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Photodegradation of the pharmaceuticals amoxicillin, bezafibrate and paracetamol by the photo-Fenton process—Application to sewage treatment plant effluent

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ABSTRACT

Photodegradation of the pharmaceuticals amoxicillin (AMX), bezafibrate (BZF) and paracetamol (PCT) in aqueous solutions via the photo-Fenton process was investigated under black-light and solar irradiation. The influences of iron source, initial H_2O_2 concentration and matrix (distilled water and sewage treatment plant effluent) on degradation efficiency were discussed in detail. The results showed that (i) the degradation of the drugs was favored in the presence of potassium ferrioxalate (FeOx) in comparison to $Fe(NO_3)_3$; (ii) the increase of the H_2O_2 concentration improved the efficiency of AMX and BZF oxidation; however, the same was not observed for PCT; (iii) the influence of the matrix was observed for the degradation of BZF and PCT; (iv) under solar irradiation, the oxidation of the BZF and PCT is faster than under black-light irradiation. All these pharmaceuticals can be efficiently degraded employing the process evaluated.

1. Introduction

Pharmaceutical substances and personal-care products have recently been recognized as an important class of organic pollutants due to their physical–chemical properties, which allow their persistence and bioaccumulation in the environment provoking negative effects in aquatic or terrestrial ecosystems in concentration down to a few nanograms per liter [1–3].

Many studies have reported a large number of pharmaceuticals such as anti-inflammatories, analgesics, betablockers, lipid regulators, antibiotics, anti-epileptics and estrogens at average concentrations of $<10\,\mu g\,L^{-1}$ in sewage treatment plant (STP) effluents, surface and groundwater and even in drinking water [4–9], indicating their poor degradability in a municipal STP [5,8,9]. A major concern about pharmaceuticals has been focused on antibiotics, which may promote resistance in natural bacterial populations, and on steroids, which may induce estrogenic responses as well as alterations in reproduction or the development of aquatic organisms [1,2,10,11].

Municipal wastewater is the main disposal route of pharmaceuticals into the environment. Nevertheless, other different sources of pharmaceutical release can be proposed to explain the appearance of these xenobiotics in waters and soils, such as inadequate treatment of manufacturing waste, direct disposal of unconsumed drugs in households and the use of manure for top soil dressing [1,4,5,10]. Since they are being continuously introduced into the environment, they are considered as “pseudo-persistent compounds” [3].

In wastewater treatment, two elimination processes are generally important: adsorption onto suspended solids (sewage sludge) and biodegradation. Adsorption depends on both hydrophobic and electrostatic interactions of pharmaceuticals with particulates and microorganisms. Although adopted as the best available technology, some studies have demonstrated that most pharmaceuticals are only partially removed by biological treatment, thus resulting in contamination of surface and groundwater [5,8,9,11]. The concern regarding water contamination and consequent human exposure to it has stimulated the development of methods capable of removing pharmaceutical residues efficiently. Based on this need, the advanced oxidation processes (AOP) have been investigated, due to their potential as alternatives or as a complement to conventional wastewater treatment, since the hydroxyl radicals generated from these processes are highly reactive and efficient in oxidizing a great variety of organic contaminants, including xenobiotics and micropollutants [12–19].

The Fenton process has attracted great interest due to its high efficiency in generating hydroxyl radicals during H_2O_2 decomposition by Fe(II) (Eq. (1)). By employing UV–vis irradiation (photo-Fenton process), the oxidation power is increased mainly due to the photoreduction of Fe(III) to Fe(II), which can react with

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H_2O_2 establishing a cycle, besides generating additional hydroxyl radicals (Eq. (2)). In addition, it is possible to use solar irradiation, eliminating the cost of UV irradiation [20].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (2)$$

