

Photo-Fenton degradation of the pharmaceuticals ciprofloxacin and fluoxetine after anaerobic pre-treatment of hospital effluent

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Abstract This work evaluated the photo-Fenton degradation of two pharmaceuticals extensively used in human medicine, ciprofloxacin (CIP), and fluoxetine (FLU) when present in an anaerobic pre-treated hospital effluent (HE) at low concentration ($100 \mu\text{g L}^{-1}$). Operational parameters such as concentration of hydrogen peroxide, iron, and initial pH as well as the effect of iron citrate complex were evaluated considering the degradation of the pharmaceuticals. Iron citrate complex (Fecit) influenced significantly FLU degradation at pH 4.5 achieving 80 % after 20 min, while with iron nitrate only 36 % degradation was obtained after the same time. However, only a slight effect was observed on CIP degradation, achieving 86 % with Fecit and 75 % with $\text{Fe}(\text{NO}_3)_3$, after 20 min. Samples of HE used in this work were previously treated in an anaerobic reactor followed by sand filtration; however, the presence of pharmaceuticals was detected. Degradation of both FLU and CIP was significantly hindered when present in HE, due to the relatively high content of organic (39.6 mg L^{-1}) and inorganic (12.5 mg L^{-1}) carbon, which may have consumed OH in side reactions. However, the iron cycle reduction was not affected by the matrix in the presence of citrate. Despite the recalcitrance of the matrix (no total organic carbon removal), it was possible to achieve over 50 % degradation of both pharmaceuticals after 90 min.

Keywords Hospital effluent · Antibiotic · Antidepressant · Citrate · Iron complex

Introduction

Due to the increasing use of pharmaceutical products, residues of these compounds have often been found at concentrations ranging from ng L^{-1} to $\mu\text{g L}^{-1}$ in wastewaters, surface waters, and even in drinking water (Rodil et al. 2012; Vázquez et al. 2013; Kosjek et al. 2013).

After ingestion, pharmaceuticals are partially converted into metabolites or excreted unchanged (Heberer 2002). Once excreted, these compounds are released directly into the environment, or pass through a wastewater treatment plant (WWTP), main route of input of pharmaceuticals waste in the aquatic environment due to inefficient elimination of these compounds (Martínez-Bueno et al. 2007). Hospitals sewage network is often directly connected to the municipal WWTP, increasing the concentration of pharmaceuticals and metabolites in the effluent to be treated, which is considered an inadequate solution (Pauwels et al. 2006; Vieno et al. 2007). Furthermore, some compounds present in hospital effluents can inhibit microbial biomass and consequently reduce the efficiency of WWTP (Verlicchi et al. 2010).

In Brazil, anaerobic systems can be employed for the treatment of hospital effluents and other health care establishments, which could be decentralized, to treat sewage on site. Anaerobic filter combined with sand filter is one of the systems suggested by the Brazilian standards. Several studies demonstrated its robustness and ability to generate a good effluent quality, with significant reduction of chemical oxygen demand (COD), total suspended solids, coliform bacteria, and viruses (Gross and Mitchell 1990; Emerick et al. 1999).

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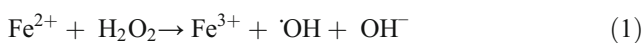
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However, the literature does not present any study of its action on removal of pharmaceuticals.

Fluoxetine (FLU) is a selective serotonin reuptake inhibitor widely used for treatment of patients with depression (Chu and Metcalfe 2007). FLU was found in university hospital effluent in concentrations in the range of 34.8–105 ng L⁻¹ in Portugal (Santos et al. 2013) and 21 ng L⁻¹ in an effluent from a psychiatric hospital in China (Yuan et al. 2013). It has been reported that exposure of medaka fish to 1–5 µg L⁻¹ concentrations of FLU during 4 weeks affected egg fertilization (Foran et al. 2004). Increase of mosquito fish lethargy has been also observed when exposed to FLU concentrations between 0.05 and 5 µg L⁻¹, although survival was not affected (Henry and Black 2008).

Ciprofloxacin (CIP) is a fluoroquinolone broad-spectrum antibiotic effective against gram-positive and gram-negative bacteria used in the treatment of diseases in humans and animals (Bongaerts and Hoogkamp-Korstanje 1993). CIP is often detected in hospital effluent at concentrations in the range of 32–99 µg L⁻¹, while in secondary wastewater and surface water ng L⁻¹ levels have been reported (Martins et al. 2008; Santos et al. 2013).

Fenton process has attracted considerable attention for the degradation of non-biodegradable and/or toxic compounds including pharmaceuticals due to the high efficiency in ·OH production from a mixture of H₂O₂ and Fe²⁺ in acid medium (Eq. 1). Degradation can be accelerated with UV-Vis irradiation due to the photo-reduction of Fe³⁺ to Fe²⁺, establishing an iron cycle besides of generating extra ·OH (Eq. 2) (Pignatello 1992).



