International Biodeterioration & Biodegradation xxx (2016) 1–10

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

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

Removal of emerging contaminant and fouling control in membrane bioreactors by combined ozonation and sonolysis

Moriel Prado [a], Laura Borea [b], Alessandra Cesaro [b], Haizhou Liu [c], Vincenzo Naddeo [b, *], Vincenzo Belgiorno [b], Florencio Ballesteros Jr. [a]

[a] Department of Environmental Engineering, University of the Philippines, Diliman, Quezon City, 1101, Metro Manila, Philippines
[b] SEED - Sanitary Environmental Engineering Division, Department of Civil Engineering, University of Salerno, via Giovanni Paolo II, 84084, Fisciano, SA, Italy
[c] Department of Chemical & Environmental Engineering University of California, Riverside, CA, 92521, United States

ARTICLE INFO

Article history:
Received 29 July 2016
Received in revised form
25 October 2016
Accepted 25 October 2016
Available online xxx

Keywords:
membrane bioreactors
Ozone
Pharmaceutical compounds
Toxicity
Ultrasound

ABSTRACT

The combination of chemical and biological treatment is a promising solution to remove emerging contaminants, *e.g.*, pharmaceuticals, from wastewater for its future reuse. In this study, the combination of ozonation and ultrasound (O_3/US) was examined as a pretreatment prior to membrane bioreactor (MBR). The effects of O_3/US on the removal of selected pharmaceuticals, including diclofenac (DCF), sulfamethoxazole (SMX) and carbamazepine (CBZ), and MBR fouling control were investigated. The variation of the toxicity potential of the MBR influent was also assessed. The O_3/US treatment was effective in reducing fouling, mainly due to its effects on the microbial metabolism products in the MBR. Extracellular polymeric substance (EPS) concentration was reduced by 50%. Improved operating conditions resulted in higher removal rates for pharmaceuticals in the MBR effluent, with removal efficiency in the range of 80–84%. However, the O_3/US treatment alone was not efficient in removing the toxicity of wastewater. This was likely due to the formation of intermediate products that are more toxic than the parent compounds. These intermediate products were observed to be biologically oxidized by MBR, with a 80% reduction of the toxicity potential in the MBR permeate compared to the influent.

1. Introduction

Emerging contaminants (ECs) are receiving increasing attention in recent years: due to their chemical physical and biological properties, such pollutants may pose serious threat to both human health and the environment (Murnyak et al., 2011; Pal et al., 2014; Xagoraraki and Kuo, 2008). Although their presence in aquatic matrices has been reported at very low concentrations, great concern about the environmental distribution and the potential effects of these substances is raising and there is widespread consensus that this kind of contaminants may be a candidate for future regulation (Álvarez et al., 2015; Combi et al., 2016; Oller et al., 2011).

Pharmaceuticals are among the most widely studied ECs (Claessens et al., 2013). Their environmental occurrence has been observed to range from nanogram to microgram per litre (trace level), but due to their resistance to degradation, high persistence in aqueous medium and high biological activity, they have been found to cause ecological threats such as endocrine disruption, increase in microbial drug resistance, plant uptake, potential for bioaccumulation in the food chain and potential increased toxicity due to synergic effects of different chemicals and metabolites (Prieto-Rodriguez et al., 2012; Rivera-Utrilla et al., 2013).

The main source of these contaminants is represented by the effluents of wastewater treatment plants (WWTPs). Due to their poor biodegradability and toxicity to various microorganisms, low removal efficiencies can be pursued by using conventional biological processes (Marcoux et al., 2013; Petrie et al., 2015). This condition can, in turn, limit the wider wastewater processing for integrated resource recovery (van der Hoek et al., 2016).

Membrane bioreactors (MBRs) represent a promising technology for wastewater treatment and reuse due to their known advantages compared to conventional wastewater treatments. They combine biological degradation with membrane filtration, using either microfiltration (MF) or ultrafiltration (UF) membranes with pore size ranges from 0.05 to 0.4 μm to separate suspended solids,

* Corresponding author.
E-mail address: vnaddeo@unisa.it (V. Naddeo).

http://dx.doi.org/10.1016/j.ibiod.2016.10.044
0964-8305/

so that secondary settlers can be avoided as well as longer sludge retention times (SRTs) applied. Additionally provision for a better disinfection capability, compactness, better resilience to shock-loading and more flexible control of operation parameters regard MBR process to be "best available" technology (Kaya et al., 2013; Hoinkis et al., 2012; Purnell et al., 2016).

An inherent problem associated with MBR is membrane fouling. It has been suggested that severe membrane fouling is often a result of organics accumulation on or in the membrane surface caused by the microbial metabolism products, both extracellular polymeric substances (EPS) and soluble microbial products (SMP) (Ding et al., 2016; Luo et al., 2015). The specific cake resistance becomes higher as the amounts of EPS and SMP increase (Wang et al., 2009). This further develops to the accumulation of a sludge cake layer causing fouling to the membranes (Zhou et al., 2015). Membrane fouling results in reduced performance, severe flux decline or rapid trans-membrane pressure (TMP) increase, high energy consumption, and need for more frequent membrane cleaning or replacement, which directly leads to the increase in maintenance and operating costs. Therefore, different conventional and advanced methods, such as the addition of carriers (Leyva-Díaz et al., 2014) and coagulants (Teli et al., 2012), the application of ultrasound (Naddeo et al., 2015a, 2015b) or the combination with electrochemical processes (Borea et al., 2016; Ensano et al., 2016), have been applied for fouling mitigation.

