



Research article

Influence of pH and ozone dose on sulfaquinoxaline ozonation



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ARTICLE INFO

Article history:

Received 15 February 2016

Received in revised form

4 August 2016

Accepted 8 August 2016

Available online 21 August 2016

Keywords:

Advanced oxidation processes

Microtox

Molecular ozone

Sulfonamides

Toxicity assays

ABSTRACT

Sulfaquinoxaline (SQX) is an antimicrobial of the sulfonamides class. Usually employed in veterinary medicine, this contaminant of emerging concern has been found in superficial and groundwater and its consequences for the environment and human health are not completely known. In this study, SQX ($C_0 = 500 \mu\text{g L}^{-1}$, 1 L) degradation by an ozonation process at pH 3, 7, and 11 was evaluated. Ozonation was effective in degrading SQX: efficiency exceeding 99% was obtained applying an ozone dose of 2.8 mg L^{-1} at pH 3. Assays were performed according to a 2^2 design of experiments (DOE) with star points and three central points for statistical validity. Minimum and maximum levels were set at 3 and 11 for pH, and 0 and 11.5 mg L^{-1} for applied ozone dose. There was no significant interaction between these variables, and the pH value played the most important role in terms of contaminant degradation. In relation to toxicity, samples ozonated at pH 3 did not inhibit the luminescence of the bacteria, even though different intermediates were formed and identified by mass spectra. At pH 7, inhibition of luminescence remained almost constant (at around 30%) according to ozonation time or ozone dose. However, the hydroxyl radical, the major oxidant at pH 11, was responsible for the formation of toxic intermediates.

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1. Introduction

Contaminants of emerging concern such as pharmaceuticals (antimicrobials and hormones) and human care products can reach municipal wastewater treatment plants, soil and water bodies (Aukidy et al., 2012; Gurke et al., 2015; Liu et al., 2015; Ma et al., 2015; Zhang et al., 2014; Zhou et al., 2013). These chemicals have been detected in treated drinking water and wastewater from treatment plants, showing that conventional treatment of water and wastewater has low efficiency in removing these compounds (Garoma et al., 2010). Moreover, many of these substances have environmental and health effects that have still not been clearly defined and reported.

Classified as contaminants of emerging concern, sulfonamides are an antimicrobial class routinely used in both human and veterinary medicine. Studies have detected and quantified sulfonamides in environmental matrices at concentrations ranging from 9 to 80 ng L^{-1} in mineral water (Perret et al., 2006),

$0.03\text{--}2978.6 \text{ ng L}^{-1}$ in surface water (Chen and Zhou, 2014; Iglesias et al., 2012; Perret et al., 2006; Wei et al., 2011; Zhao et al., 2015), $2.3\text{--}2290 \text{ ng L}^{-1}$ in effluent (Aukidy et al., 2012; Ma et al., 2015; Wei et al., 2011; Zhou et al., 2013), and $0.1\text{--}39.4 \text{ ng L}^{-1}$ in groundwater (García-Galán et al., 2011; Ma et al., 2015). Sulfaquinoxaline is a sulfonamide mainly used in veterinary treatment to prevent coccidiosis and bacterial infections (De Liguoro et al., 2010). Because of its low K_{ow} (47.9), it has been detected in surface water at concentrations ranging from 1.59 to 640 ng L^{-1} (Chen and Zhou, 2014; Iglesias et al., 2012; Wei et al., 2011; Zhao et al., 2015), in groundwater at concentrations of 39.4 ng L^{-1} (García-Galán et al., 2011), and in effluent at concentrations from 0.15 to 350 ng L^{-1} (García-Galán et al., 2010; Wei et al., 2011). This is an issue of great concern for ecosystems and human health, especially because the acute and chronic effects of antimicrobials are not well known and their presence could lead to the development of antibiotic-resistant bacteria (Lin et al., 2009; Hoa et al., 2011; Strauss et al., 2011).