The enhancement of iron photo reduction can be achieved by the use of organic ligands such as oxalic or citric acid which shows much higher quantum yield of Fe(II) generation than iron aqua complexes besides the higher molar absorption coefficients in the UV-Vis region (Trovó et al. 2008; Klammer et al. 2013). In addition, organic ligands extend the pH range that can be used in the Fenton reaction (optimum pH 2.5–3.0), allowing application at near neutral pH values (Silva et al. 2007; Perini et al. 2013; Soares et al. 2015).

The aim of this work was to study the photo-Fenton degradation of CIP and FLU at µg L⁻¹ levels present in an anaerobic pre-treated hospital effluent. Firstly, the influence of some parameters such as pH, iron, H₂O₂ concentrations, and iron complexation on pharmaceuticals degradation was evaluated in distilled water. Secondly, photo-Fenton process was evaluated when these pharmaceuticals were present in an anaerobic pre-treated hospital effluent.

Material and methods

Reagents

Ciprofloxacin hydrochloride monohydrate (99 %) (C₁₇H₁₈FN₃O₃·HCl·H₂O; MW = 385.82 g mol⁻¹) and fluoxetine hydrochloride (99 %) (C₁₇H₁₈F₃NO·HCl; MW = 345.79 g mol⁻¹) were obtained from Pharma Nostra (São Paulo, Brazil). Fe(NO₃)₃·9H₂O (Mallinkrodt, Paris, KY, USA) was used to prepare aqueous 0.25 M iron stock solution. H₂O₂ 30 % (w/w) was used (Synth, São Paulo, Brazil). Citric acid (Synth, São Paulo, Brazil) was used as iron ligand. 2,2'-bipyridyl and peroxidase (type II-A from horseradish, 1500 units/mg solid) were purchased from Sigma-Aldrich (St. Louis, MO, USA). *N,N*-diethyl-1,4-phenylene-diamine (DPD) was obtained from Fluka (Steinheim, Germany). 1,10-phenanthroline was obtained from Vetec (Rio de Janeiro, Brazil). A 1 M H₂SO₄ (Chemis, São Paulo, Brazil) solution was used for pH adjustment. Methanol, formic acid, and acetic acid (HPLC grade) were purchased from J.T. Baker (Xalostoc, Mexico). Ultrapure water (DG 500UF, Gehaka, São Paulo, Brazil) was used for dilutions and for HPLC analysis.

Hospital effluent

Effluent from a university hospital was firstly treated in an anaerobic process. As described by Tonon et al. (2015), the system consists of an upflow anaerobic filter filled with coconut shells (*C. nucifera*) followed by a sand filter. The hydraulic retention time (HRT) of the anaerobic filter was 9 h, and the hydraulic loading rate of the sand filter was 200 L m⁻² day⁻¹. The effluent from sand filters, named hereafter as hospital effluent (HE), was collected and used to carry out the photo-Fenton degradation of the pharmaceuticals after determination of pH using a pH meter (1100 series, Oakton, Vernon Hills, IL, USA), total organic and inorganic carbon concentration using a total organic carbon (TOC) analyzer (TOC-5000A-Shimadzu, Kyoto, Japan), turbidity (Turbidimeter-Quimes Q279P, São Paulo, Brazil), conductivity and total dissolved solids (pHtek-pH8b, São Paulo, Brazil), and chemical oxygen demand (COD) using COD digestion kit (HACH, Loveland, CO, USA) and then analyzed in a COD photometer (Macherey-Nagel model PF-3, Düren, Germany). The concentration of iron present in HE was measured using ICP-OES Optima 8000 spectrometer from Perkin Elmer (Waltham, MA, USA) after H₂O₂/HNO₃ digestion. The effluent was spiked with 100 µg L⁻¹ of each pharmaceutical (CIP and FLU) to evaluate the efficiency of their degradation when present in this matrix.

Experimental degradation procedures

Photo-Fenton experiments were carried out in an upflow photoreactor previously described (Nogueira and Guimarães 2000). The source of irradiation was a 15 W black-light lamp with maximum emission at 365 and 410 nm. The irradiated volume of the reactor was 280 mL, and a total volume of 500 mL of pharmaceutical solution was recirculated at a flow rate of 90 mL min⁻¹ using a peristaltic pump (Masterflex 7518-12, Vernon Hills, IL, USA). The iron complex was prepared in situ by the addition of citric acid to iron nitrate solution at 1:1 M ratio. The solution pH was then adjusted to the desired value by addition of 1 M H₂SO₄. Appropriate volume of H₂O₂ was then added to the solution under magnetic stirring and immediately pumped into the reactor. The lamp was only switched on once the reactor was completely filled, when the time started to be monitored. The initial concentration of pharmaceuticals in distilled water (DW) or HE was 100 µg L⁻¹ (0.26 µM for CIP and 0.29 µM for FLU), and concentrations of iron and hydrogen peroxide were 1 and 50 µM, respectively, unless otherwise stated.