The use of ferrioxalate (FeOx) in the photo-Fenton process for the degradation of organic pollutants was first reported by Safarzadeh-Amiri et al. [21]. Ferrioxalate is highly suitable for solar applications since it absorbs strongly between 250 and 500 nm and has a high quantum efficiency of Fe(II) generation ($\Phi_{Fe(II)} = 1.24$ at 300 nm) [22]. The Fe(III)–polycarboxylate complexes undergo rapid photochemical reaction under irradiation generating Fe(II) in the following equations [23]:

$$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4{}^{2-} + C_2O_4{}^{\bullet -} \quad (3)$$

$$[Fe(C_2O_4)_3]^{3-} + C_2O_4{}^{\bullet -} \rightarrow Fe^{2+} + 3C_2O_4{}^{2-} + 2CO_2 \quad (4)$$

$$C_2O_4{}^{\bullet -} + O_2 \rightarrow O_2{}^{\bullet -} + 2CO_2 \quad (5)$$

In the present work, the photo-Fenton degradation of amoxicillin (AMX) (antibiotic), bezafibrate (BZF) (lipid regulator) and paracetamol (PCT) (analgesic, antipyretic and anti-inflammatory) was investigated under black-light and solar irradiation, using different iron sources and initial H_2O_2 concentrations in both distilled water (DW) and STP effluent.

2. Materials and methods

2.1. Reagents

All the solutions were prepared using Millipore Milli-Q water and analytical grade reagents. $Fe(NO_3)_3{\cdot}9H_2O$ (Mallinckrodt) was used to prepare aqueous 0.25 M iron stock solution. Potassium ferrioxalate ($K_3Fe(C_2O_4)_3{\cdot}3H_2O$) was prepared and purified as described previously [22] using iron nitrate and potassium oxalate (Mallinckrodt). An aqueous potassium ferrioxalate (FeOx) stock solution was prepared at a concentration of 0.25 M and stored in the dark at room temperature for a maximum period of 1 week. H_2O_2 30% (w/w) (Synth) was used. H_2SO_4 was used for pH adjustment. Ammonium metavanadate (Vetec) solution was prepared at a concentration of 0.060 M in 0.36 M H_2SO_4. Hydrochloric acid, acetic acid (Synth), sodium acetate (Mallinckrodt), and HPLC grade methanol (Baker) were used for the HPLC analysis. The AMX, BZF and PCT (Fig. 1) used in the photodegradation experiments were obtained from a commercial source (All Chemistry) and the commercial products AMX, BZF and PCT were used as received. Analytical grade AMX and PCT (Sigma–Aldrich) were used to construct HPLC analytical curves for the determination and quantification of these pharmaceuticals.

2.2. Effluent from STP

In order to evaluate matrix effects on AMX, BZF and PCT degradation, a sample of STP effluent was collected in October 2006. This STP is based on activated sludge treatment and serves a population of almost 200,000 inhabitants in the city of Araraquara, Brazil. The sample was collected after a complete treatment and kept refrigerated for a maximum of 2 weeks until the experiments were performed, period that resulted in no significant changes in the sample characteristics in relation to total and inorganic carbon. The appropriate volume of AMX and PCT stock solution was added in separated STP samples. The STP sample was filtered though a 0.45-μm membrane only before the chemicals analysis. In the case of BZF, the same was not possible because of its low solubility in water. Therefore, it was added in excess and the sample was kept under stirring for 1 h and the suspension was filtered through a 0.45 μm membrane. The pH was adjusted to 2.5, i.e. the optimum pH value according to Nogueira and Guimarães [24], and the samples were irradiated under a black-light lamp or solar light after the addition of appropriate amounts of iron and H_2O_2.

