharmaceuticals were added to STP effluent, which was kept under magnetic stirring over 12 h for total dissolution, before irradiation.

2.4. Chemical analysis

The mineralization of the pharmaceuticals was evaluated by total organic carbon analysis (TOC) (Shimadzu – TOC 5000A) carried out immediately after sample withdrawal to avoid further reaction. During the degradation of the pharmaceuticals present in STP effluent the samples collected were filtered through 0.45 μm membrane before analysis so the dissolved organic carbon (DOC) was determined in this case.

The decay of pharmaceuticals concentration during irradiation was determined using HPLC analysis (Shimadzu LC-20AT) coupled to a DAD detector (SPD-M20A) with a Luna 5 μ C-18 (250 mm × 4.60 mm) column from Phenomenex. The detection was performed by following the UV absorption at 206 and 230 nm, maximum absorption for LCM and DZP respectively. The mobile phase used as eluent was 0.02 M of aqueous solution of potassium dihydrogenphosphate:acetonitrile:methanol (70:15:15) for LCM and methanol:acetonitrile:water (45:25:30) for DZP at a flow rate of 0.8 mL min^{-1} for both pharmaceuticals. The Fenton reaction was stopped by addition of 15 μL of catalase (2 g L^{-1}) for H_2O_2 consumption, after pH adjustment to 7 in order to precipitate the iron. The samples were then filtered through 0.45 μm membranes and kept under refrigeration until the HPLC analysis.

3. Results and discussion

3.1. Influence of iron source on the degradation of lincomycin and diazepam

The iron source has shown to be an important parameter in the photo-Fenton degradation of organic compounds. This is due to possible interactions of the target compound with iron ions, what can hinder or improve the degradation [12]. In most cases, the use of iron complexes such as the carboxilates, ferrioxalate or citrate,

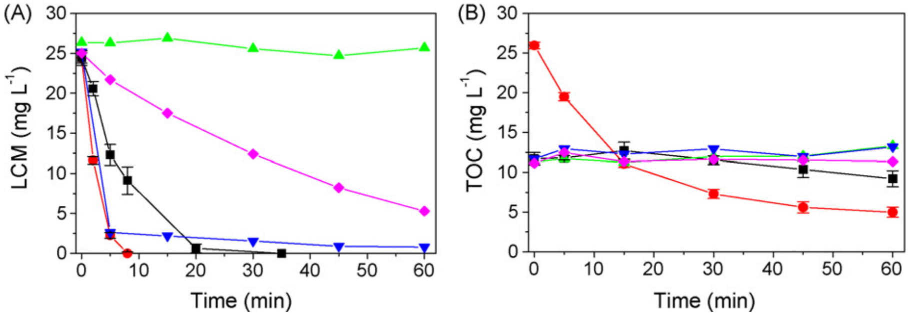

Fig. 2. Influence of the iron source on oxidation of LCM (A) and TOC removal (B) under black-light irradiation. *Experimental conditions*: [LCM] = 25.0 mg L^{-1}; [ferrioxalate] = [$Fe(NO_3)_3$] = [$FeSO_4$] = 0.20 mM; [H_2O_2] = 5.0 mM; (■) $Fe(NO_3)_3$; (—●—) ferrioxalate; (—▲—) LCM photolysis; (—▼—) dark $FeSO_4$; (—◆—) dark $Fe(NO_3)_3$.

improve the degradation efficiency due mainly to the higher quantum yield of Fe(II) generation when compared to the use of Fe^{3+} and also higher absorption of light [13].

In the case of the pharmaceuticals studied in this work, the degradation of both lincomycin and diazepam was improved when ferrioxalate was employed as iron source in comparison to $Fe(NO_3)_3$. After 8 min black-light irradiation, the concentration of lincomycin was already below its detection limit (0.29 mg L^{-1}) in the presence of ferrioxalate, while when using $Fe(NO_3)_3$, 20 min were necessary to achieve the same degradation (Fig. 2A).