Solid phase extraction

Solid phase extractions (SPEs) were carried out for pre-concentration of the pharmaceuticals, which was necessary for quantification at µg L⁻¹ levels. In this procedure, Fenton reaction is quenched since pharmaceuticals are retained in the cartridge while aqueous phase containing iron ions and residual H₂O₂ is discharged, thus interrupting the degradation. Sep-Pak-C18 (360 mg) cartridges were used for FLU extraction. In the case of CIP, recovery values with this cartridge were very low, probably due to the strong interaction of residual silanol groups with the acid group of CIP molecule. Therefore, Oasis HLB (60 mg) cartridges (Waters, Milford, MA, USA) were used for CIP extraction. Sep-Pak-C18 cartridges were previously conditioned with 5 mL methanol followed by 3 mL water. Then 15 mL of sample was percolated through the cartridge and recovered with 5 mL methanol. In the case of CIP, Oasis HLB cartridges were used after conditioning with 1 mL methanol followed by 1 mL water. Then 10 mL of sample was percolated through the cartridge and recovered with 1 mL methanol/formic acid (50:50) solution. Average recovery percentages for CIP were 105.5 ± 12.8 % in DW and 94.6 ± 5.5 in HE, while for FLU recoveries were 108.8 ± 20.2 in DW and 113.0 ± 8.5 in HE.

Chemical analysis

The decay of pharmaceuticals concentration during the experiments was determined using reversed-phase HPLC (LC 20AT Prominence, Shimadzu, Kyoto, Japan) coupled to a fluorescence detector Shimadzu (FL-20A). A C-18 column (EVO

Kinetex, 5 µm, 150 × 4.6 mm, Phenomenex, Torrance, CA, USA) was used. The mobile phase was a mixture of methanol and acetate buffer (pH = 3.6) (50:50) for FLU and methanol and formic acid (15:85) for CIP, both at 0.5 mL min⁻¹ flow rate of in isocratic mode and 40 µL injection volume. The excitation and emission wavelengths for CIP detection were 278 and 445 nm and for FLU detection 225 and 310 nm, respectively. Under these conditions, retention time was 6.8 min for FLU and 7.3 min for CIP, and the limit of quantification was 300 ng L⁻¹ for FLU and 75 ng L⁻¹ for CIP. The samples were filtered through 0.45-µm nylon membrane syringe filter (Millipore, Bedford, MA, USA) before HPLC analysis, and no decrease of pharmaceuticals concentration was observed.

Residual hydrogen peroxide concentration during photo-Fenton experiments was determined by measuring the absorbance at 551 nm after a peroxidase-catalyzed reaction with DPD (Bader et al. 1988). Concentration of ferrous ions generated during experiments was determined by measuring the absorbance at 510 nm after reaction with 1,10-phenanthroline (Fortune and Mellon 1938). A Shimadzu UV mini-1240 (Kyoto, Japan) spectrophotometer was used in both cases.

Results and discussion

Effect of iron source, pH, concentration of H₂O₂ and Fecit

Considering that the experiments were carried out with relatively low concentration of the pharmaceuticals (100 µg L⁻¹), low concentrations of iron (1 µM) and hydrogen peroxide (50 µM) were also used. Experiments were firstly carried out in DW to verify the effect of main conditions for pharmaceuticals degradation and then further applied in HE.

The iron speciation is very important in photo-Fenton degradation, as each target compound may exhibit different interactions with iron and thus interfering on Fenton reaction (Nogueira et al. 2005). Therefore, degradation of target compounds was compared using free iron (Fe(NO₃)₃), and iron citrate complex (Fecit) in photo-Fenton process at initial pH 4.5. FLU degradation was strongly influenced by the iron species with faster reaction in the presence of Fecit achieving 80 % after 20 min, while only 36 % were degraded with iron nitrate. On the other hand, only a slight difference was observed for CIP degradation achieving 75 and 86 % of antibiotic removal after 20 min, in the absence and presence of Fecit, respectively (Fig. 1). The higher degradation efficiency of pharmaceuticals, principally FLU, in the presence of Fecit in relation to Fe(NO₃)₃ can be attributed to the higher quantum efficiency in the generation of Fe^{e2+} at pH 4.0 ($\Phi_{\text{Fe(II)}} = 0.45$, for Fecit) (Abrahamson et al. 1994), much higher compared to the hydroxylated species of iron(III) ($\Phi_{\text{Fe(II)}} = 0.12$ at pH 4.0; Faust and Hoigné 1990).

