Journal of Environmental Management xxx (2017) 1–9

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

Abatement and toxicity reduction of antimicrobials by UV/H_2O_2 process

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ARTICLE INFO

Article history:
Received 5 December 2016
Received in revised form
8 February 2017
Accepted 12 February 2017
Available online xxx

Keywords:
Advanced oxidation process
Antimicrobial activity
Ofloxacin
Peroxidation
Photolysis
Sulfaquinoxaline

ABSTRACT

Antimicrobials are continuously detected in environmental waters and their removal is important to avoid health and microorganisms damage. In this work, the peroxidation assisted by ultraviolet radiation (UV/H_2O_2) was studied to verify if the process was able to degrade sulfaquinoxaline and ofloxacin antimicrobials and to remove the toxicity and the antimicrobial activity of the solution. This process was effective on degradation of the antimicrobials, despite the antimicrobial activity removal, the toxicity of the solution increased throughout the reaction time.

1. Introduction

Contaminants of emerging concern (CECs) can be defined as natural or synthetic substances which can be present in environmental matrices and their adverse effects for human health and toxicity to aquatic and terrestrial organisms are not completely known in long term (Geissen et al., 2015); most of them are unregulated. The CECs group covers human and veterinary pharmaceuticals, hormones, personal care products, surfactants, plasticizers, industrial additives, and others (Petrović et al., 2003; Sauvé and Desrosiers, 2014). Consequently, the main sources of CECs are domestic and hospital wastewater, water and wastewater from treatment plants, livestock, and agriculture.

Generally, pharmaceutical compounds such as antimicrobials are only partially metabolized by humans and other animals and are excreted in non-metabolized form or as active metabolites via feces and/or urine (Hapeshi et al., 2010; Kummerer, 2009). There is a concern on the scientific community about the presence of antimicrobials and its continuous introduction on environment, because even in low concentrations (ng L^{-1} and μg L^{-1}), they are persistent and their degradation products can be more harmful than the parent compound (Kummerer, 2009). This has given rise to significant efforts to develop effective means of minimizing exposure of environmental microbiota to antimicrobial compounds, mainly evaluating treatment technologies for effective abatement of these compounds from water. The advanced oxidation processes are technologies used for disinfection and decontamination of water, wastewater, air and soil. These processes are efficient due to the generation of oxidants species such as hydroperoxyl radical ($HO_2^{\bullet}$), superoxide radical ($O_2^{\bullet-}$), and mainly the hydroxyl radical ($HO^{\bullet}$), that is a non-selective and strong oxidant (2.8 V/SHE).

Sulfaquinoxaline (SQX) and ofloxacin (OFX) are antimicrobial agents of the sulfonamide and fluoroquinolone class, respectively (Fig. 1), two of the main classes of antimicrobials found in water (Chen and Zhou, 2014; Li et al., 2012; Ma et al., 2015). They have a broad-spectrum antimicrobial effect against Gram-positive and Gram-negative bacteria (De Liguoro et al., 2010; Dmitrienko et al., 2014; Zivanovic et al., 2006) and have been detected in raw effluent (Dorival-García et al., 2013; Wei et al., 2011), groundwater and surface water (Chen and Zhou, 2014; Li et al., 2012; Ma et al., 2015; Sun et al., 2015; Zhao et al., 2015).

One of the concerns about the presence of antimicrobials in water is the risk of bacterial resistance, which leads to the prescription of higher doses of antimicrobials. Despite this, several

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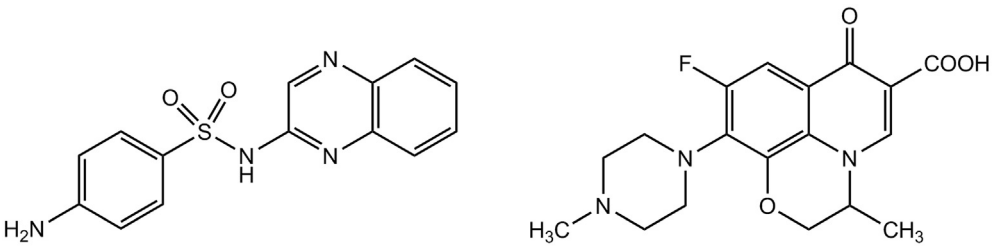
http://dx.doi.org/10.1016/j.jenvman.2017.02.028
0301-4797/



Sulfaquinoxaline
Chemical Formula: $C_{14}H_{12}N_4O_2S$
Molar Mass: 300.34 g mol^{-1}
pKa_1: 2.34 pKa_2: 5.97

Ofloxacin
Chemical Formula: $C_{18}H_{20}FN_3O_4$
Molar Mass: 361.37 g mol^{-1}
pKa_1: 6.05 pKa_2: 8.11

Fig. 1. Chemical structures of the sulfaquinoxaline (sulfonamide) and ofloxacin (fluoroquinolone) antimicrobials (Şanli et al., 2009; Barbosa et al., 1997).

studies about sulfaquinoxaline and ofloxacin degradation by advanced oxidation processes (AOPs) have been carried out. However, their focus is generally to evaluate the removal of the parent compound, and the residual toxicity and antimicrobial activity is neglected. The biological effects possibly induced by partial oxidation and/or formation of degradation products are rarely discussed (Bernabeu et al., 2011; Hapeshi et al., 2010; Klamerth et al., 2013; Liao et al., 2016; Michael et al., 2010, 2012; Miralles-Cuevas et al., 2013; Prieto-Rodriguez et al., 2012; Titouhi and Belgaied, 2016; Wols et al., 2013).