The sulfonamides, which include sulfaquinoxaline, are derivatives of sulfanilic acid (*p*-aminobenzenesulfonic acid) and comprise one of the oldest classes of antimicrobials. Since the middle of the twentieth century, these compounds have been used for the treatment of humans and other animals (Dmitrienko et al.,

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2014). The physical-chemical characteristics of sulfaquinoxaline are described in Table S1 of the Supporting Information.

Suitable treatments are required to achieve the complete elimination of these compounds present in wastewater. Some processes used for water and wastewater treatment are adsorption, photolysis, advanced oxidation (Rostamian and Behnejad, 2016), and ozonation. Adsorption has been reported as an effective treatment option on removal of persistent contaminants, such as pharmaceuticals compounds, personal care products and a wide range of organic compounds (Ali et al., 2012; Alsbaiee et al., 2015; Qin et al., 2015; Rostamian and Behnejad, 2016; Yu et al., 2015). The disadvantage of this process is that adsorbents are usually efficient on removing contaminants in order of g L^{-1} (Ali et al., 2012) and sulfonamides have been found in the environment at low concentrations ($\mu\text{g L}^{-1}$) and at high complexity matrices. Moreover, in the adsorption process the target compound is usually transferred from the matrix to the adsorbent surface.

Advanced oxidation processes (AOPs) and ozonation are technologies that can be used to degrade and mineralize micropollutants. AOPs are oxidation methods based on the generation of free radicals including hydroxyl radicals (HO^\bullet), which are extremely reactive, with reaction rates on the order of 10^{10} – $10^{13} \text{ M}^{-1} \text{ s}^{-1}$ (EPA, 1999), and are less selective than other oxidants (for example, chlorine and molecular ozone). Hydroxyl radicals are produced from oxidizing agents such as ozone and hydrogen peroxide, often combined with UV irradiation and/or metallic or semiconductor catalysts. The main advantage of this process is its capacity to oxidize organic compounds to less toxic or more biodegradable forms, or even mineralize them to CO_2 and H_2O (Homem and Santos, 2011). High degradation efficiencies of AOPs have been reported for different classes of compounds, such as fluoroquinolones (Peres et al., 2015), tetracyclines (Yamal-Turabay et al., 2013), and sulfonamides (Liao et al., 2016).

Ozonation is an effective alternative to conventional treatments when the pollutant is present in water at concentrations on the order of ng L^{-1} or $\mu\text{g L}^{-1}$. Ozone has a high reduction potential (2.07 V), making it a powerful oxidant capable of oxidizing organic and inorganic compounds present in water. Two ozone oxidation pathways in aqueous solution are known: direct oxidation, and ozone decomposition with formation of HO^\bullet (which has a reduction potential of 2.8 V). It is known that the efficiency of ozonation largely depends on the rate of ozone decay.

Given this background, the main reasons for the present study of sulfaquinoxaline are as follows: (a) Brazil is the world's largest exporter of chicken meat (MAPA, 2016) and it is likely that with increased production, there will be a rise in the use of veterinary medicines for the treatment and prevention of diseases; (b) for more than seventy years, sulfonamides have been the most commonly used antimicrobial drugs, probably due to their high efficiency, relatively low cost, and broad spectrum of activity. There is generally no legislation concerning the presence of pharmaceuticals in environmental samples or foods, and their residues, which have been reported even at low concentrations, can cause unknown damage to human health and ecosystems (Dmitrienko et al., 2014; García-Galán et al., 2011; Iglesias et al., 2012); (c) sulfaquinoxaline has been detected in environmental waters (Chen and Zhou, 2014; García-Galán et al., 2010, 2011; Iglesias et al., 2012; Wei et al., 2011; Zhao et al., 2015), but there have been few studies of effective treatments for its removal from aqueous matrices; (d) there is evidence of the efficiency of AOPs applied to contaminants of emerging concern (Liao et al., 2016; Peres et al., 2015).