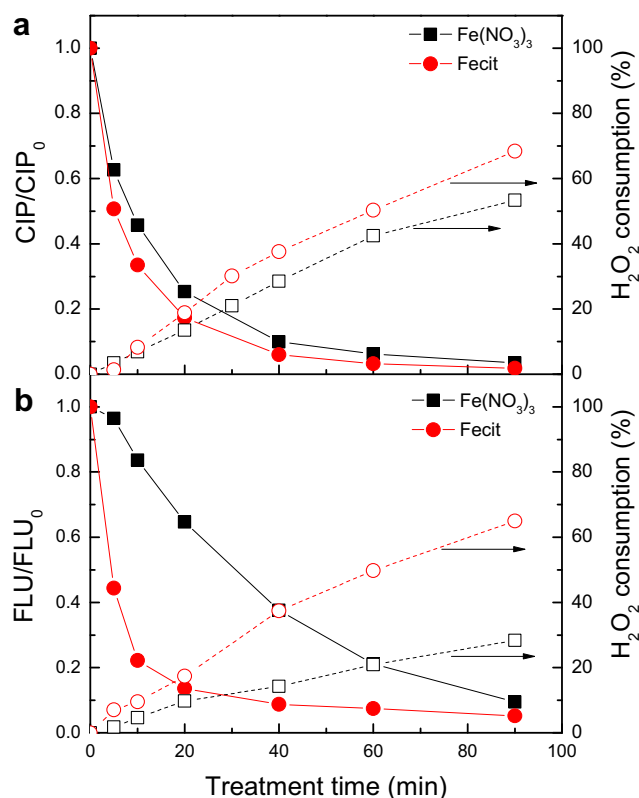


Fig. 1 Influence of iron species on degradation (solid symbols) and H_2O_2 consumption (open symbols) of CIP (a) and FLU (b) during photo-Fenton process in distilled water. Experimental conditions: $[\text{CIP}] = [\text{FLU}] = 100 \mu\text{g L}^{-1}$, $[\text{Fe}(\text{NO}_3)_3] = [\text{Fecit}] = 1 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 50 \mu\text{M}$, initial pH = 4.5

The pseudo-first-order rate constants (k_{obs}) for the removal of pharmaceuticals using $\text{Fe}(\text{NO}_3)_3$ and Fecit were determined by linear regression of $\ln(C/C_0)$ (C = concentration of pharmaceutical at time t ; C_0 = initial concentration of pharmaceutical) as a function of reaction time. All curves were linear with correlation coefficients higher than 0.95. Overall, a higher pseudo-first-order rate constant (k_{obs}) of pharmaceutical degradation in the presence of Fecit was observed,

especially for FLU ($k_{\text{obs}} = 0.097 \text{ min}^{-1}$), when compared to $\text{Fe}(\text{NO}_3)_3$ ($k_{\text{obs}} = 0.023 \text{ min}^{-1}$). On the other hand, the pseudo-first order rate constant of CIP degradation was similar with both iron sources, $k_{\text{obs}} = 0.085$ and 0.067 for Fecit and $\text{Fe}(\text{NO}_3)_3$, respectively (Table 1).

The consumption of hydrogen peroxide can be used as an indirect measure of the target compound degradation efficiency. So, the initial consumption of H_2O_2 during CIP and FLU degradation with both iron species was measured. Lower consumption of H_2O_2 occurred using $\text{Fe}(\text{NO}_3)_3$, especially in the case of FLU degradation, reaching only 28 % after 90 min reaction. On the other hand, higher hydrogen peroxide consumption was observed with Fecit, achieving around 69 % after the same reaction time for both pharmaceuticals, CIP and FLU (Fig. 1a, b, open symbol), due to the higher Fe^{2+} generation from this organic iron complex for reaction with H_2O_2 .

The photo-Fenton process depends strongly on pH, with maximum degradation efficiency in a narrow pH range (2.5–3.0) (Pignatello 1992; Nogueira and Guimarães 2000). To evaluate the pH effect, experiments were performed at three different initial pH values (3.4, 4.5, and 5.6) using Fecit complex as a source of iron. At initial pH 3.4, CIP and FLU degradation was higher than 97 % after only 20 min, with $k_{\text{obs}} = 0.20$ and 0.18 min^{-1} , respectively (Fig. 2) and decreased slightly at pH 4.5.

On the other hand, when the initial pH was 5.6, FLU degradation was significantly lower than CIP, achieving only 56 %, while 88 % CIP were removed within 90 min (Fig. 2). This different kinetics is probably due to the degradation of citrate in reaction medium at pH 5.6 (40 % TOC removal from citrate after 30 min; data not shown), which lead to iron precipitating $\text{Fe}(\text{III})$, and thus hindering FLU degradation. On the other hand, CIP can complex $\text{Fe}(\text{III})$ forming $\text{Fe}(\text{CIP})_2$ and FeCIP complexes (Eldin et al. 1996), thereby providing soluble iron for Fenton reaction, which may have favored CIP degradation compared to FLU at pH 5.6.

