



Research Paper

Simultaneous degradation of ciprofloxacin, amoxicillin, sulfathiazole and sulfamethazine, and disinfection of hospital effluent after biological treatment via photo-Fenton process under ultraviolet germicidal irradiation

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ABSTRACT

A UVC-assisted photo-Fenton process was applied to hospital wastewater that had been submitted to anaerobic treatment. Low iron ($10 \mu\text{M}$; 0.56 mg L^{-1}) and H_2O_2 ($500 \mu\text{M}$; 17 mg L^{-1}) concentrations were used at the natural pH of the effluent ($\text{pH} \approx 7.4$). Citric acid was employed as a complexation agent, at a 1:1 ratio, in order to maintain Fe^{3+} soluble at this pH, avoiding extra procedures and costs associated with acidification/basification of the final effluent. The anaerobic process quantitatively reduced the biochemical oxygen demand (BOD_5), chemical oxygen demand (COD) and total organic carbon (TOC), with low removal of antibiotics present in the wastewater. Degradation of the antibiotics ciprofloxacin, amoxicillin, sulfathiazole, and sulfamethazine was studied by spiking the anaerobic effluent at initial concentrations of $200 \mu\text{g L}^{-1}$. The antibiotics were efficiently degraded (80–95%) using UVC radiation alone, although under this condition, no DOC removal was observed after 90 min. Further additions of H_2O_2 and iron citrate increased the degradation rate constant (k_{obs}), and 8% of DOC was removed. A lower pH resulted in higher k_{obs} , although this was not essential for application of the photo-Fenton process. Irradiation with a germicidal lamp resulted in greater degradation of the antibiotics, compared to use of a black light lamp or sunlight, since the overall degradation was influenced by photolysis of the antibiotics, photolysis of H_2O_2 , and the Fenton reaction. The photo-Fenton treatment could also be applied directly to the raw hospital wastewater, since no significant difference in degradation of the antibiotics was observed, compared to the anaerobic effluent. The photo-Fenton process under UVA and solar radiation reduced total coliforms and *E. coli* after 90 min. However, quantitative disinfection of these bacteria present in the Hospital effluent was only accomplished under UVC radiation.

1. Introduction

Antibiotics are the pharmaceuticals with the highest prescription and consumption rates worldwide, in both human and veterinary medicine, and are mainly used to treat bacterial infections. Besides their medicinal use, they are also employed as growth promoters in livestock animal production [1]. However, concerns about antibiotics include their potential collateral effects on human health and aquatic ecosystems [2,3], and the emergence of resistant bacteria [2,4,5].

Most antibiotics are poorly metabolized in the human body [2,6], with the parent compounds being excreted and often transported to wastewater treatment plants (WWTPs) in sewage systems. In the case of hospital wastewater, the loads of organic material are similar to those

in urban wastewater, which has led to the discharge of this effluent into municipal sewage systems without any prior treatment. However, the average concentrations of various drugs in hospital effluents can be 2–150 times higher than the concentrations found in urban wastewater, as reported by Verlicch et al. [7]. Furthermore, hospitals are important sources of pathogens found in urban wastewaters [2,8,9].

Therefore, the treatment of hospital effluents before their disposal into urban wastewater systems is very important in order to avoid problems of contamination and inhibition of biomass growth in conventional WWTPs, which are usually based on biological treatments that are unable to completely remove pharmaceutical products including antibiotics and their metabolites [10]. The removal rates of antibiotics in WWTPs are reported to range from 80 to 90%, and the removal is mainly due to

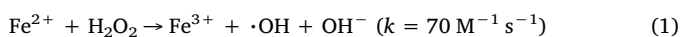
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adsorption on the sludge, rather than degradation [11–16].

An additional consideration is that there are several disadvantages associated with the traditional methods employed for the disinfection of water/wastewater, such as chlorination or ozonation. These include the production of toxic and carcinogenic halogenated byproducts, due to the reaction of chlorine with natural organic matter (NOM) and pharmaceutical compounds, as well as the high cost of O₃ and the quantities required, which make it unattractive for disinfection purposes [17,18].

There is a clear need to develop suitable methods for the treatment of hospital effluent, using new and improved technologies, in order to minimize undesirable effects in the environment. The use of advanced oxidation processes (AOPs) is an attractive option that enables the removal of non-biodegradable/toxic compounds and the inactivation of a wide range of microorganisms. AOPs are based on the generation of hydroxyl radicals ($\cdot\text{OH}$) from reactions involving oxidants such as hydrogen peroxide or ozone, UV-vis irradiation, and catalysts including metal ions or semiconductors. The Fenton process is an AOP in which $\cdot\text{OH}$ is generated from a mixture of H₂O₂ and Fe²⁺ in an acid medium (Eq. (1)). It can be applied before biological treatments, with the consequent partial oxidation of organic compounds assisting their biodegradation, or after biological treatments, in order to degrade recalcitrant compounds [19]. This process can be enhanced by UV-vis radiation (the so-called photo-Fenton process), accelerating the photo-reduction of Fe³⁺ to Fe²⁺ and establishing an Fe(II)/Fe(III) cycle in the Fenton reaction, besides generating extra $\cdot\text{OH}$ (Eq. (2)) [20].



The main challenge in application of the photo-Fenton process for wastewater treatment is that it must operate at near-neutral pH. The process is more effective under acid conditions (around pH 3), due principally to iron precipitation above this pH [21]. However, the operational costs associated with acidification/basification of the wastewater to be treated are not attractive. The photo-Fenton reaction can be enhanced by the use of organic ligands such as oxalic or citric acid, among others. Organic Fe(III) complexes have higher molar absorption coefficients in the UV-vis region, and much higher quantum yields for generation of Fe²⁺, compared to iron aqua complexes [22–24]. Furthermore, Fe³⁺-polycarboxylate complexes can extend the pH range used in the Fenton reaction, allowing operation at near-neutral pH [25–28].

The use of AOPs for the degradation of pharmaceuticals has frequently been studied using ultrapure water and/or initial concentrations of analytes in the mg L⁻¹ range, which are far from the concentration range and conditions found in natural waters and wastewaters [29–33]. Furthermore, the UVC-assisted photo-Fenton process employing iron complexation agents, at neutral pH, has not been evaluated for the treatment of hospital wastewater. Therefore, the focus of this work is to provide an option for the treatment of hospital wastewater containing high concentrations of organic carbon, pharmaceuticals, and pathogens. Firstly, the removal of COD, BOD₅, TOC, and other parameters from raw hospital wastewater (RHW) was performed using an upflow anaerobic filter. Secondly, the degradation of four antibiotics (ciprofloxacin, amoxicillin, sulfathiazole, and sulfamethazine) and bacterial disinfection (*E. coli* and total coliforms) in anaerobic hospital effluent (AHE) was carried out using UVC and a UVC-assisted photo-Fenton process with low concentrations of iron (10 μM; 0.56 mg L⁻¹) and hydrogen peroxide (500 μM; 17 mg L⁻¹), at the natural pH of the effluent (pH ≈ 7.4), avoiding the need for pH correction and making the process more attractive for practical applications.

2. Material and methods

2.1. Reagents

Ciprofloxacin hydrochloride monohydrate (CIP) (99%) (C₁₇H₁₈FN₃O₃HCl·H₂O), amoxicillin trihydrate (AMX) (97%)

(C₁₆H₁₉N₃O₅S·3H₂O), sulfathiazole (STZ) (99%) (C₉H₉N₃O₂S₂), sulfamethazine (SMZ) (99%) (C₁₂H₁₄N₄O₂S), sulfadiazine (SDZ) (99%) (C₁₀H₁₀N₄O₂S), sulfadoxin-d3 (S-d3) (C₁₂D₃H₁₁N₄O₄S), and enrofloxacin-d5 hydrochloride (E-d5) (C₁₉D₅H₁₇FN₃O₃HCl) (Table 1S) were obtained from Fluka (St. Louis, MO, USA). Fe(NO₃)₃·9H₂O (Mallinckrodt, Paris, KY, USA) was used to prepare aqueous 0.25 M iron stock solution. H₂O₂ (30% w/w) was from Synth (São Paulo, Brazil). Citric acid (Synth) was used as the iron ligand. 2,2'-bipyridyl and peroxidase (type II-A from horseradish, 1500 units/mg of 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 and formic acid (HPLC grade) were purchased from J.T. Baker (Xalostoc, Mexico). Ultrapure water from a DG 500UF system (Gehaka, São Paulo, Brazil) was used for dilutions and for HPLC analysis.