Ofloxacin degradation by UV/H_2O_2 process was previously studied by Afonso-Olivares et al. (2016), De la Cruz et al. (2012) and Lin et al. (2016). However, on these studies neither the removal of toxicity and antimicrobial activity of the samples after the degradation process nor the degradation products formed were evaluated. To the best of the author's knowledge, the remaining toxicity of sulfaquinoxaline solutions submitted to UV/H_2O_2 process was not previous reported. Thus, the present study adds important knowledge to the existing information.

UV/H_2O_2 consists of a combination of two well-known processes: direct photolysis with UV radiation and peroxidation (H_2O_2), leading to the generation of $HO^{\bullet}$ (Equation (1)), which makes this process more efficient at removing organic compounds than the application of peroxidation or photolysis separately.

$$H_2O_2 + h\nu \rightarrow 2HO^{\cdot} \quad (1)$$

The objectives of this work were to evaluate the degradation of two antimicrobials of sulfonamide and fluoroquinolone classes, and to monitor the residual toxicity and the antimicrobial activity throughout the reaction time.

2. Material and methods

2.1. Chemicals

Sulfaquinoxaline (PESTANAL®, 97.8% w/w, $C_{14}H_{12}N_4O_2S$, 300.34 g mol^{-1}), ofloxacin (99.8% w/w, $C_{18}H_{20}FN_3O_4$, 361.368 g mol^{-1}) and oxalic acid (99.5% w/w) were purchased from Sigma-Aldrich; formic acid (>98%, CH_2O_2) was from Merck; hydrogen peroxide (30% w/w, H_2O_2), sulfuric acid (97% v/v, H_2SO_4) and sodium hydroxide (97% w/w, NaOH) were from Synth; methanol (HPLC grade, CH_3OH) and $BaCl_2 \cdot 2H_2O$ (99% w/w) were from J. T. Baker; ammonium metavanadate (99%, NH_4VO_3) was from Honeywell Riedel-de Haën; potassium permanganate (99.5%, $KMnO_4$) and sodium oxalate (99.8%, $Na_2C_2O_4$) was from Ecibra; and phosphoric acid (85% v/v, H_3PO_4) was from Nuclear. *Escherichia coli* ATCC® 23716 was obtained from ATCC (Manassas); marine bacterium *Vibrio fischeri*, reconstitution solution (0.01% NaCl), diluent (2% NaCl), and osmotic adjusting solution (22% NaCl) were purchased from Modern Water Inc. Mueller-Hinton broth cultures and Mueller-Hinton Agar were purchased from Himidia. Ultrapure water was obtained from a Milli-Q water purification system (Millipore).

Sulfaquinoxaline and ofloxacin stock solutions (500 mg L^{-1}) were prepared by diluting the standards in methanol. They were stored at 4 °C and protected from light. The working solutions (500 μg L^{-1}) were obtained by appropriate dilution of the stock solution in 1 L of ultrapure water.

2.2. Experimental setup

Degradation assays were performed in duplicate, using a photochemical reactor made of borosilicate glass (38.5 cm long, 3.5 cm inner diameter) and volume of 190 mL. In the center of the tube, a low pressure mercury lamp (15 W, $\lambda_{max} = 254$ nm, internal diameter of 2.1 cm) was inserted. The irradiance of 6.95 mW cm^{-2} was measured using a radiometer calibrated at 254 nm (VLX 3W model, Cole Parmer). The lamp was in direct contact with the solution.

The operation of the system was in batches containing 1 L of the solution with recirculation at a flow rate of 0.1 L min^{-1}. The experimental system consisted of a reservoir, a magnetic stirrer to keep the solution homogeneous and a peristaltic pump to recirculate the solution to the photochemical reactor. A similar experimental system was previously used by Da Silva et al. (2011), De Oliveira et al. (2015), Guadagnini et al. (2013), and Peres et al. (2015).

The assay time varied between 0 and 60 min, which corresponded to the following irradiation times: 0; 1.9; 2.9; 5.7; 8.6 and 11.4 min. The radiation dose was calculated as previously described by Da Silva et al. (2011) and ranged between 793 mJ cm^{-2} for 10 min of assay and 4757 mJ cm^{-2} for 60 min of assay.

The hydrogen peroxide initial concentrations ranged from 0.8 to 9.0 mmol L^{-1} (27.2–306 mg L^{-1} H_2O_2). Hydrogen peroxide consumption was measured by oxidation-reduction reaction between a metavanadate ion solution (yellow color) and H_2O_2 present in the solution, resulting in red staining solution (peroxyvanadium cation formation) which exhibits maximum absorbance at 450 nm, according to the method described by Nogueira et al. (2005), with some modifications. Potassium permanganate was used instead of potassium ferrioxalate and the quantification limit was 0.03 mmol L^{-1} H_2O_2. The assays were carried out at the original pH

Please cite this article in press as: Urbano, V.R., et al., Abatement and toxicity reduction of antimicrobials by UV/H_2O_2 process, Journal of Environmental Management (2017), http://dx.doi.org/10.1016/j.jenvman.2017.02.028