Despite their recognized breakthroughs, MBRs also remain problematic for some refractory ECs (Clara et al., 2005; Reif et al., 2008; Tadkaew et al., 2011). Several studies have indeed been focused on the removal of pharmaceutical compounds by MBRs (Aubenneau et al., 2010; Cheng et al., 2015; Kimura et al., 2005; López-Fernández et al., 2012; Sipma et al., 2010; Tambosi et al., 2010) and highly variable removal have been reported (Tadkaew et al., 2011).

The application of combined treatments for the removal of ECs can be significantly valuable since it does not only combine the advantages of the constituent treatment techniques but also eliminates the challenges or drawbacks of one another: a sound, cost-effective and environment-friendly solution is the integration of chemical and biological processes. Recent findings have shown that the integration of advanced oxidation processes (AOPs) and biological treatments such as MBR offers great potentials in removing toxic and recalcitrant compounds from wastewater (Ahmed et al., n.d.; Yahiat et al., 2011).

The AOPs are known for their high versatility and, when applied as pretreatment of biological processes, they can provide the efficient conversion of biorefractory compounds to readily biodegradable intermediates that can be subsequently treated biologically: in this context, wastewater toxicity reduction can also be obtained (Cesaro et al., 2013). Therefore, this transformative technology is conceptually beneficial leading to an overall treatment efficiency higher than that of each individual stage. However, most studies limit the evaluation of combined AOPs/biological process performances to the variation in wastewater biodegradability and/or toxicity, whereas a dearth of knowledge can be recognized in the feasibility assessment of AOPs as pretreatment to MBR for both ECs removal and membrane fouling abatement.

This study aims at assessing the combined AOPs/MBR process for the simultaneous removal of selected pharmaceuticals spiked as mixture in synthetic wastewater and fouling control. Main aspects dealing with the sustainability of the combined process for its scale up are also discussed.

To this end a combined ozone (O_3)/ultrasound (US) process was considered. Ozone is a very strong oxidant, effective towards a wide range of compounds. However, it is unstable and undergoes chain decomposition to liberate hydroxyl radicals. Ultrasound rely on acoustic cavitation phenomena, involving the formation, expansion and violent collapse of microbubbles. If considering the bubble as a reactor, the sites associated with the bubble collapse and the possible generation of hydroxyl radicals are: the cavity interior, the immediate bubble vicinity, the bulk medium around the bubble and liquid droplets inside the bubble (Mason and Peters, 2002). When ozone and ultrasound are combined, ozone is decomposed thermolitically in the vapour phase of a cavitational bubble according to the following reactions (Weavers, 2001):

$$O_3 + US \rightarrow O_2 + O(^3P) \quad (1)$$

$$O(^3P) + H_2O \rightarrow 2OH^{\bullet} \quad (2)$$

The reaction products migrate to the interface of the bubble, where they are transferred into the aqueous phase. Such mechanisms result in faster degradation rates for several compounds (Guo et al., 2015; Naddeo et al., 2015c; Wang et al., 2010); increased mass transfer coefficients of ozone diffusing into solution in the presence of ultrasound has also been reported (Weavers, 2001).

Although AOPs were found to result in beneficial effects on different pharmaceutical compounds (Naddeo et al., 2009a,b,2010; Secondes et al., 2014), to the best of authors knowledge, the potential of a combined O_3/US process as treatment prior to the MBR for the simultaneous control of pharmaceutical concentrations and fouling has not been studied yet, so that this study appears to be the first attempt in this field.

2. Materials and methods

2.1. Chemicals

The experimental activity was performed using synthetic wastewater (SWW) simulating real municipal wastewater, according to a previous study (Li et al., 2005). The composition and the characteristics of the SWW is shown in Table 1.

The SWW was spiked with diclofenac (DCF), sulfamethoxazole (SMX) and carbamazepine (CBZ), selected as target compounds since they are three of the most frequently pharmaceutical compounds detected in WWTP effluents (Naidu et al., 2016; Oliveira et al., 2015; Teijon et al., 2010). A concentration of 4 μg/L was used for each compound.

2.2. Experimental set up

2.2.1. Combined O_3/US pretreatment

The O_3/US pretreatment was performed using the combined ozonation and sonolysis experimental set up plotted in Fig. 1.

The ozone generator (Procom srl, Italy) relies on a UV irradiation system. It produces ozone by splitting the oxygen molecules of the

Table 1
Composition and average characteristics of the synthetic wastewater used for the experimental activity.

Component	Concentration
Industrial glucose [mg/L]	360 ± 10
Protein [mg/L]	80 ± 5
$NaHCO_3$ [mg/L]	24 ± 5
KH_2PO_4 [mg/L]	14 ± 5
NH_4Cl [mg/L]	60 ± 5
$CaCl_2$ [mg/L]	18 ± 3
$MgSO_4 \cdot 7H_2O$ [mg/L]	24 ± 3
COD [mg/L]	442 ± 7
pH [-]	6.7 ± 0.6
DO [mg/L]	7.3 ± 1.5

Please cite this article in press as: Prado, M., et al., Removal of emerging contaminant and fouling control in membrane bioreactors by combined ozonation and sonolysis, International Biodeterioration & Biodegradation (2016), http://dx.doi.org/10.1016/j.ibiod.2016.10.044