When considering TOC results, although a higher carbon content is present when ferrioxalate is used due to the oxalate, lower residual TOC concentration is observed after 60 min irradiation when using ferrioxalate in comparison to $Fe(NO_3)_3$ which removed only 21% of TOC after the same time (Fig. 2B). This behaviour is related to the higher quantum yield of Fe(II) generation in the case of ferrioxalate (1.24 at 300 nm), far above the values for hydroxylated species of iron [13]. In the absence of irradiation, the Fenton process using $FeSO_4$ resulted in similar degradation of lyncomicin as that achieved with ferrioxalate in the first 5 min irradiation. However, the degradation was very slow after this time, indicating that Fe(II) was totally converted to Fe(III), which reaction with H_2O_2 is much slower [5]. The thermal process is much slower when using $Fe(NO_3)_3$, even so it promoted 79% of LCM oxidation after 60 min (Fig. 2A). However, no significant TOC removal was observed in the absence of irradiation using either $FeSO_4$ or $Fe(NO_3)_3$, or during LCM photolysis, indicating the generation of intermediates which were not further degraded under these conditions.

In the case of the pharmaceutical diazepam, although levels bellow detection limit (0.04 mg L^{-1}) were achieved after 20 min with both ferrioxalate and $Fe(NO_3)_3$, the degradation was much faster when ferrioxalate was used (Fig. 3A). The pseudo-first-order kinetic constant of DZP degradation increased about 6.5-fold when replacing $Fe(NO_3)_3$ with ferrioxalate (Table 2). In the case of LCM, however, ferrioxalate improved the degradation in about only 2.5-fold. The much stronger effect of ferrioxalate on degradation rate observed in the case of DZP is possibly related to the chemical structure of DZP, which has two nitrogen atoms with unshared eletron pairs available to complex iron ions reducing its reactivity with H_2O_2 and consequently the generation of $^{\bullet}$OH, as previously reported for the herbicide tebuthiuron [12]. When comparing the degradation rate of LCM and DZP, both in the presence of ferrioxalate, a slightly lower degradation rate is observed in the case of DZP, probably due to the stability of its aromatic rings. In the absence of irradiation, total DZP oxidation was achieved in 30 min using $FeSO_4$ while only 64% oxidation of DZP was achieved after 60 min when using $Fe(NO_3)_3$ due to its slower reaction with H_2O_2. The irradiation of the pharmaceuticals in the absence of iron and H_2O_2 indicated that no significant photolysis of LCM occurs, while in the case of DZP, 23% reduction of its concentration can be attributed to photolysis after 60 min irradiation. This can be attributed to the higher absorption of DZP in the UV region. In relation to mineralization, very similar results were obtained with both iron sources achieving a residual concentration of 3 mg L^{-1} (Fig. 3B).

Table 2
Pseudo-first-order kinetic constants for LCM and DZP degradation under black-light irradiation.

	Distilled water		STP effluent	
	k (min^{-1})	*R*	*k* (min^{-1})	*R*
LCM (FeOx)	0.479	0.995	0.424	0.996
LCM $Fe(NO_3)_3$	0.187	0.991	–	–
DZP (FeOx)	0.391	0.991	0.394	0.994
DZP $Fe(NO_3)_3$	0.060	0.995	–	–

Under solar irradiation, the degradation of LCM and DZP was also improved in the presence of ferrioxalate achieving concentrations

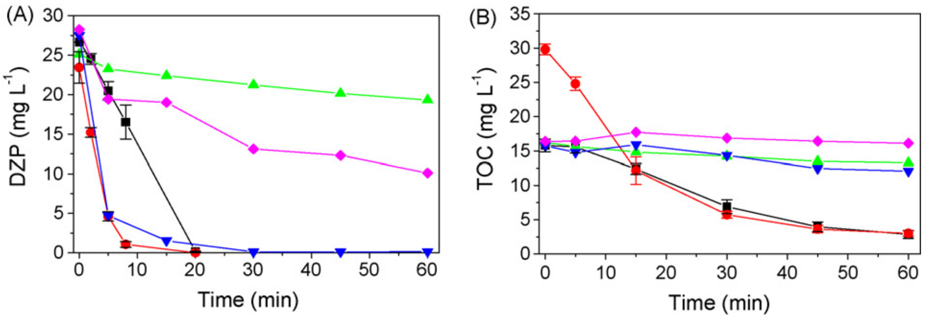

Fig. 3. Influence of the iron source on oxidation of DZP (A) and TOC removal (B) under black-light irradiation. *Experimental conditions*: [DZP] = 25.0 mg L^{-1}; [ferrioxalate] = [$Fe(NO_3)_3$] = [$FeSO_4$] = 0.20 mM; [H_2O_2] = 5.0 mM; (■) $Fe(NO_3)_3$; (—●—) ferrioxalate; (—▲—) DZP photolysis; (—▼—) dark $FeSO_4$; (—◆—) dark $Fe(NO_3)_3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