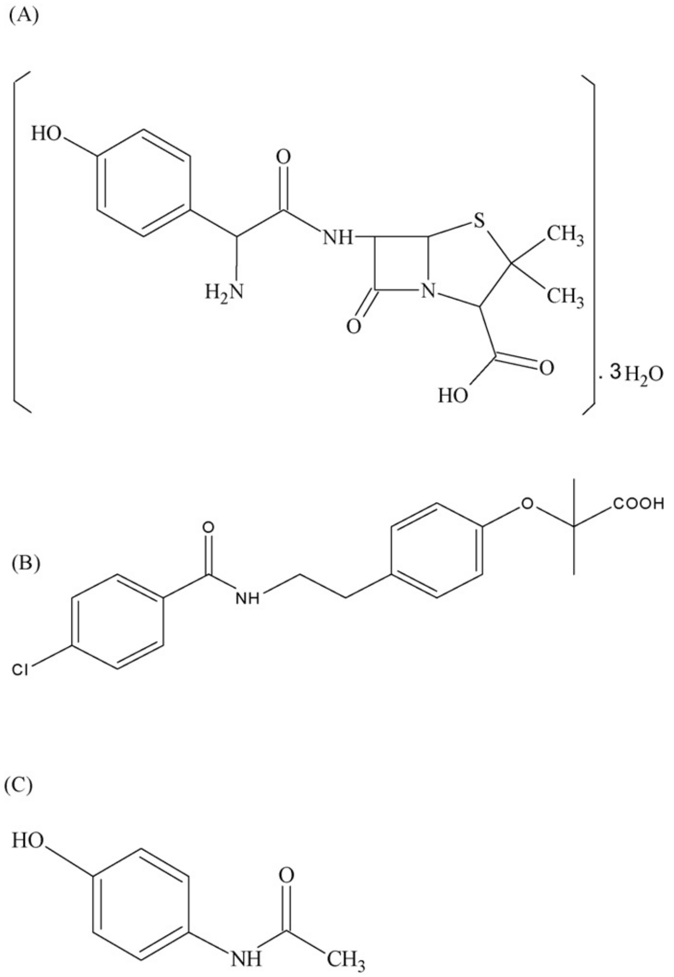

Fig. 1. Chemical structure of (A) amoxicillin trihydrate, (B) bezafibrate and (C) paracetamol.

2.3. Photodegradation procedures

2.3.1. Black-light irradiation

The experiments using black-light irradiation were carried out in an upflow photoreactor constructed using a glass cylinder of 3.8 cm internal diameter and 42 cm height, previously described by Nogueira and Guimarães [24]. The irradiation source was a 15-W black-light fluorescent lamp with a maximum emission at 365 nm, which served as the inner surface of the annulus. The irradiance of the lamp, measured using a radiometer (PMA 2100 Solar Light Co.) in the UVA region (320–400 nm) was 29 W m^{-2}. The irradiated volume of the reactor was 280 mL and a total volume of 800 mL of the pharmaceutical solution was recirculated at a flow rate of 80 mL min^{-1} using a peristaltic pump (Masterflex 7518-12) after the addition of iron solution, the adjustment of the pH and the addition of H_2O_2. The lamp was only turned on when the reactor was completely filled with the solution.

The initial concentration of AMX and PCT for all experiments was 0.1 mM. In the case of BZF, the concentration was 0.055 mM,

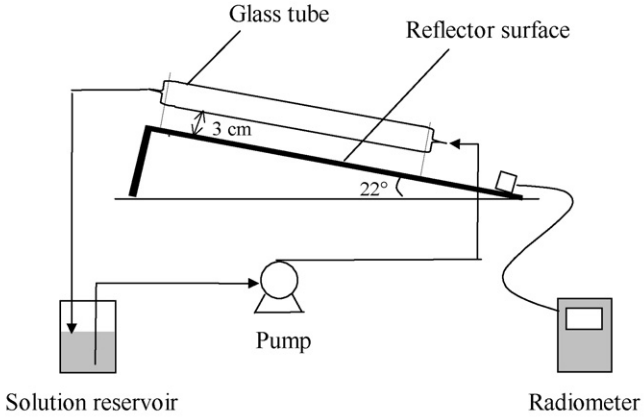

Fig. 2. Schematic representation of photodegradation system (side view).

due to its low solubility in water. These concentrations are equivalent to 42 mg L^{-1} (19 mg L^{-1} total organic carbon (TOC)) for AMX, 15 mg L^{-1} (10 mg L^{-1} TOC) for PCT and 20 mg L^{-1} (13 mg L^{-1} TOC) for BZF. Although the concentrations of the pharmaceuticals found in aquatic environments are lower than these values, these concentrations were chosen due to the difficulty in working at trace levels with HPLC-UV and to allow AMX, BZF and PCT quantification during irradiation, since the limit of quantification found for the determination of these compounds was 1.25, 0.97 and 0.064 mg L^{-1}, respectively. Besides of analytical reasons, it is expected that at lower concentrations, higher degradation percentages can be obtained for the same concentrations of Fe and H_2O_2 due to the reduction of organic matter content.

Considering the maximum concentration of iron allowed in wastewater by Brazilian legislation (15 mg L^{-1} or 0.27 mmol L^{-1}) and to avoid iron precipitation, the experiments were performed at a concentration of 0.2 mmol L^{-1} of ferric nitrate or FeOx. The initial H_2O_2 concentration ranged from 1.0 to 10.0 mmol L^{-1}.