2.2. Hospital wastewater

Wastewater from the University of Campinas hospital was firstly treated using an anaerobic process. As described by Tonon et al. [34], the system consisted of an upflow anaerobic filter filled with coconut shells (*C. nucifera*) (Fig. 1A). The hydraulic retention time of the filter was 9 h and the hydraulic loading rate was 200 L m⁻² day⁻¹. The photo-Fenton process was applied to the effluent from the anaerobic treatment (AHE) with the aim of degrading the antibiotics. The following parameters of the RHW and AHE were determined: pH, using a pH meter (1100 series, Oakton, Vernon Hills, IL, USA); total organic and inorganic carbon concentrations, using a TOC analyzer (TOC-5000A, Shimadzu, Kyoto, Japan); turbidity (Q279P turbidimeter, Quimes, São Paulo, Brazil); conductivity and total dissolved solids (pH8b, pHTek, São Paulo, Brazil); and color, using a multi-parameter photometer (HI 83200, Hanna Instruments, Barueri, Brazil). The total iron concentrations in the RHW and AHE were determined by ICP-OES, using an Optima 8000 spectrometer (PerkinElmer, Waltham, MA, USA), after digestion of the samples with H₂O₂/HNO₃. The variables COD, BOD₅, PO₄³⁻, and total nitrogen were determined according to the SMEWW (Standard Methods for the Examination of Water and Wastewater) reference methods 22 5220C, 22 5210 B, 22 4500 P-E, and 22 4500 N_{org} B, respectively [35]. The concentrations of CIP, AMX, STZ, SMT, and SDZ in the RHW and AHE were determined by LC-MS/MS analysis, as described in Section 2.4. The efficiency of the photo-Fenton degradation of the antibiotics was evaluated by spiking the AHE with 200 μg L⁻¹ of each antibiotic (CIP, AMX, STZ, and SMZ).

2.3. Solid phase extraction (SPE)

Solid phase extractions were performed in order to interrupt the degradation reactions and preconcentrate (10 ×) the antibiotics prior to analysis, which was necessary for quantification at μg L⁻¹ levels. In the SPE, Fe²⁺ and H₂O₂ were discharged with the aqueous phase, without interacting with the solid phase, while the analytes were retained in the cartridge for subsequent elution, hence stopping the Fenton reaction.

In the photo-Fenton experiments, the extraction procedure was as described previously [36]. Oasis HLB cartridges (60 mg; Waters, Milford, MA, USA) were first conditioned with 5 mL of methanol, followed by 5 mL of water (pH 2.5). A 10 mL volume of aqueous sample (pH 2.5, with 0.1% w/v EDTA) was then percolated through the cartridge. Finally, the cartridge was washed with water (pH 7.0) and eluted with 1 mL of methanol. The eluate was filtered through a 0.45 μm nylon membrane syringe filter (Millipore, Bedford, MA, USA) and was then analyzed using HPLC-DAD. No decreases of the antibiotics concentrations were observed after filtration. The average percentage recoveries of AMX, CIP, STZ, and SMZ from the hospital effluent were

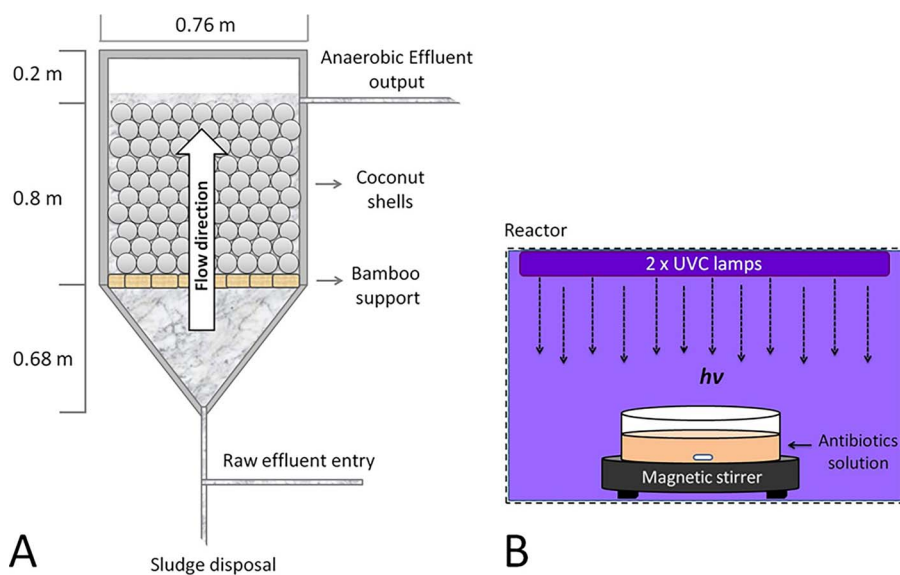


Fig. 1. Schematic illustrations of the anaerobic filter with coconut shells (A) and the reactor with UVC lamps used in the photo-Fenton process (B).

68.2 ± 12.8 , 103.8 ± 15.2 , 92.3 ± 8.5 , and 88.5 ± 9.8 , respectively.

Preparation of the samples for quantification of the selected antibiotics in the RHW and AHE (without spiking) was performed using the same type of cartridge (Oasis HLB). However, in this case, 50 mL volumes of the effluents were first filtered through glass fiber filters (Sartorius-Stedim, Göttingen, Germany) and then through cellulose acetate filters ($0.45 \mu\text{m}$), prior to SPE extraction. The samples were subsequently acidified to pH 2.5, followed by the addition of EDTA (0.1% w/v) and sulfadoxin-d3 (S-d3), used as a surrogate. The cartridge was eluted twice with 5 mL methanol, evaporated with N_2 , recovered in 0.5 mL of 0.1% v/v formic acid:MeOH (90:10, v/v), with enrofloxacin-d5 (E-d5) as internal standard, and analyzed by LC–MS/MS. The recoveries of the surrogate (at $5 \mu\text{g L}^{-1}$) were $86 \pm 7\%$ for the RHW and $63 \pm 7\%$ for the AHE.

2.4. Analytical methods

The decays of the antibiotics concentrations during the photo-Fenton experiments were determined using a reversed-phase high performance liquid chromatography (HPLC) system (LC 20AT Prominence, Shimadzu, Kyoto, Japan) equipped with a diode array detector (DAD). Separation was achieved using a C-18 column (EVO Kinetex, $5 \mu\text{m}$, $150 \times 4.6 \text{ mm}$; Phenomenex, Torrance, CA, USA) and guard column ($4 \times 3 \text{ mm}$; Phenomenex). The mobile phase was a mixture of methanol (A) and 0.1% v/v formic acid (B), at a flow rate of 0.5 mL min^{-1} . Gradient elution was performed using 5% A and 95% B for 8.0 min, followed by 15% A and 85% B for 12.0 min, and an equilibration time of 3 min. The injection volume was $40 \mu\text{L}$ and the detection wavelengths were 275 nm (CIP, STZ, and SMZ) and 230 nm (AMX). The oven temperature was maintained at $40 \text{ }^\circ\text{C}$. Under these conditions, the retention times of AMX, STZ, CIP, and SMZ were 5.0, 13.8, 15.7, and 18.3 min, respectively. The wastewater samples (AHE and RHW) were filtered through $0.45 \mu\text{m}$ nylon membrane syringe filters before the HPLC-DAD analyses, and no decreases of the pharmaceutical concentrations were observed. The instrumental detection limits for AMX, CIP, STZ, and SMZ were 12, 31, 6.9, and $8.6 \mu\text{g L}^{-1}$, respectively.

Carboxylic acids were quantified in the AHE and RHW, as well as after the photo-Fenton process, using a Rezex ROA-Organic Acid H^+ (8%) ion-exclusion column ($8 \mu\text{m}$, $300 \times 7.8 \text{ mm}$; Phenomenex, Torrance, CA, USA) in the same HPLC system, with detection at 210 nm and 2.5 mM H_2SO_4 as the mobile phase, at a flow rate of 0.5 mL min^{-1} .