Table 1 Kinetic parameters obtained for CIP and FLU degradation under different experimental conditions

Matrix	pH	iron (μM)	H_2O_2 (μM)	k_{CIP} (min^{-1})	$t_{1/2\text{CIP}}$ (min)	k_{FLU} (min^{-1})	$t_{1/2\text{FLU}}$ (min)
DW	4.5	1 ^a	50	0.067	10	0.023	30
DW	3.6	1 ^b	50	0.20	3.4	0.18	3.9
DW	4.5	1 ^b	50	0.085	8.2	0.097	7.7
DW	5.6	1 ^b	50	0.045	15	0.022	32
DW	4.5	1 ^b	100	0.13	5.3	0.16	4.3
DW	4.5	2 ^b	50	0.44	1.6	0.26	2.8
HE	4.5	2 ^b	100	0.022	32	0.0075	92
HE	4.5	2 ^b	100 + 100 ^c	0.020	35	0.0073	95

^a $\text{Fe}(\text{NO}_3)_3$

^b Fecit

^c Second addition of H_2O_2 after 40 min

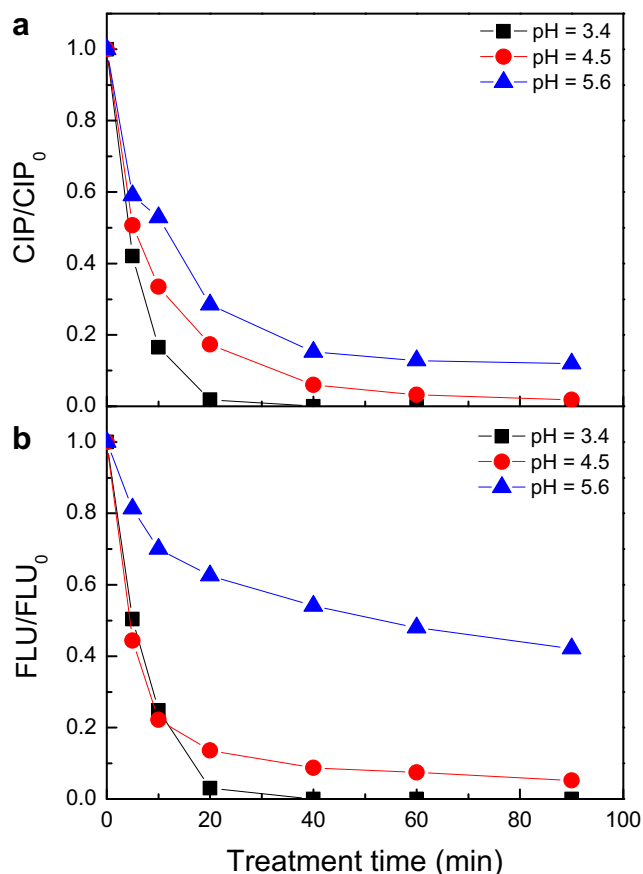


Fig. 2 Influence of pH on CIP (a) and FLU (b) degradation during photo-Fenton process in distilled water. Experimental conditions: [CIP] = [FLU] = 100 μg L⁻¹, [Fecit] = 1 μM, [H₂O₂] = 50 μM

At pH 5.6, there is a predominance of less photoactive species as Fe(OH)(cit)⁻ (Faust and Zeep 1993; Abrahamson et al. 1994; Ou et al. 2008). Using the public domain program Visual MINTEQ 3.1, it was calculated that at pH 4.5, 83 % of the Fe(III) is in the form of iron citrate complex, while 66 % of the iron concentration is complexed at pH 5.6, favoring degradation at lower pH values. Consequently, pharmaceutical degradation efficiency using Fecit is practically independent of pH up to pH 4.5, decreasing considerably at pH 5.6, especially in the case of FLU, showing the importance of using complexed iron in detriment to free iron, due to the low solubility-product constant of Fe(III) ($K_{sp} = 2 \times 10^{-39}$).

The effect of H₂O₂ and iron concentration is another important parameter for photodegradation of contaminants, since the excess or lack of these reagents may reduce the efficiency of the process. Firstly, experiments were carried out at pH 4.5 with two different H₂O₂ concentrations (50 and 100 μM), while the concentration of Fecit was maintained at 1 μM, resulting in a H₂O₂/Fe molar ratio of 50 and 100, respectively.

The use of 100 μM hydrogen peroxide lead to an increase in process efficiency achieving more than 95 % degradation of CIP and FLU after 20 min (Fig. 3). In this case, the H₂O₂ concentration was approximately eight times the