2.3.2. Solar irradiation

The photodegradation experiments were carried out in Araraquara, Brazil (22°S 48°W) using a solar reactor composed of a glass tube with an internal diameter of 3.6 and 49.5 cm long and a capacity of 510 mL placed over a reflective surface fitted at an angle of 22° and at a distance of 3 cm from it (Fig. 2). The experiments were performed during spring and summer between 10 a.m. and 2 p.m.

As described before for the black-light irradiation, 800 mL of the solution were pumped to the solar reactor after adding iron solution, adjusting the pH and adding an appropriate volume of H_2O_2. The reactor remained covered while the glass tube was being filled. Once the tube was completely filled, it was exposed to the sunlight. 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. The average irradiance measured during the experiments was 20 W m^{-2}.

It is important to mention that the time shown in the *x*-axis of the plots corresponds to the irradiation time, which differs from the total experiment time, since the volumes of the reactor and the solution are not same in the experiments using black-light lamp and solar irradiation. The irradiation time was calculated according to the following equation:

$$t_{\text{irradiation}} = t_{\text{total}} \times \left(\frac{V_{\text{reactor}}}{V_{\text{total}}}\right) \qquad (6)$$

where t is the time in min and V is the volume in mL.

2.4. Chemical analysis

The mineralization of the pharmaceutical solutions during the experiments was evaluated by measuring the decay of the TOC using a carbon analyzer (TOC 5000A: Shimadzu). The TOC concentration includes the carbon content of the target compound, intermediates generated during the experiments, oxalate when ferrioxalate was used and also natural organic matter, in the case of STP effluent. The samples of STP wastewater were filtered through 0.45 μm membranes prior to analysis so that only the dissolved organic carbon (DOC) was determined. The TOC analysis was always performed immediately after the sample withdrawn.

The concentration of AMX, BZF and PCT was monitored during the experiments using reversed phase HPLC (Shimadzu SCL-10Avp) with a diode array detector (SPD-M10Avp) and a C-18 column (Luna 5 μm, 250 × 4.60 mm from Phenomenex). The elution was performed with 0.01 M sodium acetate (pH 4.0) and methanol (95:5) for AMX, 0.09 M acetic acid and methanol (30:70) for BZF and 3 mM HCl and methanol (87:13) for PCT, at a flow rate of 1 mL min^{-1}. The wavelengths of 274, 228 and 242 nm were used to monitor the degradation of AMX, BZF and PCT, respectively.

The compounds were firstly extracted from aqueous samples using solid phase extraction cartridges, Sep-Pack C-18 360 mg (AMX and PCT) and Oasis HLB 60 mg (BZF), both previously conditioned with methanol and water. The samples were withdrawn and immediately applied to the cartridges to extract the organic compounds and discard the aqueous phase containing iron and residual hydrogen peroxide in order to interrupt the reaction and allow for the storage of the sample for further analysis. After extraction, the cartridges were eluted with methanol (PCT and BZF) and distilled water (AMX). The recovery percentages, in three concentration levels, ranged from 80 to 108% for AMX (2.19–438.5 mg L^{-1}), from 78 to 98% for BZF (5.0–20.0 mg L^{-1}) and from 97 to 110% for PCT (0.181–181.2 mg L^{-1}). These results include the tests undertaken in the presence and absence of FeOx.

The residual hydrogen peroxide left over from degradation of the pharmaceuticals was measured during the experiments using the spectrophotometric method employing ammonium metavanadate (Shimadzu mini-1240 UV spectrophotometer) as described by Nogueira et al. [25].

3. Results and discussion

3.1. Influence of the iron source and H_2O_2 concentration on the degradation of AMX, BZF and PCT

Previous works have demonstrated that the iron source can influence considerably the degradation of different compounds [26–28]. Nogueira et al. [26] evaluated the photo-Fenton degradation efficiency of different classes of organic compounds in the presence of $Fe(NO_3)_3$ and FeOx, under solar irradiation. While the 4-chlorophenol degradation was favored by using $Fe(NO_3)_3$, the degradation of formaldehyde, dichloroacetic acid and the herbicides diuron and tebuthiuron was more efficient when FeOx was used.

In order to evaluate the influence of the iron source (FeOx or $Fe(NO_3)_3$) on the photo-Fenton degradation of pharmaceuticals, a series of experiments was carried out to compare their oxidation using fixed concentrations of iron (0.20 mM) and H_2O_2 under black-light irradiation for AMX and PCT and solar irradiation for BZF. It is important to mention that no photolysis of the pharmaceuticals was observed either under black-light or solar irradiation in the absence of iron and H_2O_2 due to the lack of absorption of the three pharmaceuticals above 300 nm, where solar and black-light emissions start to be significant.