Quantification of the pharmaceuticals in the unspiked AHE and

RHW was performed using an LC–MS/MS system (1200 series, Agilent Technologies, Santa Clara, CA, USA) equipped with a triple quadrupole QqQ 6410 B detector, an electrospray ionization source, and a StableBond C-18 column ($3.5 \mu\text{m}$, $2.1 \times 30 \text{ mm}$; Agilent Technologies, Santa Clara, CA, USA). The mobile phase was methanol (A) and 0.1% v/v formic acid (B), at a flow rate of 0.3 mL min^{-1} . The gradient elution was from 5% to 30.5% A during 9.0 min, followed by an increase to 65% A during 15 min, a hold for 2 min, and finally column re-equilibration during 6 min. The retention times of AMX, SDZ, STZ, SMZ, S-d3, CIP, and E-d5 were 1.8, 2.2, 3.3, 6.2, 8.3, 8.6, and 9.2 min, respectively. The mass spectrometer ionization source was operated in positive mode. The capillary and fragmentation voltages were 4000 and 100 V, respectively, the nebulizer pressure was 40 psi, and the temperature was $350 \text{ }^\circ\text{C}$. The triple quadrupole mass spectrometer acquired data in multiple reaction monitoring mode. The mass spectrometer operating parameters and the performance of the LC–MS/MS method are described in Tables 2S and 3S of the Supplementary Material. For all compounds, the instrumental detection limit was 10 pg and the method detection limit was 100 ng L^{-1} .

The mineralization of organic matter after the photo-Fenton process was evaluated by measuring the decay of dissolved organic carbon (DOC) using a TOC 5000A analyzer (Shimadzu, Kyoto, Japan). The concentrations of ferrous ions generated during the photodegradation experiments were measured using a spectrophotometric method employing 1,10-phenanthroline, with maximum absorbance at 510 nm [37]. The hydrogen peroxide consumption during the photo-Fenton experiments was determined by measuring the absorbance at 551 nm after a peroxidase-catalyzed reaction with DPD [38]. For both Fe^{2+} and H_2O_2 analyses, the absorbances were recorded using a UVmini-1240 spectrophotometer (Shimadzu, Kyoto, Japan).

The global degradation of the antibiotics was calculated as the average removal percentage of the four antibiotics (Eq. (3)).

$$\text{Global degradation(\%)} = \frac{\% \text{Removal(AMX)} + \% \text{Rem(CIP)} + \% \text{Rem(SMZ)} + \% \text{Rem(STZ)}}{4} \quad (3)$$

2.5. Quantification of bacteria

Total coliforms and *E. coli* present in the RHW and AHE samples were determined according to standard methods SMEWW 22 9222 B and G [35]. In both cases, the detection limit was 1 CFU mL^{-1} .

2.6. Experimental degradation procedures

Photo-Fenton experiments were carried out using the photoreactor shown in Fig. 1B. Two 15 W germicidal lamps with maximum emission at 254 nm were used as the radiation source. The irradiated volume of the solution was 250 mL and the path length was 1.5 cm. The sample was agitated at 500 rpm using a magnetic stirrer (model 751, Fisatom, São Paulo, Brazil). The iron citrate complex was prepared *in situ* by the addition of citric acid to iron nitrate solution, at a 1:1 molar ratio, resulting in a concentration of 10 μM in the effluent. In the experiments performed at pH 2.5 and 4.7, the sample pH was adjusted to the desired value by addition of 1 M H_2SO_4 . An appropriate volume of H_2O_2 was then added in order to obtain a concentration of 500 μM in the effluent. The initial spiked concentration of each antibiotic in the hospital effluent was 200 $\mu\text{g L}^{-1}$ (0.52 μM for CIP, 0.48 μM for AMX, 0.79 μM for STZ, and 0.72 μM for SMZ).

The apparatus used for the solar photo-Fenton experiments was the same as for the photo-Fenton/UVC experiments, but with direct exposure to sunlight. The experiments were carried out in Araraquara, Brazil (22°S, 48°W), during winter, under clear sky conditions between 11 am and 2 pm. The irradiation and the accumulated solar energy dose during the experiments were measured in the UVA region (320–400 nm) using a radiometer (PMA 2100, Solar Light Co., Glenside, PA, USA), with the sensor placed at the same angle as the reactor.

3. Results and discussion

3.1. Biological treatment for removal of TOC, COD, and BOD

The physical-chemical parameters determined for characterization of the hospital wastewater are summarized in Table 1. The biological process used for the pretreatment employed an upflow anaerobic filter, with a mantle of microorganisms supported on the surfaces of green coconut shells. Removal of TOC, COD and BOD_5 exceeded 90%. These results showed that the anaerobic process provided efficient removal of the more labile organic matter, in agreement with the findings of Tonon et al. [34]. The removal efficiencies for turbidity and color were 90 and 57%, respectively. No changes in total dissolved solids or conductivity were observed after the anaerobic process.

The total iron concentration increased from 6.3 μM in the RHW to

Table 1
Main parameters determined for the raw hospital effluent (RHW) and the anaerobic hospital effluent (AHE).

Parameters	Units	RHW	AHE
Total carbon	mg L^{-1}	185.9	94.51
Inorganic carbon	mg L^{-1}	70.71	83.37
Total organic carbon	mg L^{-1}	115.1	11.14
pH	–	7.6	7.4
Dissolved Fe	$\mu\text{M}/\text{mg L}^{-1}$	6.3/0.350	41/2.29
*Dissolved Fe	$\mu\text{M}/\text{mg L}^{-1}$	2.2/0.12	4.1/0.230
Total nitrogen	mg L^{-1}	106.8	73
PO_4^{3-}	mg L^{-1}	1.72	9.6
COD	$\text{mg O}_2 \text{L}^{-1}$	168	14.0
BOD_5	$\text{mg O}_2 \text{L}^{-1}$	118	< DL
Turbidity	NTU	79.9	7.87
UV at 254 nm	–	0.880	0.587
Color	mg PtCo L^{-1}	464	198
Odor	–	Very strong	Very strong
Total dissolved solids	mg L^{-1}	339	337
Conductivity	$\mu\text{S cm}^{-1}$	680	678

*Dissolved Fe without acid digestion.

DL – Detection limit.

NTU – Nephelometric turbidity unit.

COD – Chemical oxygen demand.

BOD_5 – Biochemical oxygen demand.

41 μM in the AHE after the anaerobic treatment. Since the iron concentration in the AHE was much higher than in the RHW, it was also measured without acid digestion (using HNO_3 and H_2O_2) of the sample, resulting in a 90% lower iron concentration in the AHE (4.1 μM). This indicated that iron particles derived from abrasion of the reactor were dissolved during the acid digestion and contributed to the higher concentration in the AHE. A higher PO_4^{3-} concentration after the anaerobic treatment could have been due to dissolution of the phospholipid membranes of the bacteria.

3.2. Occurrence of antibiotics in the RHW and AHE

Various studies have reported the presence of antibiotic residues in wastewaters, typically at $\mu\text{g L}^{-1}$ levels, including CIP at concentrations ranging from 0.03 to 11 $\mu\text{g L}^{-1}$ [36,39,40], AMX at 0.03 $\mu\text{g L}^{-1}$ [36], STZ at 5×10^{-4} –0.05 $\mu\text{g L}^{-1}$ [36,41], SMZ at 0.005 $\mu\text{g L}^{-1}$ [9], and SDZ at 0.029–0.38 $\mu\text{g L}^{-1}$ [41]. In this work, the concentrations of AMX, SDZ, and CIP in the RHW were 2.5 ± 0.4 , 1.3 ± 0.1 , and $13.0 \pm 0.4 \mu\text{g L}^{-1}$, respectively, while SMZ and STZ were not detected in either the RHW or the AHE (Table 2). The occurrence of CIP, AMX, and SDZ at $\mu\text{g L}^{-1}$ levels in the RHW could be explained by the high consumption of these antibiotics in the hospital, estimated at 7.3, 26.1, and 3.0 kg y^{-1} , respectively. On the other hand, use of SMZ and STZ was much lower and the concentrations were below the detection limits.