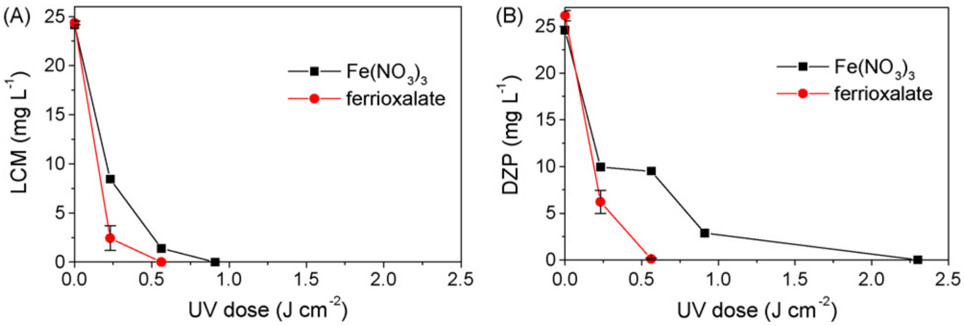

Fig. 4. Influence of the iron source on oxidation of LCM (A) and DZP (B) under solar irradiation. *Experimental conditions*: [DZP] = [LCM] = 25.0 mg L^{-1}; [ferrioxalate] = [Fe(NO$_3$)$_3$] = 0.20 mM; [H_2O_2] = 5.0 mM.

below detection limits after 0.56 J cm^{-2} UV dose, what corresponds to about 5 min solar irradiation (Fig. 4).

Considering that higher degradation rates were observed with ferrioxalate, further experiments were carried out with this iron source.

3.2. *Influence of H_2O_2 concentration on the degradation of lincomycin and diazepam*

The initial concentration of hydrogen peroxide plays an important role in the oxidation of organic compound in photo-Fenton process. The degradation efficiency may be limited either with low or excess of H_2O_2. In this work, three H_2O_2 concentrations were evaluated for the degradation of the pharmaceuticals in the presence of 0.20 mM ferrioxalate, 1.0, 5.0 and 10 mM, which correspond to the molar ratios Fe:H_2O_2 1:5, 1:25, 1:50, respectively. LCM and DZP were fastly oxidized in the presence of the three H_2O_2 concentrations. Both LCM and DZP were already below detection limits after 8 min irradiation. However, then using 1.0 mM TOC removal from DZP was only 73% after 60 min while 5.0 and 10.0 mM H_2O_2 removed 90% after the same time (Fig. 5). The same behavior was observed for LCM, reason why 5 mM H_2O_2 were used in further experiments for both pharmaceuticals.

It is interesting to note that 50% TOC removal was achieved in the absence of H_2O_2 during DZP degradation after 60 min, probably due to the generation of hydroxyl radicals through iron complexes photolysis [14], besides of DZP photolysis, as previously discussed.

3.3. *Influence of sewage treatment plant effluent on the degradation of lincomycin and diazepam*

The constituents of a matrix can influence the degradation of target compounds during the photo-Fenton process. Either the organic matter or inorganic species, such as carbonate (Eqs. (1) and (2)) [15] and chloride ions (Eq. (3)) [16], may contribute to hydroxyl radical scavenging and consequently hinder the overall efficiency of degradation of the target compound:

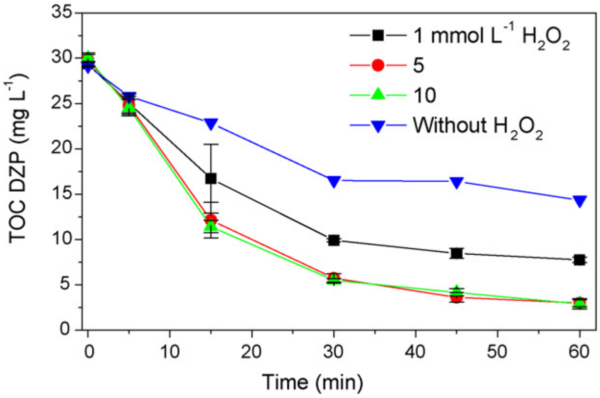

Fig. 5. Influence of H_2O_2 concentration on TOC removal of DZP under black-light irradiation. *Experimental conditions*: [DZP] = 25.0 mg L^{-1}; [ferrioxalate] = 0.20 mM.