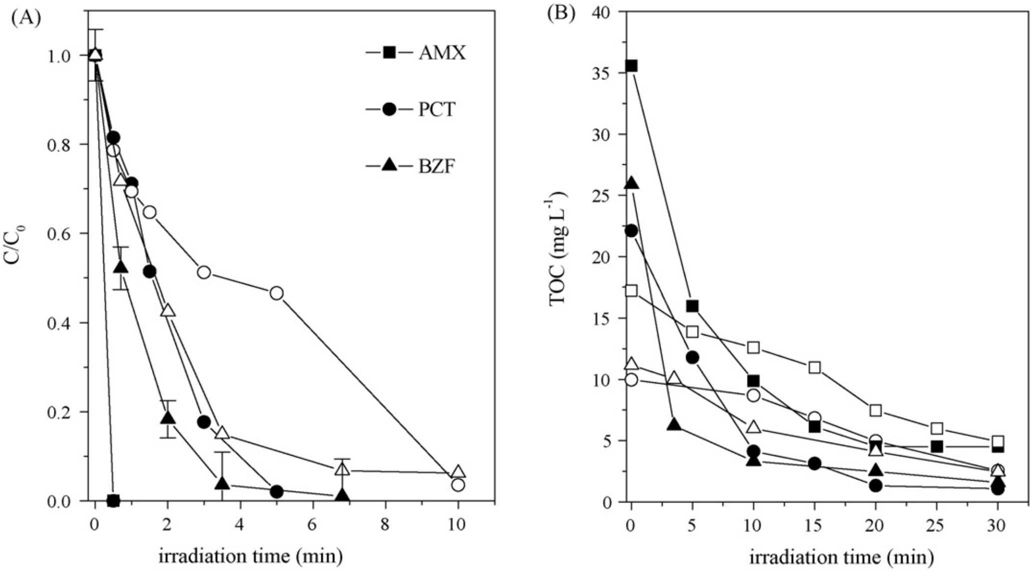

Fig. 3. Influence of the iron source on the (A) oxidation and (B) mineralization of AMX, PCT (black-light irradiation) and BZF (solar irradiation). Initial concentrations: [AMX] = 42 mg L^{-1} = 19 mg L^{-1} TOC; [PCT] = 15 mg L^{-1} = 10 mg L^{-1} TOC; [BZF] = 20 mg L^{-1} = 13 mg L^{-1} TOC; [FeOx] = [Fe(NO$_3$)$_3$] = 0.20 mM; [H_2O_2] = 5.0 mM; pH 2.5. FeOx (solid symbols) and Fe(NO$_3$)$_3$ (open symbols). Typical standard deviations are shown.

The results displayed in Fig. 3 shows that the photodegradation of BZF and PCT was influenced by the iron source. For both pharmaceuticals, the degradation is favored when FeOx is used (Fig. 3A). A removal of 98% for BZF and PCT was achieved after 5 min irradiation as opposed to using Fe(NO$_3$)$_3$ where 89 and 53% of the initial concentration of these compounds were removed after the same irradiation times. On the other hand, no difference was observed for the oxidation of AMX, for which total degradation was reached for both iron sources after 0.5 min of irradiation time. Therefore, this experiment was repeated increasing the initial concentration of AMX to 210 mg L^{-1} under solar irradiation. From the results of the AMX degradation under this condition, it was observed that AMX degradation is favored in the presence of FeOx, reaching 84% of oxidation after 1 min while 62% was observed using Fe(NO$_3$)$_3$ (data not shown).

It was observed that the TOC removal rate was higher when using FeOx for all target compounds (Fig. 3B). However after 30 min, both iron sources reached the same result. Although the presence of FeOx contributes to the organic matter content (14 mg L^{-1} of carbon), a control experiment demonstrated that it was completely mineralized after 20 min of irradiation.

The high efficiency of FeOx in degrading the pharmaceuticals can be attributed to its high quantum yield of Fe(II) generation, besides the radicals formed during its photolysis (Eqs. (3)–(5)) which can enhance the oxidative process. Zhou et al. [27] observed the same behavior during the photo-oxidation of the synthetic estrogen diethylstilbestrol and related that the production rate of hydroxyl radicals by the photolysis of Fe(III)–oxalate complex system is higher than that of the Fe(III)–OH complex system.