After the anaerobic treatment, the concentration of AMX decreased to below the detection limit (0.1 $\mu\text{g L}^{-1}$). However, the concentrations of CIP and SDZ were 4.5 ± 0.1 and $5.3 \pm 1.2 \mu\text{g L}^{-1}$, respectively. The results indicated that although the anaerobic process was effective for TOC, COD and BOD_5 removal, antibiotics were still present at $\mu\text{g L}^{-1}$ levels (with the exception of AMX), showing the need for further treatment of the effluent. A substantial increase in the SDZ concentration was observed, probably due to desorption from the sludge, or variability in the amounts discharged. The inefficiency of anaerobic treatment for the removal of antibiotics has also been reported elsewhere [42,43].

The differences between the concentrations of antibiotics in the inputs and outputs (removal efficiencies) of WWTPs vary according to the type of wastewater, the chemical structures and properties of the antibiotics, and the technology employed [44]. Complete removal of antibiotics is often not achieved, resulting in the discharge of these compounds into the aquatic environment. Therefore, AOPs such as the photo-Fenton process could be employed as treatments complementary to those already used in WWTP, in order to eliminate these antibiotic residues.

3.3. Antibiotics degradation using photo-Fenton and UVC processes

3.3.1. Comparison of UVC, UVC/ H_2O_2 , and photo-Fenton/UVC processes for antibiotics degradation

Technologies employing anaerobic reactors are attractive for the removal of organic and nitrogen loads from different types of effluents, as described in Section 3.1. However, the efficiency of removal of micro-contaminants, such as antibiotics, is questionable. In contrast,

Table 2
Concentrations of antibiotics, expressed in $\mu\text{g L}^{-1}$, for the raw hospital wastewater (RHW) and the anaerobic hospital effluent (AHE).

Antibiotics	Raw wastewater (RHW)	Anaerobic effluent (AHE)
CIP	13 ± 0.4	4.5 ± 0.1
AMX	2.5 ± 0.4	< DL
SMZ	< DL	< DL
STZ	< DL	< DL
SDZ	1.3 ± 0.1	5.3 ± 1.2

DL – Detection limit.

the high oxidizing power of the photo-Fenton process can effectively remove pharmaceutical compounds from water/wastewater systems.

FeCit was used as the iron source, since it was shown to provide more efficient degradation of CIP and fluoxetine, even at low iron concentrations, compared to free iron ($\text{Fe}(\text{NO}_3)_3$) [45]. Selection of the initial FeCit and hydrogen peroxide concentrations was based on a previous study [45]. The photo-Fenton experiments were carried out at the natural pH of the effluent (≈ 7.4), except when the effect of the initial pH on the degradation efficiencies was evaluated. It should be noted that the concentrations of AMX and CIP found in the anaerobic effluent were up to 10 times lower than the concentrations used in the removal experiments.

In the AHE, the background TOC concentration was approximately 10 mg L^{-1} , while the sum of all the antibiotics added to the effluent (each at $200 \mu\text{g L}^{-1}$) corresponded to less than 0.4 mg L^{-1} of carbon. Therefore, it was important to determine whether the proposed processes were able to degrade these compounds present at $\mu\text{g L}^{-1}$ levels in a complex matrix with a much higher concentration of TOC. The TOC could be also oxidized, hence competing with the antibiotics present at very low concentrations, which could reduce the efficiency of the photo-Fenton process. Additionally, in the absence of acid digestion, the AHE had an initial iron content of $4.1 \mu\text{M}$ (0.230 mg L^{-1}) (Table 1), probably due to corrosion of the material used to construct the anaerobic reactor.

Treatments were performed using (a) UVC lamps emitting at 254 nm, (b) UVC/ H_2O_2 without iron addition, and (c) the photo-Fenton process (UVC/ H_2O_2 /FeCit). After 30 min under UVC irradiation, between 45 and 65% of the initial concentrations of the antibiotics was removed, and at the end of the experiment (after 90 min), the global degradation of the antibiotics was 80% (Fig. 2A). Despite the presence of 11.14 mg L^{-1} of TOC and 83.37 mg L^{-1} of inorganic carbon (IC) at near-neutral pH, the UVC irradiation alone provided significant degradation of the antibiotics, although no DOC removal was observed at the end of the experiment, reflecting the inability of UVC irradiation to mineralize the effluent organic matter.

Direct photolysis of organic pollutants due to electronic excitation of the molecules results in electron transfer from the excited state to the ground state of molecular oxygen [46,47], as well as homolysis to form organic radicals that also react with oxygen [48]. The presence of dissolved organic matter (DOM) can lead to the indirect degradation of organic pollutants by absorption of radiation and the consequent promotion of a photosensitive molecule to its first singlet state ($^1\text{DOM}^*$), where excited humic substances accelerate the degradation rate of ciprofloxacin and decrease its antimicrobial activity as reported previously [49]. The singlet excited state generally has a short lifetime, so consequently there is no significant interaction with pollutant molecules. However, the singlet state can be transformed to the longer-lived excited triplet state (Eq. (4)), which can decay to the ground state or react with O_2 to form singlet oxygen ($^1\text{O}_2$) (Eq. (5)), a photo-oxidant that can contribute to pollutant degradation [50,51].



The effect of hydrogen peroxide photolysis was also evaluated, with the pseudo-first order rate constants for degradation of the antibiotics mixture ranging from 0.035 to 0.063 min^{-1} (Table 3). Total degradation of AMX and STZ was achieved after 60 min, while over 80% degradation of CIP and SMZ was observed during the same time (Fig. 2B). The higher rate of antibiotics degradation achieved using UVC/ H_2O_2 , compared to irradiation with a germicidal lamp (254 nm wavelength emission) alone, was due to the photolysis of hydrogen peroxide to produce two hydroxyl radicals [48]. However, the absolute contribution of the UVC/ H_2O_2 process could not be measured, because the AHE contained $4.1 \mu\text{M}$ of soluble iron, which could have contributed to hydrogen peroxide decomposition by means of the Fenton reaction.

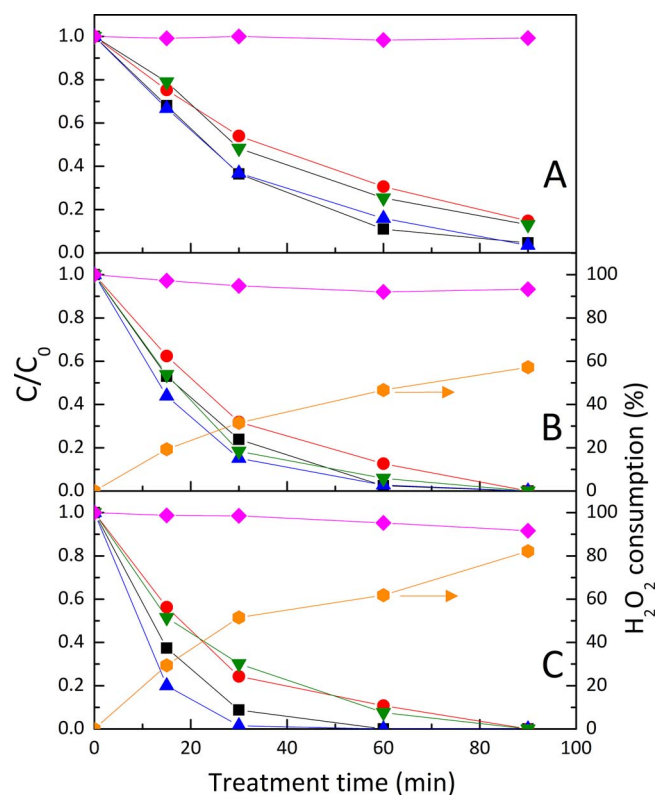


Fig. 2. Comparison of the UVC (A), UVC/ H_2O_2 (B), and UVC/ H_2O_2 /FeCit (C) processes for degradation of the antibiotics mixture in the AHE. Experimental conditions: $[\text{H}_2\text{O}_2] = 500 \mu\text{M}$; $[\text{FeCit}] = 10 \mu\text{M}$; $\text{pH}_{\text{initial}} = 7.4$; $\text{TOC}_{\text{initial}} = 10.1 \text{ mg L}^{-1}$; $\text{IC}_{\text{initial}} = 74.5 \text{ mg L}^{-1}$; $[\text{AMX}] = [\text{CIP}] = [\text{STZ}] = [\text{SMZ}] = 200 \mu\text{g L}^{-1}$. Symbols: (■) AMX; (●) CIP; (▲) STZ; (▼) SMZ; (◆) DOC; (○) H_2O_2 .