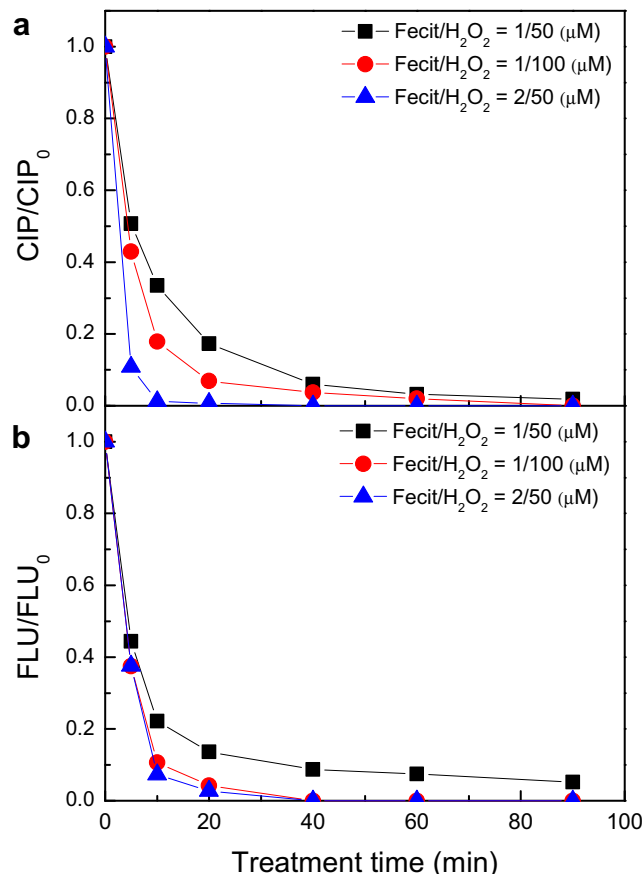


Fig. 3 Influence of H₂O₂ and Fecit concentration on CIP (a) and FLU (b) degradation during photo-Fenton process in distilled water. Experimental conditions: [CIP] = [FLU] = 100 μg L⁻¹, initial pH = 4.5

stoichiometric amount (13 μM) for total degradation of 0.26 μM CIP and 0.29 μM FLU (100 μg L⁻¹) into CO₂, water, and inorganic ions. Moreover, when a lower concentration of the oxidant was used (50 μM, approximately four times the theoretical stoichiometric H₂O₂ concentration), total degradation of the pharmaceuticals was not achieved until 90 min (Fig. 3). As can be seen in Table 1, the rate constants of CIP and FLU degradation increased with the increment of hydrogen peroxide concentration.

The influence of iron concentration in pharmaceuticals degradation was assessed using two different Fecit concentrations (1 and 2 μM) and initial H₂O₂ concentration fixed at 50 μM, which corresponds to a H₂O₂/Fe molar ratio of 50 and 25, respectively. The degradation efficiency of pharmaceuticals was increased with increasing initial Fecit concentration from 1 to 2 μM (Fig. 3). The kinetic constant for CIP degradation enhanced 5.2 times and FLU 2.7 times, with a reduction of half-life time from 8.2 to 1.6 min for CIP and 7.7 to 2.8 min for FLU (Table 1).

Therefore, using 2 μM Fecit concentration resulted in higher degradation rates in comparison to the higher concentration of H₂O₂ (100 μM), which shows that the iron

concentration is more important to the oxidation of pharmaceuticals than the concentration of hydrogen peroxide.

Photo-Fenton degradation of CIP and FLU in HE samples

The analysis of Table 2 shows that the anaerobic system applied as pre-treatment of the hospital effluent was able to generate an effluent with a similar quality to those generated from more complex systems (Tonon et al. 2015). This demonstrates the viability of onsite treatment of hospital sewage, with respect to environmental parameters traditionally evaluated. However, in relation to pharmaceutical compounds and its metabolites, the anaerobic treatment was not able to remove it completely. A qualitative analysis of the HE (after anaerobic treatment and sand filter), two pharmaceuticals, CIP, and diclofenac was detected with high intensity in LC-MS/MS analysis in the effluent pre-concentrated 40 times using Sep-Pak-C18 cartridges. The quantification of these pharmaceuticals and others in treated and raw HE will be discussed in a future work. The concentration of total carbon (TC) in HE at natural pH 5.6 is 52.1 mg L^{-1} of which 12.5 mg L^{-1} due to inorganic carbon (IC) corresponds to approximately 24 % of the total carbon and a COD of 100 mg L^{-1} (Table 2). However, the pH adjustment to 4.5 and magnetic stirring during 30 min in all experiments with HE reduced the TC and IC content to 45.2 and 7.3, respectively, due to evolution of CO_2 (Table 2).

The experiments with HE were performed using higher Fecit and H_2O_2 concentrations, 2 and $100 \mu\text{M}$, respectively, due mainly to the IC content of HE, which even after pH adjustment could reduce the process efficiency by consumption of $\cdot\text{OH}$ in side reactions. Although the calculated stoichiometric amount of H_2O_2 necessary for complete oxidation of the HE is 6.25 mM, lower H_2O_2 concentration was used considering that the objective of the photo-Fenton treatment proposed in this work was the degradation of pharmaceuticals

Table 2 Main parameters determined for pre-treated hospital effluent (HE)

Parameters	Before pH adjustment	After pH adjustment
Total carbon (mg L^{-1})	52.1	45.2
Inorganic carbon (mg L^{-1})	12.5	7.3
Total organic carbon (mg L^{-1})	39.6	37.9
pH	5.6	4.5
Dissolved Fe ($\text{mg L}^{-1}/\mu\text{M}$)	3.72/66.6	nd
Turbidity (nephelometric units)	6.06	nd
Total dissolved solids (mg L^{-1})	493	nd
COD ($\text{mg O}_2 \text{ L}^{-1}$)	100	nd
Conductivity ($\mu\text{S cm}^{-1}$)	1054	nd

COD chemical oxygen demand, nd not determined

present at low concentrations ($100 \mu\text{g L}^{-1}$) and not the mineralization of the effluent.