$$HO^{\bullet} + HCO_3{}^{-} \rightarrow H_2O + CO_3{}^{\bullet -} \quad (1)$$

$$HO^{\bullet} + CO_3{}^{2-} \rightarrow HO^{-} + CO_3{}^{\bullet -} \quad (2)$$

$$HO^{\bullet} + Cl^{-} \rightleftarrows HOCl^{\bullet -} \overset{H^{+}(-H_2O)}{\rightleftarrows} Cl^{\bullet} \overset{Cl^{-}}{\rightleftarrows} Cl_2{}^{\bullet -} \quad (3)$$

The degradation of pharmaceuticals can be differently affected by the STP. Previous work has demonstrated that photo-Fenton degradation of the antibiotic tetracycline can be significantly hindered when present in STP effluent [17]. However, no detrimental effect of STP effluent was observed in the case of the antibiotic amoxicillin and the analgesic paracetamol in comparison to the removal obtained in distilled water under black-light irradiation [11].

In the present work, the influence of STP on LCM and DZP degradation was evaluated comparing the results obtained in

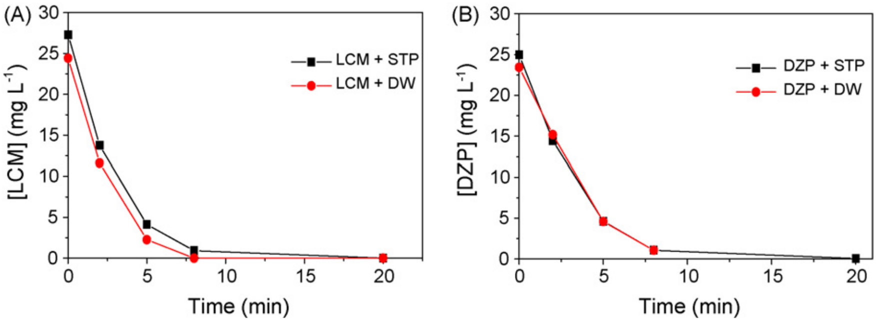

Fig. 6. Oxidation of LCM (A) and DZP (B) in distilled water (DW) and STP effluent (STP) under black-light irradiation. *Experimental conditions*: [DZP] = [LCM] = 25.0 mg L^{-1}; [ferrioxalate] = 0.20 mM; [H_2O_2] = 5.0 mM.

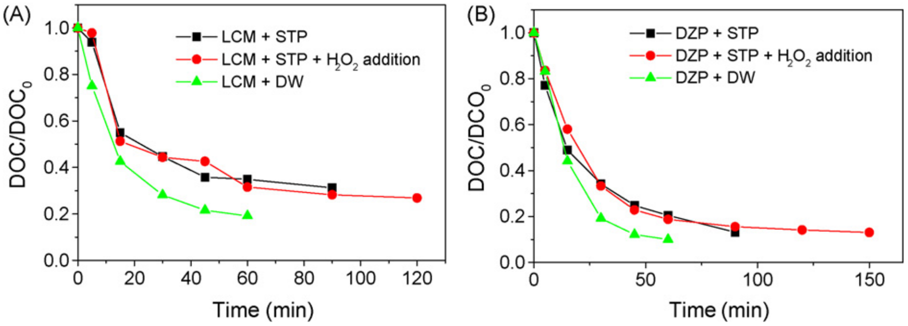

Fig. 7. DOC removal during LCM (A) and DZP degradation (B) in distilled water (DW) and STP effluent (STP) under black-light irradiation. *Experimental conditions*: [DZP] = [LCM] = 25.0 mg L^{-1}; [ferrioxalate] = 0.20 mM; [H_2O_2] = 5.0 mM; H_2O_2 addition: 1.23 × 10^{-3} mol in 30 min. DOC [LCM] = 12 mg L^{-1}; DOC [LCM + STP] = 56 mg L^{-1}.

experiments carried out in STP effluent to those obtained in distilled water, both using ferrioxalate as iron source. No significant difference in the oxidation of LCM and DZP was observed when these pharmaceuticals were present in STP effluent in comparison to the experiments carried out in distilled water (Fig. 6), since very similar degradation kinetic rate constants were observed (Table 2).

In relation to the DOC removal, a slightly lower rate of DOC removal for LCM in the presence of STP effluent was observed already at the beginning of the reaction in relation to DW achieving 80% after 60 min, while in STP effluent this percentage was 65% even with fresh H_2O_2 additions (Fig. 7A).