Although degradation of the antibiotics to levels below the detection limits was achieved after 90 min, only 7% of the DOC was removed and 60% of the H_2O_2 was consumed at the end of the experiment.

The efficiency of the photo-Fenton process for degradation of the pharmaceuticals was also evaluated using UVC lamp irradiation and the results were compared with those obtained for the UVC/ H_2O_2 and UVC processes. Photo-Fenton degradation is usually carried out in acid media. However, in the present work, the experiments could be conducted at the natural pH of the effluent ($\text{pH} \approx 7.4$), due to the low iron concentration and the use of citrate, which acts as a polydentate ligand and complexes iron, hence keeping it soluble. This has the advantage of avoiding the need for acidification/neutralization of wastewater, which could be unfeasible in large-scale applications. Furthermore, citrate presents higher molar absorption coefficients in the UV-vis region, compared to iron aqua complexes, producing Fe^{2+} via ligand-to-metal charge transfer [25].

The photo-Fenton process in the presence of citrate was able to degrade the antibiotics to levels below the detection limit after 30 min (STZ), 60 min (AMX), and 90 min (CIP and SMZ) (Fig. 2C). The addition of iron to the effluent improved the degradation, as can be seen by the higher k_{obs} values, compared to the UVC/ H_2O_2 system, with the greatest increase in k_{obs} (2.33-fold) being obtained for STZ (Table 3). The global degradation of the antibiotics after treatment for 30 min increased from 57% for the UVC system to 79% with the addition of H_2O_2 and 83% with the addition of H_2O_2 and FeCit. It is noteworthy that very similar degradations were obtained for the UVC/ H_2O_2 and UVC/ H_2O_2 /FeCit systems, due to the presence of iron in both cases.

The generation of Fe^{2+} in the presence of FeCit was very fast, reaching about $12.5 \mu\text{M}$ within 15 min of irradiation and decreasing to less than $2 \mu\text{M}$ after 90 min following reaction with H_2O_2 (Fig. 3A). The oxidation of Fe^{2+} was accompanied by citrate degradation, as reported

Table 3
Kinetic parameters obtained for degradation of the antibiotics under different experimental conditions.

Matrix	pH	FeCit (μM)	H ₂ O ₂ (μM)	Light source	k _{AMX} (min ⁻¹)	k _{CIP} (min ⁻¹)	k _{STZ} (min ⁻¹)	k _{SMZ} (min ⁻¹)
AHE	7.4	–	–	UVC	0.036	0.021	0.037	0.023
AHE	7.4	–	500	UVC	0.063	0.035	0.060	0.048
AHE	7.4	10	500	UVC	0.081	0.038	0.14	0.043
AHE	4.7	10	500	UVC	0.22	0.091	0.17	0.087
AHE	2.5	10	500	UVC	0.29	0.12	0.27	0.11
AHE	7.4	10	500	UVA	0.018	0.019	0.0033	0.0024
AHE	7.4	10	500	Solar	0.017	0.018	0.011	0.0065
RHW	7.6	10	500	UVC	0.054	0.039	0.075	0.033

AHE – anaerobic hospital effluent.
RHW – raw hospital wastewater.

in previous work [45]. A decrease of the citrate concentration leads to iron precipitation, strongly harming the photoreduction and decreasing the rate of degradation of target compounds. The complete consumption of 500 μM H₂O₂ was observed after 90 min of reaction.

The Fenton reaction is strongly dependent on the iron and hydrogen peroxide concentrations, and in the absence of these reagents, the reaction rate decreases to a minimum. Therefore, an experiment was performed with a second addition of 500 μM H₂O₂ and 10 μM FeCit at 60 min, in order to increase the removal of DOC. This resulted in 18% DOC removal after 120 min (Fig. 3B), equivalent to a two-fold higher mineralization, compared to the single addition of Fenton reagents.

3.3.2. Influence of pH on antibiotics degradation

The photo-Fenton/UVC process was evaluated at pH 2.5, 4.7, and 7.4. A lower efficiency at high pH values is related to the formation and precipitation of iron hydroxide, which affects the degradation process.

At pH 2.5, the global degradation of the antibiotics reached 100% after only 30 min of treatment, with k_{obs} increasing in the order 0.11 (SMZ), 0.12 (CIP), 0.27 (STZ), and 0.29 min⁻¹ (AMX) (Table 3). The DOC removal was 38%, and the H₂O₂ was completely consumed in 90 min (Fig. 4A). In this case, acidification of the sample before the

start of the experiments removed most of the carbonate/bicarbonate present in the effluent (83.37 mg L⁻¹), which would otherwise have scavenged the hydroxyl radicals formed. The acidified sample required stirring for 30 min in order to decrease the carbonate concentration to 2.5 mg L⁻¹ IC.

At pH 4.7, the initial IC concentration was 8.2 mg L⁻¹, while the TOC concentration remained almost constant. The global removal of the antibiotics was 85% after 30 min, with k_{obs} values ranging from 0.087 to 0.22 min⁻¹ for the different compounds (Table 3). The DOC removal was 25% at 90 min, with 94% consumption of the hydrogen peroxide (Fig. 4B). At the natural pH, the global degradation of the antibiotics after 30 min was slightly lower than at pH 2.5, with 8.5% removal of DOC (Fig. 4C). Overall, it could be seen that the decrease of pH from 7.4 to 4.7 and to 2.5 resulted in higher rates of degradation of the antibiotics, as well as greater mineralization.

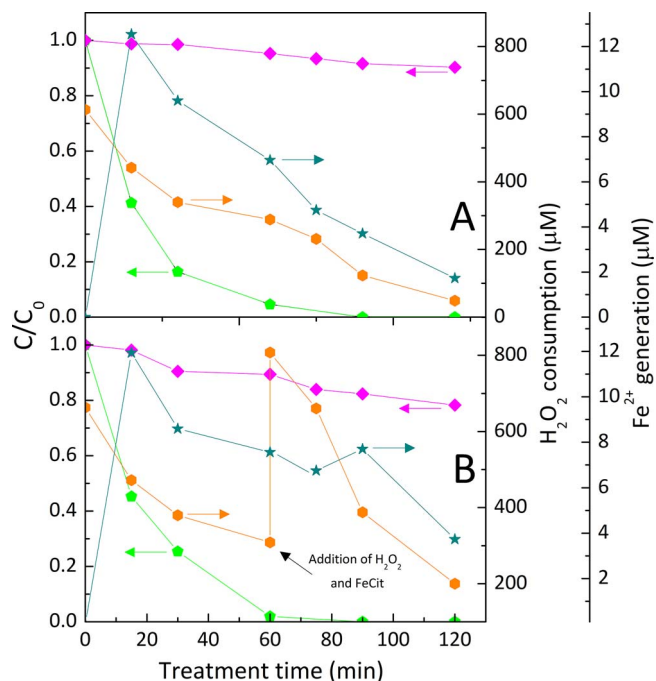


Fig. 3. Influence of single (A) and double (B) addition of H₂O₂ and FeCit on degradation of the antibiotics mixture in the AHE by the photo-Fenton process. Experimental conditions: [H₂O₂] = 500 μM; [FeCit] = 10 μM; [AMX] = [CIP] = [STZ] = [SMZ] = 200 μg L⁻¹; pH_{initial} = 7.4; TOC_{initial} = 10.1 mg L⁻¹; IC_{initial} = 74.5 mg L⁻¹. Symbols: (●) Σ antibiotics; (◆) DOC; (★) Fe²⁺; (●) H₂O₂.