Lower efficiency of CIP and FLU degradation (Fig. 4a, b) was observed in HE at pH 4.5, achieving 69 and 47 % after 90 min, with half-life time of 32 and 92 min (Table 1), respectively, even using twice the concentration of Fenton reagents compared to DW. Considering the relatively high TOC and IC content of the effluent when compared to low H_2O_2 added for the pharmaceuticals degradation, an experiment was carried out with a second addition of H_2O_2 ($100 \mu\text{M}$) after 40 min reaction. However, this procedure did not improve the removal of CIP and FLU, reaching the same removal level when compared to a single addition of oxidant, i.e., 72 and 40 % for CIP and FLU, respectively after 90 min (Fig. 4a, b), indicating that the hydrogen peroxide was not the limiting factor of the degradation reaction.

No significant decrease of TOC was observed during 90 min reaction. However, despite the low concentration of hydrogen peroxide ($100 \mu\text{M}$), only 25 % was consumed during photo-Fenton degradation in HE (Fig. 4c), much lower consumption compared to DW (69 %). Accordingly, the effect of HE on H_2O_2 consumption and, consequently, on pharmaceutical degradation, could be associated to the presence of recalcitrant compounds in this effluent. As reported by

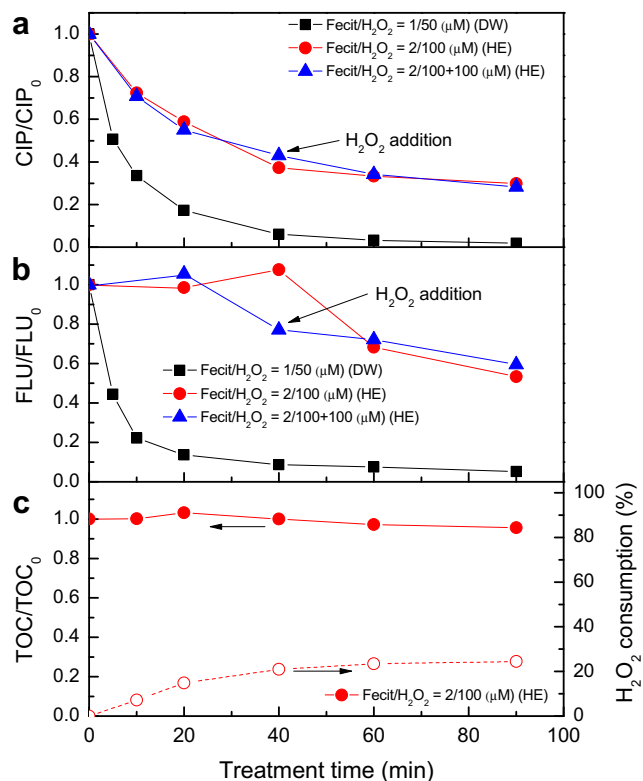
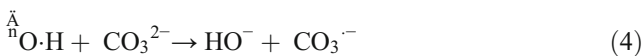
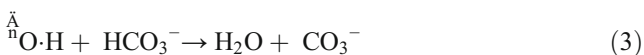


Fig. 4 Influence of matrix on CIP (a) and FLU (b) degradation. TOC removal (solid symbols) and H_2O_2 consumption (open symbols) (c) during photo-Fenton process. Experimental conditions: $[\text{CIP}] = [\text{FLU}] = 100 \mu\text{g L}^{-1}$, initial $\text{TOC} = 37.8 \text{ mg L}^{-1}$, initial $\text{pH} = 4.5$. DW distilled water, HE hospital effluent

Ruppert et al. (1993), both mineralization and hydrogen peroxide consumption are greatly affected by the recalcitrance of target compounds. Probably, in the case of HE, recalcitrant products formed during anaerobic degradation process (low molecular weight carboxylates and alcohols) can inhibit the Fenton reaction (Michael-Kordatou et al. 2015). Furthermore, the presence of IC (carbonate and bicarbonate) in HE can also scavenge OH radicals (Eqs. 3 and 4):



It was also considered that the compounds present in HE could be suppressing the generation of Fe²⁺ due to its complexation with organic compounds in the sample and consequently, decreasing the Fenton reaction efficiency. Therefore, experiments were performed to compare the generation of Fe²⁺ in DW and HE during irradiation. Initial iron (III) concentration was 116 μM in DW and HE (50 + 66 μM already present in the effluent, totaling 116 μM) (Table 2), and the citrate added was 50 μM. It was observed that the generation of Fe²⁺ in HE was higher than in DW reaching 60 μM in the presence of Fecit within the first 10 min, while in DW it reached 45 μM after the same time (Fig. 5). This indicates that HE did not hindered Fe³⁺ reduction and recalcitrance of its components, and the inorganic carbon present is the main cause for the lower degradation of pharmaceuticals in this matrix. However, in the absence of Fecit, the generation of Fe²⁺ was significantly lower in both DW and HE, achieving approximately 7 μM after 10 min, showing the importance of organic complex in iron reduction cycle.

