

CONTROL OF EMERGING COMPOUNDS IN BIOLOGICAL TREATMENT OF WASTEWATER BY ADVANCED PRE-OXIDATION

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ABSTRACT

The ubiquitous occurrences of pharmaceuticals in the environment have resulted to emerging adverse effects to both humans and animals. The integration of chemical and biological processes is deemed as a sound, cost-effective and environment-friendly alternative of removing emerging contaminants such as pharmaceuticals found in municipal wastewaters. This study investigates the impacts of the pre-oxidation treatment using enhanced ozonation by sonolysis (O₃/US) on the performance of a membrane bioreactor (MBR) to remove selected pharmaceuticals - diclofenac (DCF), sulfamethoxazole (SMX) and carbamazepine (CBZ). The influence of chemical pre-oxidation in terms of its performance in the membrane fouling control and its biological toxicity were also investigated. The enhanced O₃/US using a constant power density of 370 W/L and an ozone flow of 3.3 g/h was employed as the pre-oxidation treatment. The results indicate that the removal efficiencies of MBR with O₃/US pre-oxidation were observed to be 83%, 84% and 80%, for DCF, CBZ and SMX, respectively. The transmembrane pressure (TMP) was found to be relatively lower for the MBR with pre-oxidation compared to conventional MBR (without pre-oxidation). Based on the toxicity test results, the O₃/US pre-oxidation did not significantly lead to complete elimination of toxicity in wastewater.

Keywords: advanced oxidation processes, degradation, emerging contaminants, ozone, ultrasound, membrane bioreactors

1. Introduction

More and more pharmaceuticals residues in their unchanged form or in its metabolites are detected and identified in the aquatic environment. Their environmental occurrences are reported in measurable concentrations usually in ng/L to µg/L, but due to their resistance to degradation, high persistence in aqueous medium (Rivera-Utrilla, Sánchez-Polo, *et al.*, 2013) and high biological activity, they are found to cause ecological threats such as endocrine disruption (Sipma, Osuna, *et al.*, 2010), increase in microbial drug resistance, plant uptake, potential for bioaccumulation in the food chain (Secondes, Naddeo, *et al.*, 2014) and potential increased toxicity due to synergic effects of different chemicals and metabolites (Rizzo, 2011). Thus, they are currently considered as emerging compounds (ECs) because these are mostly unregulated compounds that may be candidate for future regulation depending on the reported potential adverse effects in humans and wildlife and monitored data on their occurrence (Rivera-Utrilla, Sánchez-Polo, *et al.*, 2013; Oller, Malato, *et al.*, 2011).

A sound, cost-effective and environment-friendly alternative to reduce inputs of pharmaceuticals to the environment is the integration of chemical and biological processes. This offers great potentials in removing toxic and recalcitrant compounds such as that of pharmaceuticals in water and in wastewater. The chemical oxidation partial treatment selectively removes the more bioresistant contaminants and their conversion to readily biodegradable intermediates can be subsequently treated biologically (Mantzavinos and Psillakis, 2004; Klavarioti, Mantzavinos, *et al.*, 2009). This was also found to remove toxicity from wastewater (Cokgor, Alaton, *et al.*, 2004). The biological step serves to lower the costs of chemical pretreatment by converting

biorefractory pollutants into biodegradable compounds as well as biodegrading the by-products generated during oxidation process (Benoit Guieysse, 2013). Therefore, the combination of chemical pre-oxidation and biological post-treatment is conceptually beneficial as it can lead to increased overall treatment efficiencies compared with the efficiency of each individual stage. The influence of chemical pre-oxidation to biological treatments is usually evaluated in terms of biodegradability and toxicity tests. Also, the application of this combined process to the degradation of pharmaceuticals has not been explored. Deemed as a possible solution, the aim of this study was to assess the impacts of the combined O_3/US pre-oxidation on the performance of a membrane bioreactor (MBR): (1) to remove pharmaceuticals; (2) to control the membrane fouling; and (3) to reduce biological toxicity to the wastewater.

2. Materials and methods

2.1. Chemicals

Three pharmaceuticals were selected as model compounds: diclofenac (DCF), sulfamethoxazole (SMX) and carbamazepine (CBZ) obtained from Sigma Aldrich, Inc. (USA). For the preparation of the mixture as the feed for all tests, a concentration of 4 ppb each of DCF, SMX and CBZ was used to spike synthetic wastewater (SWW) (Li, Gao, *et al.*, 2005).