In the case of DZP, similar removal rate was observed in the first 15 min irradiation (Fig. 7B) in the presence of DW or STP effluent. However, after this time, lower degradation rate is observed in the presence of STP effluent, probably due to the higher DOC content of the STP sample, achieving 90% in DW and 80% removal in STP effluent after 60 min irradiation. In order to attempt an improvement in the DOC removal, further additions of H_2O_2 were made, but no significant improvement of DOC removal was observed.

The residual DOC concentration either in DZP (10 mg L^{-1}) or in LCM degradation (17 mg L^{-1}) in STP effluent can be due to recalcitrant compounds present in this matrix. In order to verify this hypothesis, an experiment was carried out only to evaluate STP effluent mineralization using the same concentrations of H_2O_2 and ferrioxalate. Fig. 8 shows that only 50% of DOC concentration was removed after 90 min treatment, what suggests that recalcitrant compounds were formed.

Considering that the concentration of inorganic carbon in STP effluent is relatively high, even higher than organic carbon, and that carbonates can scavenger hydroxyl radicals, another experiment was carried out in the absence of inorganic carbon with the attempt to increase the DOC removal. The STP effluent was stirred after pH adjustment to 2.5, until complete inorganic carbon removal. However, the gain in DOC removal was only 16% after 90 min of treatment, what confirms that besides of the scavenging of hydroxyl radicals by inorganic carbon, recalcitrant intermediates from STP effluent may be formed during this process. Considering that the STP effluent contributes to an initial organic load of 44 mg C L^{-1}, considerably higher than the organic content of the two pharmaceuticals (12 and 16 mg L^{-1}), these results suggest that the recalcitrant compounds are not products from the target compounds but generated from the STP effluent.

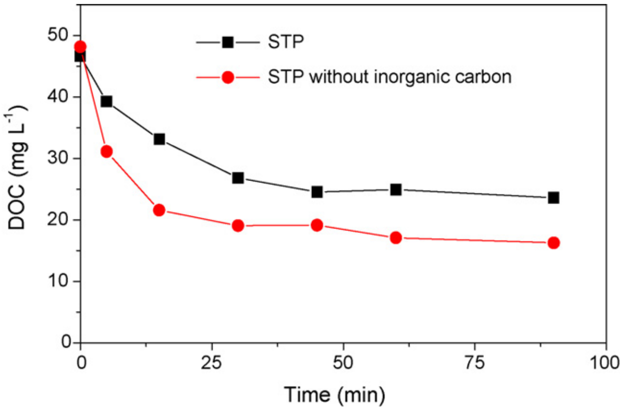

Fig. 8. DOC removal in STP degradation under black-light irradiation. *Experimental conditions*: [STP] = 44.0 mg L^{-1} C; [ferrioxalate] = 0.20 mM; [H_2O_2] = 5.0 mM.

Although chloride ions may also scavenge hydroxyl radicals (Eq. (3)), the low concentration in the STP sample (~1.5 mM) suggests that it does not interfere in the degradation process since significant detrimental effect is usually observed above 100 mM [15].

The great advantage of the photo-Fenton process besides the simplicity of operation is the possibility of using solar radiation as irradiation source. The use of solar radiation reduces considerably the costs of the process, especially for the treatment of high volumes such as effluents from STPs. Many studies have demonstrated the high efficiency of ferrioxalate when using solar radiation, which is mainly related to its high absorption in the UV–vis region and its high quantum yield of Fe(II) generation [13]. Therefore, the DZP degradation in STP effluent was evaluated under solar radiation in the same experimental conditions and the results obtained were very similar to the results obtained under black-light irradiation (data not shown) achieving a residual organic carbon concentration of 13 mg L^{-1}. These results indicate that the process may also be performed using solar radiation what decreases considerably the treatment costs.

4. Conclusions

The photo-Fenton degradation of LCM and DZP was improved in the presence of ferrioxalate in comparison to $Fe(NO_3)_3$, resulting in complete oxidation of both pharmaceuticals in few minutes. The STP effluent did not interfere significantly in the initial oxidation of the pharmaceuticals. However, DOC removal during LCM and DZP degradation was slightly affected by the matrix due probably to the formation of recalcitrant compounds from STP effluent and the presence of inorganic carbon. Even though, significant DOC removal percentages were obtained, 65% for LCM and 80% for DZP after 60 min reaction.

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