Despite the recalcitrance of organic compounds present in the HE studied in this work, it was possible to achieve more than

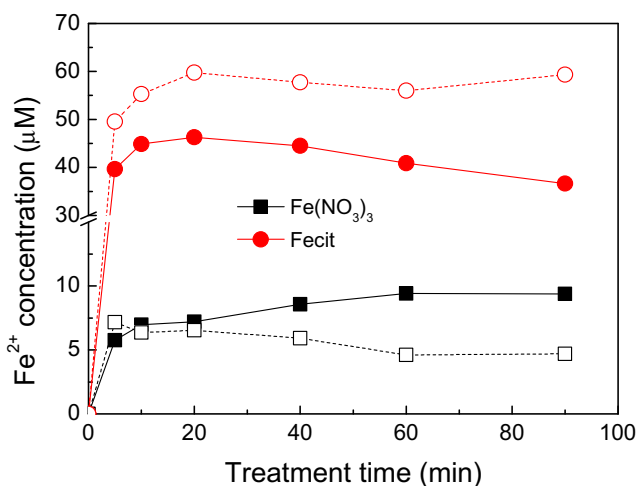


Fig. 5 Generation of Fe²⁺ during irradiation of Fecit and Fe(NO₃)₃ in distilled water (solid symbols) and hospital effluent (open symbols). Experimental conditions: [Fe(NO₃)₃] = 166 μM, [citrate] = 50 μM, initial pH = 4.5

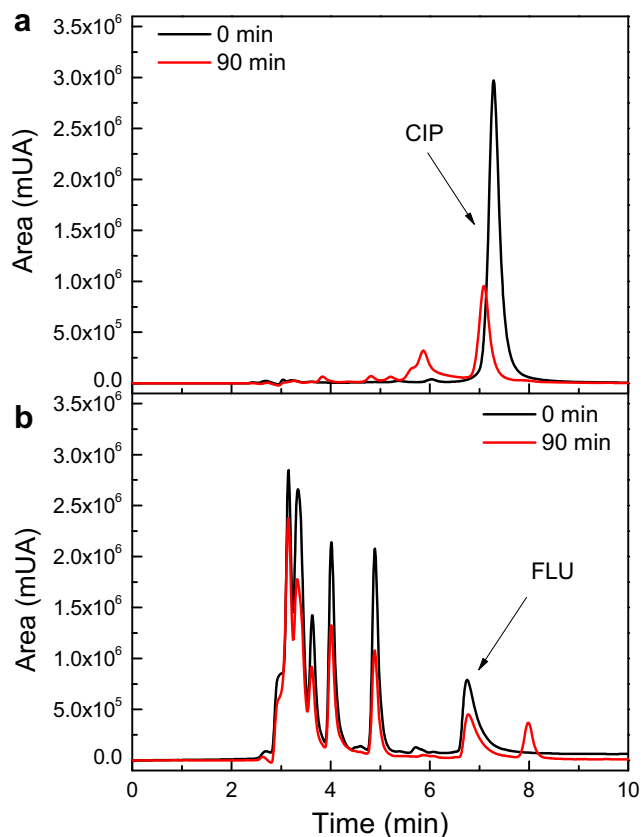


Fig. 6 HPLC-FL chromatograms before and after 90 min photo-Fenton degradation of CIP (a) and FLU (b) by in pre-treated hospital effluent. Experimental conditions: [CIP] = [FLU] = 100 μg L⁻¹, [Fecit] = 2 μM, [H₂O₂] = 100 μM, initial pH = 4.5

50 % degradation of CIP and FLU after 90 min at pH 4.5 using very low concentration of Fenton additives. Moreover, from the chromatograms before and after 90 min photo-Fenton degradation, it can be observed that the intensity of the main peaks decreased considerably indicating that photo-Fenton process was able to degraded compounds already present in HE (Fig. 6).

Conclusions

The photo-Fenton process was efficient for the degradation of the pharmaceuticals even when using very low concentrations of reagents (Fe(III) and H₂O₂). The FLU degradation was strongly favored with iron citrate (Fecit) when compared to iron nitrate, while CIP degradation was only slightly improved with iron citrate. The pharmaceutical degradation rates were higher at more acid pH (3.4 and 4.5) when compared to pH 5.6. The HE strongly hindered the degradation of pharmaceuticals in relation to DW, since in this case, the high ratio of carbon to CIP and FLU content resulted in a consumption of hydroxyl radical in side reactions. However, the redox iron cycle was not influenced by the HE content during photo-Fenton process. Despite the recalcitrance

of the matrix, more than 50 % of pharmaceuticals were degraded within 90 min of experiment by photo-Fenton process.

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