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Research article

Multistage ozone and biological treatment system for real wastewater containing antibiotics

Rafaela B.P. Marcelino [a], Mônica M.D. Leão [a], Rochel M. Lago [b], Camila C. Amorim [a, *]

[a] Universidade Federal de Minas Gerais – UFMG, Department of Sanitary and Environmental Engineering, Av. Antônio Carlos nº 6627 Bairro Pampulha, Belo Horizonte, Brazil

[b] Universidade Federal de Minas Gerais – UFMG, Chemistry Department, Av. Antônio Carlos nº 6627 Bairro Pampulha, Belo Horizonte, Brazil

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ABSTRACT

In this study, a multistage treatment system was proposed to treat real pharmaceutical wastewater containing the antibiotic amoxicillin. Ozonation (O_3), and ozonation combined with aerobic biodegradation, were performed. The real pharmaceutical wastewater presented a high concentration of organic matter (TOC: 803 mg $C \cdot L^{-1}$ and COD: 2775 mg $O_2 \cdot L^{-1}$), significant amoxicillin content (50 mg L^{-1}) and acute ecotoxicity (Aliivibrio fischeri aTU: 48.22). Ozonation proved to be effective for amoxicillin degradation (up to 99%) and the results also indicated the removal of the original colour of the wastewater, with average consumption of 1 g of ozone. However, the ozonation system alone could not achieve complete mineralization. Therefore, a combination of ozonation and biodegradation in a multistage system was proposed in order to improve cost and treatment efficiency. The multistage treatment system presented promising results, achieving degradation of more than 99% of the amoxicillin, more than 98% of the original chemical oxygen demand (COD), and 90% of initial toxicity, with the consumption of approximately 500 mg of ozone. This indicates that this system could prevent dangerous and bio-recalcitrant antibiotics from entering water resources.

1. Introduction

There is growing concern about the currently specifically unregulated groups of pollutants, which, because of their toxic effects on the environment and human health, coupled with their high occurrence, render them subject to future regulation (Miralles-Cuevas et al., 2013). Such groups of pollutants include various globally widespread organic compounds, such as pesticides, dyes, pharmaceuticals, personal care products, polymers, and plastics. Antibiotics are chemical, natural, or synthetic pharmaceuticals that can eliminate or prevent the multiplication of pathogenic microorganisms. These drugs have been used extensively in human and veterinary medicine to treat diseases caused by bacteria and, in some cases, to prevent bacterial infections (Akmehmet Balcıoğlu and Ötker, 2003; Monteagudo et al., 2013).

The β-lactam antibiotics (penicillin derivatives, cephalosporins, monobactams and carbapenems) are one of the most important antibiotic groups, with their consumption in medicinal and veterinary therapy reaching 50–70% of the total amount of antibiotics applied in medicine in most countries (Gozlan et al., 2013). However, the complete metabolization of these pharmaceuticals by their consumers is extremely difficult to achieve. Consequently, they occur in municipal wastewater, as well as surface, ground, and drinking water, and in the soil. (Li et al., 2015; Wang et al., 2011). Moreover, the wastewater generated by the manufacturing operations of the pharmaceutical industry could be regarded as important sources of the antibiotics found in the natural water systems (Zheng et al., 2010).

Conventional WWTPs use biological processes to treat wastewater; however, these techniques are inefficient for the degradation of recalcitrant and dangerous compounds. In addition, the techniques are unable to remove effectively all the potentially hazardous constituents present in pharmaceutical wastewaters (Mascolo et al., 2010; Monteagudo et al., 2013).

Technologies have been studied for degrading antibiotics in synthetic solutions and for treating pharmaceutical wastewater. Interest has been growing in the application of Advanced Oxidation Processes (AOPs) for the treatment of antibiotics in water matrices. Ozonation, in particular, has been considered capable of oxidizing a

* Corresponding author.
E-mail address: camila@desa.ufmg.br (C.C. Amorim).

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wide range of antibiotics to simpler and more easily biodegradable compounds (Wang et al., 2011).

An extensive literature survey has pointed to a large amount of research on antibiotic ozonation. However, most of this research was conducted either by using pure antibiotic solutions or by using synthetic wastewaters containing a mix of these substances. Ozonation in pure antibiotic solutions such as amoxicillin (Andreozzi et al., 2005; Li et al., 2015), norfloxacin (Santos et al., 2015), clarithromycin (Lange et al., 2006), sulfamethoxazole (Dantas et al., 2008), oxytetracycline (Li et al., 2008), ciprofloxacin (De Witte et al., 2009), enrofloxacin (Guinea et al., 2009), tetracycline (Wang et al., 2011), and ampicillin (Jung et al., 2012), has been studied. Synthetic wastewater containing a mixture of ceftriaxone sodium, penicillin, and enrofloxacin (Akmehmet Balcıoğlu and Ötker, 2003), and sulfamethoxazole, sulfadimethoxine, sulfamethazine, tylosin, and erythromycin (Lin et al., 2009), were studied for treatment by ozonation.

However, fewer studies have focused on real pharmaceutical wastewater, a complex matrix with high organic and inorganic content that could compete with the target pollutant for the oxidizing agents; thus reducing the effectiveness of the removal of the antibiotic molecules (Lin et al., 2009; Xing et al., 2014).