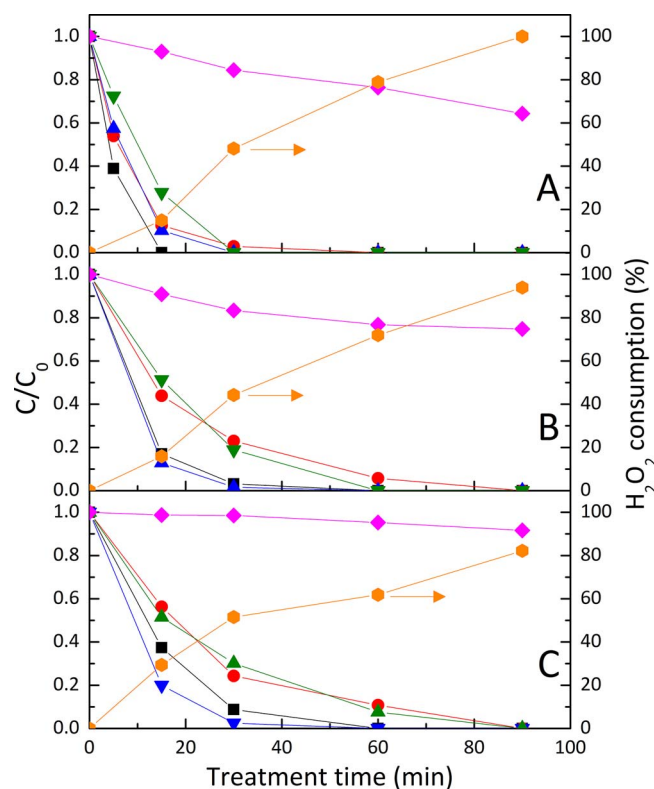


Fig. 4. Effect of pH on degradation of the antibiotics mixture in the AHE by the photo-Fenton process. Experimental conditions: [H₂O₂] = 500 μM; [FeCit] = 10 μM; [AMX] = [CIP] = [STZ] = [SMZ] = 200 μg L⁻¹. (A) pH_{initial} = 2.5; TOC_{initial} = 8.6 mg L⁻¹; IC_{initial} = 2.5 mg L⁻¹. (B) pH_{initial} = 4.7; TOC_{initial} = 8.3 mg L⁻¹; IC_{initial} = 8.2 mg L⁻¹. (C) pH_{initial} = 7.4; TOC_{initial} = 10.1 mg L⁻¹; IC_{initial} = 74.5 mg L⁻¹. Symbols: (■) AMX; (●) CIP; (▲) STZ; (▼) SMZ; (◆) DOC; (●) H₂O₂.

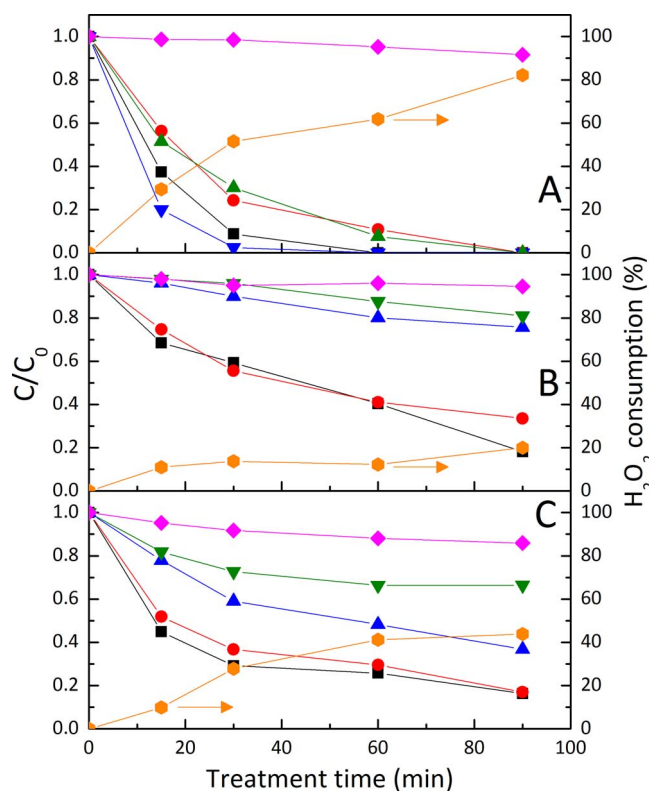


Fig. 5. Comparison of photo-Fenton processes using UVC lamp (A), UVA lamp (B), and sunlight irradiation (C) for degradation of the antibiotics mixture in the AHE. Experimental conditions: $[H_2O_2] = 500 \mu M$; $[FeCit] = 10 \mu M$; $[AMX] = [CIP] = [STZ] = [SMZ] = 200 \mu g L^{-1}$; $pH_{initial} = 7.4$; $TOC_{initial} = 10.1 mg L^{-1}$; $IC_{initial} = 74.5 mg L^{-1}$. Symbols: (■) AMX; (●) CIP; (▲) STZ; (▼) SMZ; (◆) DOC; (○) H_2O_2 .

3.3.3. Effect of irradiation source on antibiotics degradation

Iron complexes absorb in the near UV and up to 450 nm, suggesting that solar irradiation could be used to promote the degradation of the antibiotics, hence reducing the cost of irradiation. Therefore, the efficiency of degradation of the antibiotics at the natural pH of the effluent (AHE) was compared using three sources of radiation: UVC lamp, UVA lamp, and solar.

Use of the UVC/ H_2O_2 / $FeCit$ system resulted in total degradation of the antibiotics and 8.5% mineralization after 90 min, with 82% consumption of the hydrogen peroxide (Fig. 5A). Under these conditions, there were synergistic effects among the photo-Fenton reaction, H_2O_2 photolysis, and photolysis of the antibiotics. The germicidal lamp with maximum emission at 254 nm could photolyze both hydrogen peroxide and the target compounds, as well as photochemically reduce Fe^{3+} to Fe^{2+} , hence enhancing the Fenton reaction. In control experiments at pH 7.4, using only hydrogen peroxide or $FeCit$, in the absence of UVC light, no degradation of the antibiotics was observed after 60 min.

Using the black light lamp as the radiation source, with maximum emission at 365 nm, global degradation of the antibiotics at the end of the experiment was only 47%, much lower than the value obtained with the germicidal lamp (100%). The DOC removal was 4.5% and only 20% of the H_2O_2 was consumed after 90 min (Fig. 5B). The calculated kinetic parameters (Table 3) indicated that degradation of the sulfonamide antibiotics (STZ and SMZ) was severely restricted when the black light lamp was used, with rate constants of 0.0033 and 0.0024 min^{-1} , respectively. These values were approximately 40 and 20 times lower than the k_{obs} values of 0.14 and 0.043 min^{-1} obtained using the germicidal lamp.

Under solar irradiation, global antibiotics degradation of 66% was obtained after 90 min, with 43% consumption of H_2O_2 and 11% mineralization (Fig. 5C). Higher degradation of the antibiotics was

observed under sunlight than under the black light lamp. In this case, the sunlight UVA energy dose during treatment for 90 min was 14.1 $J cm^{-2}$, while the energy dose provided by the black light lamp was only 4.62 $J cm^{-2}$, approximately three times lower. Solar radiation has a much broader spectral range than the radiation from black light lamps, resulting in greater photoreduction of $Fe(III)$ following absorption of the radiation by the $Fe(III)$ -citrate complex. Although the predominant $FeCit$ species at pH 4–6 ($Fe(OH)(Cit)^-$) shows lower photoactivity (with a quantum yield of $Fe(II)$ of 0.28–0.21 at 436 nm [25,52]), the values are higher than those observed with iron aqua complexes.

The UVC radiation provided the best degradation of the antibiotics, since it played an important role in various individual processes, resulting in greater overall efficiency. However, despite the lower efficiency of the solar process, the possibility of saving energy costs is an important advantage. Despite the inherent variability of solar radiation, the results indicated that it could be effective for removal of antibiotics from hospital effluents using the photo-Fenton process.

3.3.4. Effect of the matrix on antibiotics degradation

Evaluation was made of the photodegradation of the antibiotics present in the AHE and RHW media. These effluents differ considerably, especially in terms of TOC, IC, and BOD, so comparison of the degradation behaviors could provide information concerning the influence of these parameters. Both CO_3^{2-}/HCO_3^- and organic carbon can hinder the efficiency of the process, due to $\cdot OH$ scavenging in side reactions, hence decreasing the process efficiency.