The influence of the initial H_2O_2 concentration on the degradation of the pharmaceuticals was further studied in the presence of FeOx using black-light irradiation for AMX and PCT and solar irradiation for BZF, since this iron source gave better results. The hydrogen peroxide concentration ranged from 1.0 to 5.0 mM for the AMX and PCT experiments and from 3.0 to 10.0 mM for BZF. The first-order kinetic constants for the degradation of all the pharmaceuticals are presented in Table 1. The results demonstrated that when the initial H_2O_2 concentration increased from 1.0 to 2.0 mM, the degradation constant of AMX increased more than two times, from 0.91 to 2.0 min^{-1}. It was not possible to calculate the degradation constant for the experiment using 5.0 mM H_2O_2, as after 0.5 min, the AMX concentration was lower than its limit of quantification (1.25 mg L^{-1}). In the case of BZF, when the H_2O_2 concentration was increased within the range of 3.0–10.0 mM, the degradation constant increased from 0.61 to 1.5 min^{-1}.

The same was not observed for PCT, which degradation kinetics was independent from the initial concentration of the H_2O_2 within the range of 1.0–5.0 mM. A comparison of the degradation of the pharmaceuticals under the same experimental conditions showed that PCT was the one that presented lowest degradation constants, suggesting that PCT is more recalcitrant than AMX and BZF.

When considering TOC removal, increasing the initial H_2O_2 concentration from 1.0 to 2.0 mM, the AMX mineralization efficiency increased from 67 to 85% (data not shown). Increasing to 5.0 mM H_2O_2, no considerable improvement was obtained, reaching 87% TOC removal after 30 min of irradiation, which suggests that 1.0 mM is not sufficient to promote the same degree of mineralization as with 2.0 mM, due to the total consumption of the H_2O_2 in 5 min, while for 2.0 mM H_2O_2, total consumption was reached only after 15 min. For BZF and PCT, TOC removal was not influenced by the initial concentration of the H_2O_2 in the range studied.

3.2. Matrix effects on AMX, BZF and PCT degradation in the photo-Fenton process under black-light and solar irradiation

Degradation processes are developed aiming their potential application at eliminating the target compound from environmental matrixes. In the case of pharmaceuticals, which are found in STP

Table 1
Influence of initial H_2O_2 concentration on the degradation rate constant of the pharmaceuticals AMX, BZF and PCT using 0.20 mM FeOx

Initial H_2O_2 concentration (mmol L^{-1})	k (min^{-1})		
	AMX	BZF	PCT
1.0	0.91	–	0.60
2.0	2.0	–	0.75
3.0	–	0.61	–
5.0	–	0.94	0.70
10.0	–	1.5	–

