Applied Catalysis B: Environmental 224 (2018) 761–771

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

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

João A. Lima Perini[a,*], Adriano L. Tonetti[b], Cristiane Vidal[c], Cassiana C. Montagner[c], Raquel F. Pupo Nogueira[a]

[a] Department of Analytical Chemistry, Institute of Chemistry of Araraquara UNESP, São Paulo State University, P.O. Box 355, 14801-970, Araraquara, SP, Brazil
[b] School of Civil Engineering, Architecture and Urban Design-FEC, UNICAMP, University of Campinas, P.O. Box 6021, 13083-852, Campinas, SP, Brazil
[c] Department of Analytical Chemistry, Institute of Chemistry of Campinas, UNICAMP, University of Campinas, P.O. Box 6154, 13083-970, Campinas, SP, Brazil

ARTICLE INFO

Keywords:
Anaerobic treatment
Hydroxyl radical
Photolysis
Pharmaceuticals
Bacterial disinfection

ABSTRACT

A UVC-assisted photo-Fenton process was applied to hospital wastewater that had been submitted to anaerobic treatment. Low iron (10 μM; 0.56 mg L^{-1}) and H_2O_2 (500 μM; 17 mg L^{-1}) concentrations were used at the natural pH of the effluent (pH ≈ 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 μg 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

* Corresponding author.
E-mail address: joaoperini@gmail.com (J.A.L. Perini).

https://doi.org/10.1016/j.apcatb.2017.11.021
Received 21 August 2017; Received in revised form 7 November 2017; Accepted 9 November 2017
Available online 10 November 2017
0926-3373/

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 O_3 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 (•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 •OH is generated from a mixture of H_2O_2 and Fe^{2+} 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 photoreduction of Fe^{3+} to Fe^{2+} and establishing an Fe(II)/Fe(III) cycle in the Fenton reaction, besides generating extra •OH (Eq. (2)) [20].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \quad (k = 70\ M^{-1}\,s^{-1}) \qquad (1)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \cdot OH \qquad (2)$$

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 Fe^{2+}, compared to iron aqua complexes [22–24]. Furthermore, Fe^{3+}-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, BOD_5, 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%) ($C_{17}H_{18}FN_3O_3 \cdot HCl \cdot H_2O$), amoxicillin trihydrate (AMX) (97%) ($C_{16}H_{19}N_3O_5S \cdot 3H_2O$), sulfathiazole (STZ) (99%) ($C_9H_9N_3O_2S_2$), sulfamethazine (SMZ) (99%) ($C_{12}H_{14}N_4O_2S$), sulfadiazine (SDZ) (99%) ($C_{10}H_{10}N_4O_2S$), sulfadoxin-d3 (S-d3) ($C_{12}D_3H_{11}N_4O_4S$), and enrofloxacin-d5 hydrochloride (E-d5) ($C_{19}D_5H_{17}FN_3O_3 \cdot HCl$) (Table 1S) were obtained from Fluka (St. Louis, MO, USA). $Fe(NO_3)_3 \cdot 9H_2O$ (Mallinckrodt, Paris, KY, USA) was used to prepare aqueous 0.25 M iron stock solution. H_2O_2 (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 H_2SO_4 (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 H_2O_2/HNO_3. The variables COD, BOD_5, PO_4^{3-}, 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, Fe^{2+} and H_2O_2 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