WATER RESEARCH 65 (2014) 307–320

Available online at www.sciencedirect.com

ScienceDirect

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

Solar photocatalytic oxidation of recalcitrant natural metabolic by-products of amoxicillin biodegradation

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ARTICLE INFO

Article history:
Received 8 May 2014
Received in revised form
19 July 2014
Accepted 26 July 2014
Available online 7 August 2014

Keywords:
β-Lactam
Amoxicilloic acid
TiO_2 photocatalysis
Photo-Fenton mediated by ferrioxalate
Solar radiation
Compound parabolic collectors (CPCs)

ABSTRACT

The contamination of the aquatic environment by non-metabolized and metabolized antibiotic residues has brought the necessity of alternative treatment steps to current water decontamination technologies. This work assessed the feasibility of using a multi-stage treatment system for amoxicillin (AMX) spiked solutions combining: i) a biological treatment process using an enriched culture to metabolize AMX, with ii) a solar photocatalytic system to achieve the removal of the metabolized transformation products (TPs) identified via LC-MS, recalcitrant to further biological degradation. Firstly, a mixed culture (MC) was obtained through the enrichment of an activated sludge sample collected in an urban wastewater treatment plant (WWTP). Secondly, different aqueous matrices spiked with AMX were treated with the MC and the metabolic transformation products were identified. Thirdly, the efficiency of two solar assisted photocatalytic processes (TiO_2/UV or Fe^{3+}/Oxalate/H_2O_2/UV–Vis) was assessed in the degradation of the obtained TPs using a lab-scale prototype photoreactor equipped with a compound parabolic collector (CPC). Highest AMX specific biodegradation rates were obtained in buffer and urban wastewater (WW) media (0.10 ± 0.01 and 0.13 ± 0.07 $g_{AMX}\ g_{biomass}^{-1}\ h^{-1}$, respectively). The resulting TPs, which no longer presented antibacterial activity, were identified as amoxicilloic acid ($m/z = 384$). The performance of the Fe^{3+}/Oxalate/H_2O_2/UV–Vis system in the removal of the TPs from WW medium was superior to the TiO_2/UV process (TPs no longer detected after 40 min ($Q_{UV} = 2.6\ kJ\ L^{-1}$), against incomplete TPs removal after 240 min ($Q_{UV} = 14.9\ kJ\ L^{-1}$), respectively).

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http://dx.doi.org/10.1016/j.watres.2014.07.037
0043-1354/

1. Introduction

In the last decades, the use of antibiotics has evolved from preventing and treating human and veterinary infections to other applications in diverse areas, such as agriculture, aquaculture and animal husbandry (Martinez, 2009). To this date, β-lactams remain one of the most important and prescribed group of antibiotics (Sun et al., 2012; Versporten et al., 2011), with amoxicillin (AMX), a broad-spectrum and semi-synthetic penicillin, as one of most relevant of its class. AMX is poorly metabolized in the organism and, consequently, around 80–90% is excreted in its original form (Hirsch et al., 1999). Despite the high consumption, AMX is infrequently detected in environmental samples. Raw wastewater concentrations can vary from 0.02 to 6.9 μg L^{-1} and are easily eliminated by conventional treatments (Michael et al., 2013). The infrequent detection of AMX in the environment may be explained by low efficiency and sensitivity of extraction and detection methods, combined with the highly reactive β-lactam ring, which is broken under environmental conditions, such as alkaline conditions (pH 7.5–9.0), water hardness and by β-lactamase action (Babington et al., 2012; Deshpande et al., 2004; Hirsch et al., 1999; Jerzsele and Nagy, 2009). Nevertheless, the low persistence of AMX in water matrices may be compensated by its intensive use and continuous discharge into the environment (Daughton and Ternes, 1999).