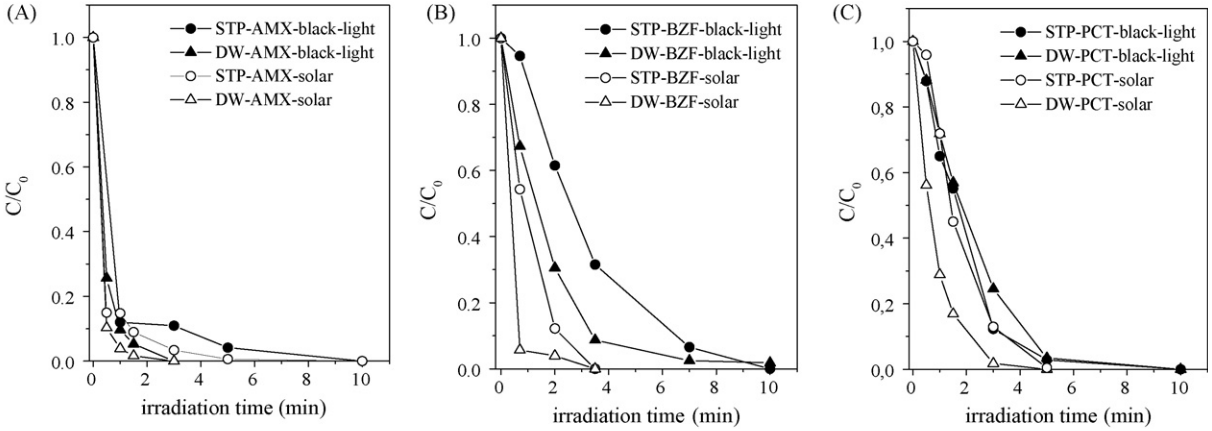

Fig. 4. Influence of the matrix on oxidation of (A) AMX; (B) BZF and (C) PCT during black-light and solar irradiation. Initial concentrations: [AMX] = 42 mg L^{-1} = 19 mg L^{-1} TOC; [BZF] = 20 mg L^{-1} = 13 mg L^{-1} TOC; [PCT] = 15 mg L^{-1} = 10 mg L^{-1} TOC; pH 2.5; [FeOx] = 0.20 mM; [H_2O_2] = 2.0 mM (AMX and PCT) and 10.0 mM (BZF).

effluent, it is important to evaluate the possible influence of this matrix on the process efficiency.

The photo-Fenton process was evaluated as to its oxidizing potential of AMX, BZF and PCT present in STP effluent under black-light and solar irradiation using FeOx. The results were then compared with those obtained in distilled water (Fig. 4). The STP effluent contains 78 mg L^{-1} of dissolved carbon, of which 50 mg L^{-1} are inorganic carbon, resulting in 28 mg L^{-1} of organic carbon. The presence of chloride and inorganic carbon (carbonate and bicarbonate) can strongly decrease the degradation efficiency by scavenging hydroxyl radicals [13,29]. After the pH adjustment to 2.5, it was possible to eliminate the interference of the carbonate and bicarbonate, since the inorganic carbon was reduced to 2–4 mg L^{-1}.

The AMX degradation is neither affected by the matrix nor by the type of irradiation (Fig. 4A). Under black-light irradiation, 90 and 89% of AMX oxidation was obtained after 1 min of irradiation in distilled water and in STP effluent, respectively; while under solar irradiation, 96 and 85% was reached after the same time. These differences are considered within the standard deviation of the analysis, which is typically between 3 and 5%. The irrelevant influence of matrix and irradiation on AMX degradation can be attributed to AMX susceptibility to hydrolysis, becoming the influence of the matrix and the irradiation source less important. In the control experiments no hydrolysis of AMX occurred at natural pH (4.2–4.5) while at pH 2.5 a decrease of 30% after 5 min was observed, which remained constant for 48 h. In both cases, no TOC removal was observed.

The matrix influenced the degradation rate of BZF and PCT to a greater extent under black-light than under solar irradiation (Fig. 4B and C). The presence of organic compounds that present absorbance in the same region as the FeOx can diminish its radiation absorption, hindering its photolysis and the availability of free iron. On the other hand, although the concentration of organic matter in STP effluent is 28 mg L^{-1}, which is comparable to the concentration of the pharmaceuticals, the recalcitrance of its components is probably low. Furthermore, the dissolved iron concentration of 2 mg L^{-1} of this sample [28] can also contribute to the photo-Fenton degradation in relation to distilled water resulting in only a slight influence in the overall efficiency and complete oxidation after 3.5 min (BZF) and 5 min (PCT) under solar irradiation. When using black-light irradiation, 10 min were necessary to achieve the same result.

Bautitz and Nogueira [28] also observed a lower efficiency of tetracycline degradation in STP effluent under black-light irradiation, indicating that there was interference from the sample constituents on the overall efficiency of the process. However, under solar irradiation with FeOx, no influence from the matrix was observed, demonstrating the importance of evaluating the parameters of the process for each target compound.

When evaluating TOC removal, no differences were observed when black-light or solar light were employed in distilled water for all the pharmaceuticals tested. However, for AMX and BZF in STP effluent, a faster mineralization was observed when solar light was used in comparison to black-light (data not shown).

4. Conclusions

The results presented in this work demonstrate that the photo-Fenton process could be successfully applied to the degradation of AMX, BZF and PCT even when present in complex samples, such as STP effluent, where they are often encountered. The use of solar irradiation favored the degradation of BZF and PCT, achieving complete degradation in a shorter time than that obtained with black-light irradiation. Although AMX degradation was not influenced by the source of the irradiation, the use of solar irradiation is more advantageous because it reduces the operating costs. These results offer the possibility of treatment of STP effluents contaminated with pharmaceuticals using low concentrations of reagents and low energy costs since solar light can be applied.

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