The AHE contained 94.51 $mg L^{-1}$ of TC, of which 83.37 $mg L^{-1}$ was IC, and 14.0 $mg L^{-1}$ COD. The RHW showed higher TC of 185.9 $mg L^{-1}$, with 70.71 $mg L^{-1}$ of IC, and 168 $mg L^{-1}$ COD. No adjustment of pH was applied, with the experiments being performed at the natural pH values of 7.4 (AHE) and 7.6 (RHW).

Global degradation of the antibiotics in the AHE reached 83% in 30 min, with removal of approximately 1 mg of TOC (corresponding to 8.5% mineralization of AHE) and 82% hydrogen peroxide consumption at the end of the experiment (Fig. 6A). The initial rate constants, in ascending order, were 0.038, 0.043, 0.081, and 0.14 min^{-1} for CIP, SMZ, AMX, and STZ, respectively (Table 3). The H_2O_2 concentration used was approximately 5 times higher than the stoichiometric amount (111 μM) required for total degradation of 2.5 μM of the antibiotics ($4 \times 200 \mu g L^{-1}$) to CO_2 , water, and inorganic ions. Although the stoichiometric amount of hydrogen peroxide necessary for complete oxidation of the organic matter in the AHE was 8.75 mM, a much lower H_2O_2 concentration was used, since the main goal of the tertiary photo-Fenton treatment proposed in this work was the degradation of antibiotics present at very low concentrations, rather than total mineralization of the effluent.

Despite the greater complexity of the RHW, compared to the AHE, the rate constants for degradation of the antibiotics were very similar for CIP and SMZ, while the value decreased by 50% in the case of STZ (Table 3). The initial rate constants, in ascending order, were 0.033, 0.039, 0.054, and 0.075 min^{-1} for SMZ, CIP, AMX, and STZ, respectively. The global degradation achieved after 30 min was 74%, with 66% consumption of H_2O_2 and 16% mineralization at the end of the experiment.

It is possible that the presence of nitrate may have increased the degradation rates of the contaminants, due to the formation of OH radicals by nitrate photolysis. This effect was observed previously using irradiation at wavelengths shorter than 280 nm [53], as in the case of the germicidal lamp employed in this work. It has also been found that the presence of DOM can accelerate the degradation of contaminants by the formation of oxidizing species such as singlet oxygen, H_2O_2 , and $\cdot OH$ [54].

In addition, adsorption onto particulate matter has been reported for some classes of antibiotics, including tetracyclines, sulfonamides, and fluoroquinolones [55]. Aristilde and Sposito [56] observed

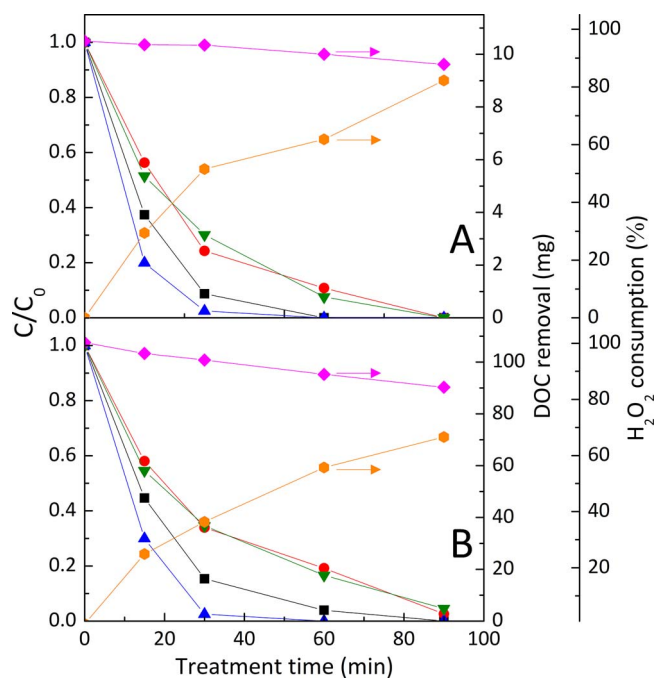


Fig. 6. Influence of the matrix on degradation of the antibiotics mixture in the AHE (A) and RHW (B) using the photo-Fenton process. Experimental conditions: $[H_2O_2] = 500 \mu M$; $[FeCit] = 10 \mu M$; $[AMX] = [CIP] = [STZ] = [SMZ] = 200 \mu g L^{-1}$. (A) $pH_{initial} = 7.4$; $TOC_{initial} = 10.1 mg L^{-1}$; $IC_{initial} = 74.5 mg L^{-1}$. (B) $pH_{initial} = 7.6$; $TOC_{initial} = 105.1 mg L^{-1}$; $IC_{initial} = 64.6 mg L^{-1}$. Symbols: (■) AMX; (●) CIP; (▲) STZ; (▼) SMZ; (◆) DOC; (○) H_2O_2 .

complexation of the zwitterionic form of CIP in protonated humic substances. Given that antibiotics of the fluoroquinolone class (such as CIP) have sorption coefficients (k_d) ranging from 70 to 353,000 $kg L^{-1}$, the sorption of CIP onto solid matrices could be the primary mechanism for its removal from effluent [57,58], since the concentration of total dissolved solids was in the region of 340 $mg L^{-1}$ (Table 1).

However, the concentrations of the spiked antibiotics in RHW did not alter significantly after stirring in the dark for 1 h, indicating that sorption/complexation of the antibiotics involving the constituents of this matrix did not occur and that the main removal mechanisms were oxidation by photogenerated $\cdot OH$ and photolysis during irradiation.

The chromatograms obtained for the RHW and AHE before the photo-Fenton treatment revealed the presence of several compounds with high intensity peaks, especially for the AHE, with retention times of 6.6, 7.3, and 16.9 min, while the RHW chromatogram showed major peaks at retention times of 15.2, 15.9, and 16.8 min (Fig. 7A). After application of the photo-Fenton process to the AHE, resulting in treated hospital effluent (THE), the aforementioned peaks disappeared and a new peak appeared at 17.9 min, possibly due to a degradation product of contaminants present in the effluent.

The UV-vis spectra of the RHW, AHE, and THE samples (inset of Fig. 7A) showed a slight decrease of absorbance after the anaerobic treatment and the photo-Fenton/UVC process, indicating the degradation of absorbing organic matter.

The chromatogram for the spiked AHE (using 200 $\mu g L^{-1}$ of each antibiotic and 10-fold preconcentration) showed peaks at 5.0, 13.8, 15.7, and 18.3 min, corresponding to AMX, STZ, CIP, and SMZ, respectively, together with other peaks for compounds already present in the effluent. After 15 min of photo-Fenton treatment, the intensities of the antibiotic peaks showed sharp decreases, while no antibiotics were detected after 90 min, indicating their oxidation to levels below the detection limit (Fig. 7B). Carboxylic acids including citric, succinic, and acetic acids were identified in the AHE (data not shown), which were also degraded to levels below the detection limit during the photo-Fenton process. These acids present in the AHE were formed during the