2.2. Experimental set-up

2.2.1. Combined O_3/US pre-oxidation

The combined O_3/US experiments were performed using the ozonation setup combined with an ultrasonic generator (750 W, 20 kHz, Sonics Vibracell™ VCX-750, Sonics & Materials Inc., USA) equipped with a titanium horn with a 1.3 cm in diameter tip; and a temperature probe to keep the temperature around 25°C. The combined O_3/US tests were carried out at a constant power density of 370 W/L, using ozone flow of 3.3 g/h and a reaction time of 40 min. These operating conditions were based on previous work (Naddeo, Uyguner-Demirel, *et al.*, 2015). Figure 1 shows the combined O_3/US experimental setup.

2.2.2. Laboratory-scale MBR system and operation protocol

The laboratory-scale MBR is composed of a glass reactor with active volume of 8 L, two air pumps (one for the membrane and one for the diffuser), a pressure transducer connected to a computer, two mixers (one for the influent tank and the other is for the membrane bioreactor), and two pumps (influent and permeate pumps) as shown in Figure 2.

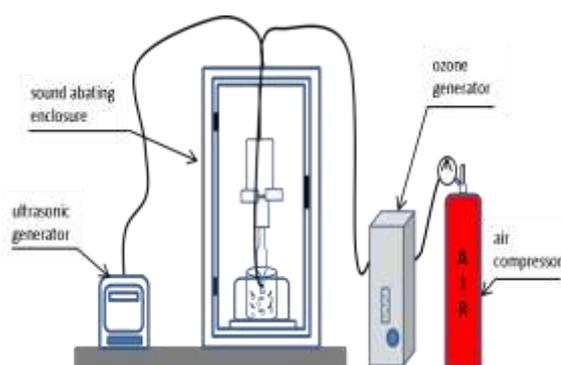


Figure 1: Combined O_3/US Experimental Setup

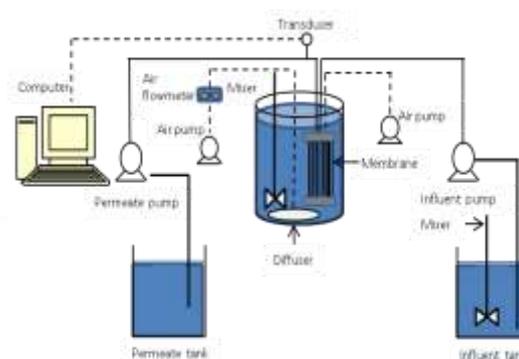


Figure 2: Schematic Diagram of the MBR Experimental Setup

The submerged hollow fiber microfiltration membrane module used in the study was supplied by Zenon. The reactor was seeded with activated sludge from the sludge recirculation line of a full-scale UWWTP in Salerno, Italy. The raw SWW was initially fed to the MBR until the steady state was achieved in terms of COD removal. After the start-up period, ECs were added to the SWW. During this period, the feed and the effluent was collected for evaluating the conventional MBR (without O_3/US pre-oxidation). After this phase, the feed of SWW spiked with ECs was evaluated by matching the continuous operation of the MBR with a batch, off-line O_3/US pre-oxidation

process. Samples of MBR influent, O₃/US effluent and MBR effluent were analyzed to monitor the performance of the combined systems.

2.3. Analytical Methods

The degradation extent of DCF, SMX and CBZ in synthetic solutions was measured by 4000 Q Trap LC-126 MS/MS System (Applied Biosystems, Foster City, USA) with electro-spray ionization (ESI) - positive and negative ionization modes using a mobile phase composed of 0.1% formic acid in water and acetonitrile-water (1:1 v/v) solution. The acute toxicity of the feed SWW spiked with the studied compounds (with and without O₃/US pre-oxidation) and generated permeates were evaluated to *Daphnia magna* immobilization tests (ISO, 1996; Naddeo, Belgiorno, *et al.*, 2010)

3. Results and discussion

3.1. Removal of pharmaceuticals in MBR

In Figure 3, it appears that the removal efficiency of the MBR without pre-oxidation were reported as 77%, 75% and 74% for DCF, CBZ and SMX, respectively. It should be noted that there was a noticeable improvement in the removal rates for the studied compounds in the permeate after employing the pre-oxidation. The removal rates for DCF, CBZ and SMX in the pretreated permeate were as follows: 83%, 84% and 80%, respectively. This remarkably confirms that the pretreatment contributed on the partial chemical oxidation of the pharmaceuticals which leads to the enhancement in their biodegradability in the MBR (Pollice, Laera, *et al.*, 2012).