Despite its high efficiency to degrade complex organic molecules, ozonation employed for the complete mineralization of organic matter could be expensive. Therefore, combining this method with other types of treatment, such as biodegradation in a multistage system, has been widely reported to reduce operating costs and enhance efficiency, and are usually applied as pretreatment in the combined treatment (Arimi et al., 2016; Oller et al., 2011).

Although the utilization of AOPs to treat wastewater containing pharmaceuticals compounds has been widely studied, the studies with cost-effective chemical and biological treatment combinations are incipient and scarce (Oller et al., 2011). In this context, if the original wastewater contained a considerable amount of biodegradable compounds, the pre-oxidation step with AOP would only cause the unnecessary consumption of chemicals, increasing the overall cost of the treatment (Arimi et al., 2016; Jochimsen et al., 1997; Oller et al., 2011).

Preliminary study indicated that the wastewater used in this study had a high concentration of biodegradable organic matter (Marcelino et al., 2016 #27); therefore, the aim of this study was to apply a multistage treatment system, comprising a combination of aerobic biological and ozonation processes, to treat real wastewater with amoxicillin.

2. Material and methods

2.1. Wastewater sampling and characterization

The wastewater in this study was a mixture of water, cleaning products, antibiotics, solvents, and excipients, which had been generated during the formulation of amoxicillin-based medicines. The samples were collected during one week-long of amoxicillin production at a pharmaceutical production facility. After collection, the samples were stored at 4 °C until the conduction of the tests.

The wastewater samples were characterized by measures of pH, conductivity, dissolved oxygen, turbidity (HACH 2100AN), total organic carbon (TOC) (Shimadzu, TOC-V CPN), chemical oxygen demand (COD, mg $O_2 \cdot L^{-1}$) (APHA, 2005), alkalinity (potentiometric method), total suspended solids (TSS) and volatile suspended solids (VSS) (APHA, 2005). Moreover, phosphate and chloride were determined using ion chromatography (850 Professional IC Methrom) (APHA, 2005).

2.2. Analytical methods

The degradation of organic matter was monitored by periodic sample collection, filtration with quantitative paper filters (125 mm C40, QUANTY) and subsequent analysis of TOC.

Amoxicillin was determined using HPLC (Agilent Technologies, Model 1260 Infinity), equipped with a reverse-phase Zorbax Eclipse Plus® C18 (4.6 × 150 mm, 5.0 μm). The mobile phase was methanol:water (55:45, v/v) at isocratic elution. The flow was maintained at 0.750 mL min^{-1}, and the monitored wavelength was 210 nm. The aliquots were filtered through 0.20 μm syringe filters (Millexs-GN, 25 mm, Millipore) before HPLC injection. The injection volume was 20 μL and the total run time was 10 min.

Spectrophotometric measurements (200–900 nm by a UV/Vis Lambda XLS – PerkinElmer – spectrophotometer) were performed to evaluate the aromaticity at 254 nm (Akmehmet Balcıoğlu and Ötker, 2003), and absorbance removal.

2.3. Aerobic biodegradability and acute ecotoxicity assays

The inherent aerobic biodegradability assays were performed according to the Zahn-Welles test methodology (OECD, 1992), with high nutrient and biomass concentrations (Marcelino et al., 2016).

The test was performed under aeration, in darkness and at room temperature (~25 °C), for 28 days. The degradation of the organic matter was monitored by periodic TOC analysis. The percentage of biodegradation (Dt) at time t was determined as follows (Eq. (1)):

$$D_t = \left[1 - \left(\frac{C_t - C_B}{C_A - C_{BA}}\right)\right] \times 100 \quad (1)$$

where C_A and C_{BA} are the TOC (mg L^{-1}) in the sample and in the blank, respectively, measured 3 h after the starting time, and C_t and C_B are the TOC (mg L^{-1}) in the sample and in the blank, respectively, measured at the sampling time t. According to the definition of the method, wastewater samples were considered biodegradable by the Zahn-Wellens methodology when D_t was higher than 70%.

Acute ecotoxicity tests were conducted using the luminescent marine bacteria *Aliivibrio fischeri*, according to the methodology described by De Souza Santos et al. (2014). The ecotoxicity results were analysed and compared, using the acute toxicity unit (aTU) after 30 min of exposure.

2.4. Ozonation conditions

The ozonation experiments were performed in a 1000 mL borosilicate glass bubble column reactor for 180 min at semi-batch conditions, in which the ozone-containing gas was continuously sparged through a cylindrical porous-stone diffuser, at ambient temperature (25 °C ± 6). The reactor was connected to an O_3 generator and an O_2 concentrator from air (Fig. 1). The O_3 outlet was forced into two gas absorption bottles, containing 500 mL of 1% KI solution, and the oxidant was quantified by the iodometric titration method (Poole and Cord-Ruwisch, 2004).

The amount of ozone consumed was determined from the difference between the inlet concentration (iodometric titration), the excess ozone dissolved in the wastewater (DPD colorimetric method) (Buchan et al., 2005) and the outlet concentrations. The average ozone-production rate in each oxygen flow was measured experimentally, and is presented in Table S1.

In order to infer the effects of the parameters that could be controlled and monitored in the ozonation system, oxygen flow rate and pH, on the removal of TOC from the wastewater, experimental design was performed, as described in Table S1.

The response surface methodology was used, together with the

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