Amoxicillin has low toxicity and, for that reason, direct effects in the environment are highly unlikely (Andreozzi et al., 2004). Nevertheless, indirect effects, such as propagation of β-lactam resistant bacteria (Martinez, 2009) and the impact of metabolites are more pressing concerns. Several studies reported an increasing proportion of β-lactam resistant organisms after wastewater treatment, which suggests that conventional WWTP may promote the spread of antibiotic resistance (Rizzo et al., 2013; Zhang et al., 2009). This could also explain the frequent presence of resistance genes in different environmental compartments such as surface and drinking water, a tendency reported for all the major antibiotic classes, including penicillins (Vaz-Moreira et al., 2014). Resistance against AMX and other penicillins can occur by different mechanisms, and deactivation of this group of antibiotics through the action of β-lactamases is one of the most common and relevant (Drawz and Bonomo, 2010). The products of AMX chemical or β-lactamase hydrolysis are, to some extent, more recalcitrant than the parent compound and for that reason, have been frequently detected in both environmental samples and animal tissue (Lamm et al., 2009; Pérez-Parada et al., 2011; Reyns et al., 2008). Amoxicilloic acid is one of the major metabolites and in addition to its recalcitrant behaviour, this compound retains allergenic properties that can cause adverse reactions in sensitive individuals (Torres et al., 2010).

Given the aforementioned detrimental effects, the development of treatment methods able to remove antibiotic residues and their by-products is henceforth an environmental priority. Advanced oxidation processes (AOPs) are known as highly efficient methods to treat otherwise recalcitrant organic pollutants. They are characterized by different ways of generating the highly reactive and non-selective hydroxyl radical (•OH) and other reactive oxygen species (Gogate and Pandit, 2004a, b). As a way of reducing operating costs, recent research has been focussing on the combination of AOPs able to use solar radiation as the source of UV photons, such as TiO_2/UV and the photo-Fenton process, with biological degradation as a pre- or post-treatment stage (Elmolla and Chaudhuri, 2011; González et al., 2008; Oller et al., 2011). Our research groups have previously dealt with each of these processes separately. Barreiros et al. (2003) and Lopes et al. (2013) successfully isolated bacteria commonly found in contaminated sites and applied them, *in situ*, for the biodegradation of an organic pollutant. Additionally, Pereira et al. (2013a, 2013b); Pereira et al. (2014) reported on the removal of antibiotics such as Amoxicillin, Oxytetracycline and Oxolinic Acid from aqueous solutions by solar TiO_2-assisted photocatalysis and by the ferrioxalate-mediated solar photo-Fenton process using a pilot-plant equipped with compound parabolic collectors (CPCs). Although Amoxicillin has been previously subject to several degradation studies via various AOPs (Ay and Kargi, 2011; Dimitrakopoulou et al., 2012; Homem et al., 2010; Mavronikola et al., 2009; Trovó et al., 2011), none has focused on the removal of common transformation products resulting from the slow transformation that the parent compound undergoes in aquatic environments (Gozlan et al., 2013; Längin et al., 2009; Nägele and Moritz, 2005). In this way, the aim of this study was to evaluate a multistage treatment for AMX-spiked solutions combining: i) a biological treatment step to metabolize the AMX molecule, with ii) a solar photocatalytic system to achieve the mineralization of the transformation products (TPs), recalcitrant to further biological removal. Firstly, a mixed culture (MC) was obtained through the enrichment of an activated sludge sample collected in a WWTP treating urban wastewater in order to optimize AMX biotransformation. Secondly, different aqueous matrices spiked with AMX were treated with the MC, which constituted a surrogate of activated sludge, and the metabolic transformation products were identified. Thirdly, the efficiency of the photocatalytic step was assessed in the removal of the metabolized TPs in a lab-scale photoreactor prototype equipped with a compound parabolic collector (CPC). The two proposed solar AOPs are the well-known photocatalytic system mediated by TiO_2 (TiO_2/UV) and a modification of the conventional photo-Fenton process in order to work with near-neutral pH levels, the Fe^{3+}/Oxalate/H_2O_2/UV–Vis system. To the best of the authors' knowledge, this is the first study dealing exclusively with the application of AOPs to remove recalcitrant transformation products resulting from the natural degradation of antibiotics, which are often overlooked.

2. Materials and methods

2.1. Reagents

Amoxicillin (MW: 365.4, CAS# 26787-78-0, HPLC-UV chromatogram and MS/MS spectrum in Fig. 1a and b, respectively) was purchased from Sigma–Aldrich. HPLC-grade methanol was from Prolabo, H_3PO_4 (85% p.a.), KH_2PO_4 and $(NH_4)_2SO_4$