Recent studies have concluded that the ozonation process can effectively remove sulfonamides from water matrices (Bai et al., 2016; Garoma et al., 2010; Guo et al., 2015; Lin et al., 2009; Prieto-Rodríguez et al., 2013). However, the degradation of

sulfaquinoxaline by ozonation has not been reported in the literature. Due to this lack of information, the objectives of the present study were to evaluate sulfaquinoxaline ($C_0 = 500 \mu\text{g L}^{-1}$, 1 L) degradation and toxicity reduction, as a function of applied ozone dose, at different pH values. The effects of the variables pH and ozone dose were investigated using a design of experiments. Finally, evaluation was made of the degradation products formed during ozonation.

2. Methods

2.1. Chemicals

Sulfaquinoxaline (PESTANAL[®] analytical standard, $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_2\text{S}$, $300.34 \text{ g mol}^{-1}$) was purchased from Sigma-Aldrich; formic acid (98–100%, CH_2O_2) was from Merck; potassium iodide (KI), and sulfuric acid (97%, H_2SO_4) were from Synth; sodium hydroxide (97%, NaOH) was from Ecibra, and methanol (HPLC grade, CH_3OH) was from J.T. Baker. A culture of the luminescent bacterium *Vibrio fischeri* was purchased from Modern Water Inc. (Newark, Delaware, USA), together with the reconstitution solution (0.01% NaCl), diluent (2% NaCl), and osmotic adjusting solution (22% NaCl). Ultrapure water was obtained from a Milli-Q water purification system (Millipore).

2.2. Experimental setup

To evaluate sulfaquinoxaline degradation, working solutions ($500 \mu\text{g L}^{-1}$ or $1.67 \mu\text{mol L}^{-1}$) were prepared in 1 L of ultrapure water. This initial concentration was chosen to be closer to the concentration of SQX level found in the environment and because of the quantification limit of the equipment (Section 2.3.1). The experimental setup for the study consisted of an ozone generator (O3R Philozon), a glass contact column (50 cm height x 7 cm diameter, volume of 1000 mL), and a reaction vessel containing 2% potassium iodide, for ozone gas measurement. The ozone generator was able to produce $5.52 \pm 0.32 \text{ mg min}^{-1} \text{ L}^{-1} \text{ O}_3$, using ambient air (flow rate of 4.0 L min^{-1}) and an oxygen concentration unit. A glass diffuser was used to sparge ozone gas into the solution.

The initial sulfaquinoxaline concentration ($500 \mu\text{g L}^{-1}$) and ozone generation ($5.52 \pm 0.32 \text{ mg min}^{-1} \text{ L}^{-1} \text{ O}_3$) were kept constant during the experiments. Different initial pH values (pH 3, 7, and 11) were used during the evaluation of sulfaquinoxaline degradation. Sulfuric acid and sodium hydroxide were used to adjust the initial pH of the working solutions. The pH range used in this study was chosen to study the most effective oxidation mechanism of ozonation process to SQX degradation (ozonation by molecular ozone or hydroxyl radicals). This pH range was also evaluated by Caianelo et al. (2016), Lin et al. (2009) and Sumegová et al. (2013).

The experiments were conducted at room temperature ($20 \pm 1^\circ\text{C}$). The gaseous ozone concentration in the contact column was determined by a potassium iodide method (Method 2350 E; APHA, 2012). The applied ozone dose was obtained by multiplying the ozonation time (0–15 min) by the ozone generation ($5.52 \pm 0.32 \text{ mg min}^{-1} \text{ L}^{-1} \text{ O}_3$), and then dividing by the sample volume (van Leeuwen, 2015). The consumed ozone concentration was the difference between the ozone dosage at the inlet and outlet of the bubble column, measured using the KI solution, and varied according to the pH used and the ozonation time (between 0 and 15 min).

In the control experiment, oxygen gas was continuously bubbled into the solution at the same flow rate used in the ozonation experiments, and the results indicated that sulfaquinoxaline was not stripped from the aqueous phase.

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