3.2. Membrane Fouling

It can be seen from Fig. 4 that for the MBR pretreated with O₃/US, the transmembrane pressure (TMP) remained stable for the first 20 minutes followed by an abrupt jump to 0.04 bar. Similar observations were noted in literature (J. Zhang, 2006). The TMP continued to increase gradually up to 0.1 bar. The permeate flux obviously declined when the TMP of MBR reached 0.1 bar. On the other hand, when the MBR was not provided with O₃/US pre-oxidation, the TMP initially started from 0.04 bar and continuously increased up to 0.1 bar. The TMP was found relatively lower for the MBR with pre-oxidation compared to conventional MBR. It was thus believed that O₃/US pre-oxidation was an effective pretreatment strategy to reduce the increasing rate of TMP to lower energy requirement for the membrane filtration process at a constant flux.

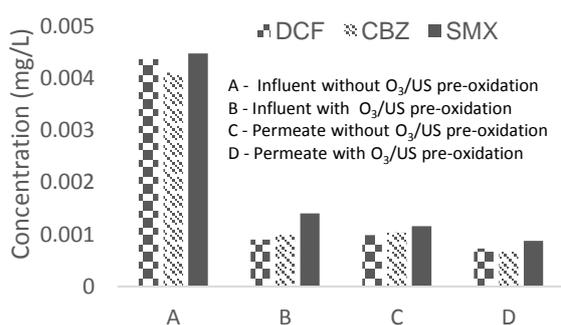


Figure 3: Removal of DCF, SMX and CBZ in the MBR influent and permeate with and without O₃/US pre-oxidation

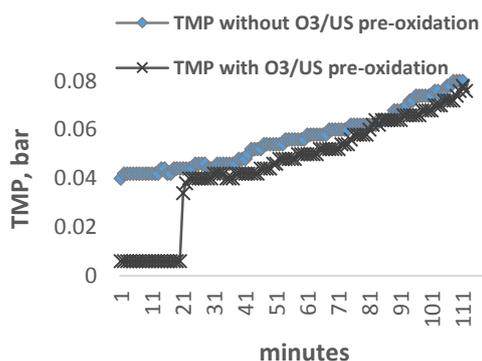


Figure 4: TMP profile in the MBR with and without O₃/US pre-oxidation

3.3. Toxicity Results

The acute toxicity of the feed SWW spiked with the studied compounds (with and without O₃/US pre-oxidation) and generated permeates were evaluated using 24-h test with *Daphnia magna* immobilization tests. As shown in Table 3, the feed SWW has been observed to have 100% toxicity. No toxicity removal was noted after the O₃/US pre-oxidation. Higher toxicity (20%) has been found for the generated permeate from the MBR with O₃/US pre-oxidation which could be

attributed to the formation of some intermediate by-products but less toxic than the parent compound (Zhiqiao He, 2009; de O. Martins, Canalli, *et al.*, 2006; Espejo, Aguinaco, *et al.*, 2014).

Table 3: Ecotoxicity results of *Daphnia magna* immobilization tests

Samples	Immobility (24 h)	% toxicity (24 h)
Influent without O ₃ /US pre-oxidation	10	100
Influent with O ₃ /US pre-oxidation	10	100
Permeate without O ₃ /US pre-oxidation	1	10
Permeate with O ₃ /US pre-oxidation	2	20

4. Conclusions

The results showed that O₃/US pre-oxidation was proven to be an effective pretreatment strategy to reduce ECs in MBRs. In fact, the combination of O₃/US as pre-oxidation and MBR has resulted in improved effluent quality as demonstrated by the improvement in removal rates for ECs which could be possibly related to the partial oxidation of the ECs which leads to the enhancement in their biodegradability. Moreover, the O₃/US pre-oxidation was reported to reduce the increasing rate of TMP suggesting that this can potentially control membrane fouling. The applied pre-oxidation process did not result to complete elimination of toxicity of the wastewater. The remaining toxicity could have possibly caused by the formations of the intermediate by-products. Nonetheless, these intermediates are believed to be less toxic than the parent compound.

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