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

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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.

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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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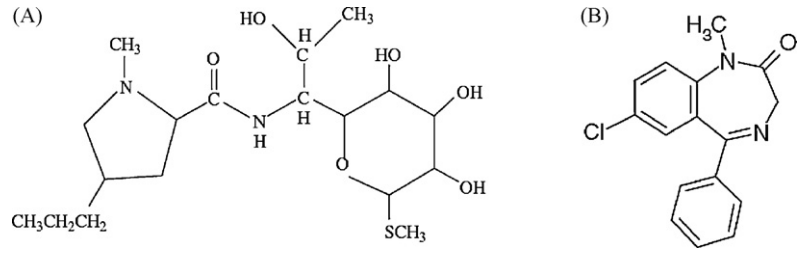

Fig. 1. Chemical structure of lincomycin (A) and diazepam (B).

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,

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