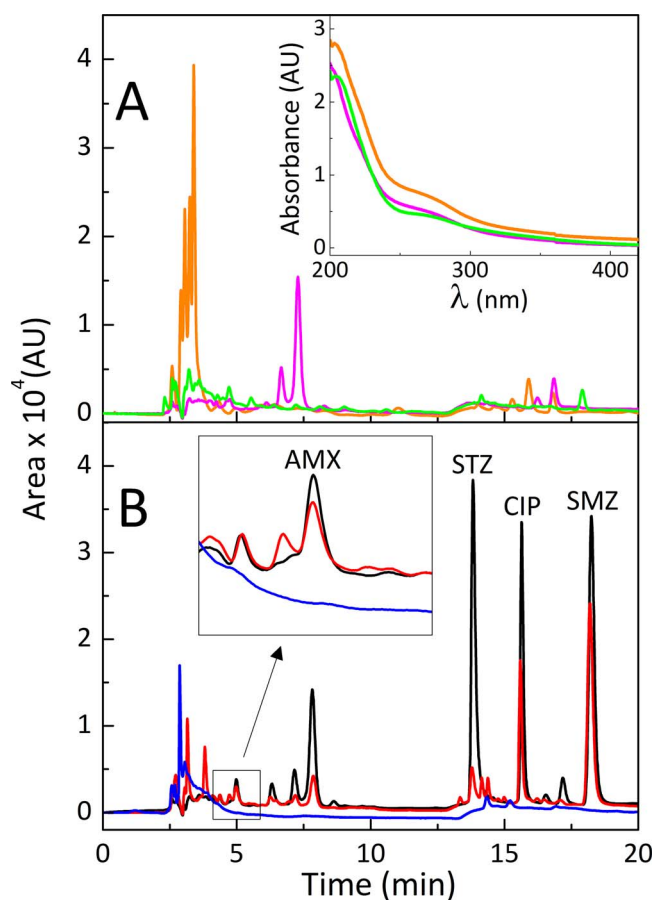


Fig. 7. Chromatograms obtained for the RHW, AHE, and THE (A). Chromatograms for the AHE fortified with antibiotics during the photo-Fenton process ($\lambda = 254 nm$) (B). Inset: UV spectra of the RHW, AHE, and THE. Experimental conditions: $[H_2O_2] = 500 \mu M$; $[FeCit] = 10 \mu M$; $[AMX] = [CIP] = [STZ] = [SMZ] = 200 \mu g L^{-1}$. Symbols: (A) (—) RHW; (—) AHE; (—) THE. (B) (—) 0 min; (—) 15 min; (—) 90 min.

biological treatment process applied to the RHW. In the particular case of succinic acid, succinate could be released because it is a counter ion used in certain pharmaceuticals in order to increase their solubility in water.

After 90 min of photo-Fenton/UVC treatment, the RHW and AHE both became more translucent (Fig. 1S), with significant reductions of their strong odors, hence improving the quality of the final effluent to be discharged.

3.4. Disinfection of anaerobic hospital effluent by the photo-Fenton/UVC process

In addition to the antibiotics content of hospital effluents, another important hazard concerns the presence of pathogens. Therefore, it is important to employ a treatment process able to efficiently remove both antibiotics and pathogens. The quantification of total coliforms and *E. coli* in the RHW revealed the presence of 2.6×10^8 and 7.0×10^6 colony-forming units per 100 mL (CFU/100 mL), respectively. The AHE showed slightly lower values of 3.8×10^7 and 2.5×10^5 CFU/100 mL for total coliforms and *E. coli*, respectively, confirming the inefficiency of anaerobic treatment for the disinfection of hospital effluent (Fig. 8A).

The photo-Fenton treatment decreased the bacterial concentration of the *E. coli* and total coliforms (Fig. 8B). The photo-Fenton process assisted by UVA irradiation caused only slight reductions of total coliforms and *E. coli*, of 1-log and 0.4-log, respectively, in the AHE after 90 min of treatment. Considerably higher disinfection of the bacteria was obtained under solar irradiation (14.1 $J cm^{-2}$ energy dose), with 3.7-log and 2.4-log reductions achieved for total coliforms and *E. coli*,

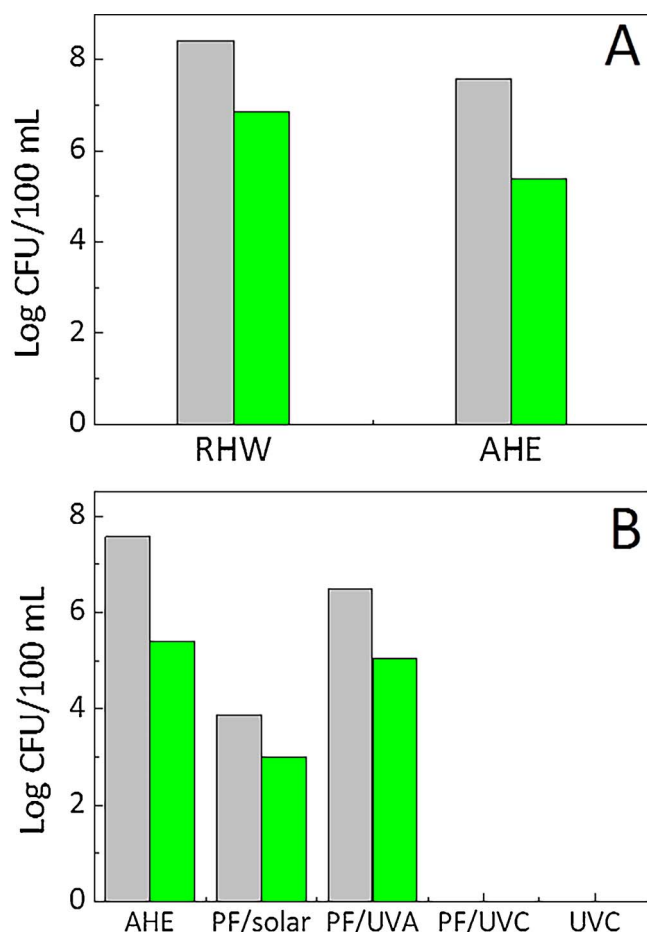


Fig. 8. Counts of bacteria present in the RHW and AHE (A). Inactivation of bacteria present in the AHE after UVC and photo-Fenton (UVC, UVA, and solar) processes (B). Experimental conditions: $[H_2O_2] = 500 \mu M$; $[FeCit] = 10 \mu M$; $pH_{initial} = 7.4$; treatment time = 90 min. Symbols: (grey) total coliforms; (green) *E. coli*.

respectively. However, as already mentioned, the accumulated energy dose provided by the UVA lamp was lower ($4.62 J cm^{-2}$), which contributed to the lower bacterial disinfection. The $\cdot OH$ formed in the photo-Fenton reaction can induce reactions involving lipids, proteins, and DNA, causing lethal effects in bacteria [59,60]. In addition, the bacterial disinfection during photo-Fenton treatment can be caused by the diffusion of Fe^{2+} into the cells, where $\cdot OH$ can then be produced during internal Fenton reactions [61].

Irradiation with UVC alone or in the presence of FeCit ($10 \mu M$) and hydrogen peroxide ($500 \mu M$) resulted in the quantitative disinfection of total coliforms and *E. coli* present in the AHE to levels below the quantification limits after 90 min (Fig. 8B). The exposure of bacteria to UVC radiation results in damage to the nucleic acids, causing inactivation [62].

A previous study reported the incomplete inactivation of total coliforms present in a sewage treatment plant effluent, using a solar photo-Fenton system at natural pH, with $0.2 mM$ of iron and $1.5 mM$ of H_2O_2 [63]. Elsewhere, total disinfection of *E. coli* in Milli-Q water was obtained using a solar photo-Fenton system with concentrations of additives ($10.7 \mu M Fe^{2+/3+}$ and $300 \mu M H_2O_2$) similar to those employed in the present work [59]. The disinfection efficiency of UVC is highly dependent on the type of matrix. In the present case, the proposed system (UVC/ H_2O_2 /FeCit) was effective for the disinfection of total coliforms and *E. coli* in the effluent matrices evaluated.

4. Conclusions

UVC-assisted photo-Fenton treatment of anaerobic hospital effluent spiked with four antibiotics at $\mu g L^{-1}$ levels was successfully applied at near-neutral pH (7.4), with the use of citric acid as a complexation agent. Although prior anaerobic treatment of raw hospital wastewater was able to efficiently remove the biochemical oxygen demand, chemical oxygen demand, total organic carbon, and total nitrogen, the concentrations of the antibiotics ciprofloxacin and sulfadiazine remained at $\mu g L^{-1}$ levels, demanding further treatment.

Although the highest rates of degradation of the antibiotics were achieved at pH 2.5, application of the FeCit/ H_2O_2 /UVC treatment at pH 7.4 resulted in complete degradation of all the antibiotics and disinfection of total coliforms and *E. coli* after 90 min.

The photo-Fenton treatment could also be applied directly to the raw hospital wastewater, without any significant difference in degradation of the antibiotics. In addition, the ability to use solar irradiation is attractive due to the potential savings in the energy costs of photo-Fenton treatment.

The photo-Fenton/UVC process was effective for the treatment of hospital wastewater, where high organic loads and the presence of pharmaceuticals and pathogens can lead to harm to the aquatic environment and human health.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.11.021>.

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