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Influence of volumetric reduction factor during ozonation of nanofiltration concentrates for wastewater reuse

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HIGHLIGHTS

- Pharmaceuticals rejections by tight-NF membranes are not impacted by the VRF.
- Ozone treatment lead to more biodegradable concentrates.
- Ozonation of ozone-reactive PhACs is effective for low ozone doses.

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ABSTRACT

Global population growth induces increased threat on drinking water resources. One way to address this environmental issue is to reuse water from wastewater treatment plant. The presence of pathogenic microorganisms and potentially toxic organic micropollutants does not allow a direct reuse of urban effluents. Membrane processes such reverse osmosis (RO) or nanofiltration (NF) can be considered to effectively eliminate these pollutants. The integration of membrane processes involves the production of concentrated retentates which require being disposed. To date, no treatment is set up to manage safely this pollution. This work focuses on the application of ozonation for the treatment of NF retentates in the framework of the wastewater reuse. Ozonation is a powerful oxidation process able to react and degrade a wide range of organic pollutants. Four pharmaceutical micropollutants were selected as target molecules: acetaminophen, carbamazepine, atenolol and diatrozic acid. This study highlighted that NF represents a viable alternative to the commonly used RO process ensuring high retention at much lower operating costs. Ozonation appears to be effective to degrade the most reactive pollutants toward molecular ozone but is limited for the reduction of refractory ozone pollutants due to the inhibition of the radical chain by the high content of organic matter in the retentates. The ozonation process appears to be a promising NF retentate treatment, but additional treatments after ozonation are required to lead to a zero liquid discharge treatment scheme.

1. Introduction

NF and RO processes are recognized as effective technologies to remove micropollutants as pharmaceutically active compounds (PhACs) during advanced wastewater treatment for surface water augmentation and groundwater injection projects using reclaimed water (Alturki et al., 2010). Indeed, Umar et al. (2015) have identified at least fifty water reclamation plants worldwide above 10 MLJ (10^6 L j^{-1}) using integrated membrane systems (IMS), such as microfiltration (MF) or ultrafiltration (UF) pretreatment followed by reverse RO (Umar et al., 2015). Some of the best known examples are those of Sulabaiya plant in Kuwait (375 MLJ), Orange County in United States (328 MLJ) and Changi in Singapore (232 MLJ). However, although RO is a well-established technology, this process suffers from significant drawbacks as a high energy requirement and a severe fouling propensity due to an almost complete rejection of the effluent organic matter (EfOM) and salts from pretreated wastewater treatment plant (WWTP) effluents. Consequently, some authors have recently promoted NF for wastewater reuse instead of RO which is still the industry standard (Bellona et al., 2012; Yangali-Quintanilla et al., 2010). NF provides a number of advantages as higher permeate flux rates for lower energy requirements, high to moderate rejections of emerging contaminants and smaller rejections of monovalent salts than RO thus less

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problematic membrane concentrates (Bellona and Drewes, 2007). Based on these observations and those obtained from a previous work, the present study proposes to use NF in place of RO for wastewater reuse (Azais et al., 2014).

One significant inherent disadvantage of the use of these membrane processes for water reuse is the need to dispose the concentrate (brine) ranging usually between 15 and 50% of the feed volume. A first solution would be to reduce the volume of concentrates by increasing the conversion rate (the ratio of permeate flow on influent flow) from 85 to 98% (Bozkaya-Schrotter et al., 2009; Flyborg et al., 2010). However, the main limitation of this practice remains the membrane fouling especially by the precipitation of salts. Hence, a second solution would be to considerer the concentrate recirculation back to the biological treatment. This scheme is not a long-term option due to the impact of salinity on biological activity (Reid et al., 2006). The most widely used strategy for membrane concentrate disposal is the direct discharge into the environment. Obviously, the discharge into sea or surface waters is not to encourage due to the average composition of urban membrane concentrates: conductivity from 2 to 20 mS cm^{-1}, DOC from 20 to 55 mg L^{-1} and micropollutants concentrations multiplied by a factor of 3–7 compared to those encountered in WWTP effluent (Solley et al., 2010). As a consequence, further treatment of the concentrate should be investigated to transform wastewater into resources.

Several studies have focused on the application of single reactants such as UV radiation, ozone (O_3), hydrogen peroxide (H_2O_2) or their combination as advanced oxidation processes (AOPs) to remove recalcitrant organic traces in wastewater effluents (Arnold et al., 2012; Esplugas et al., 2007; Sarkar et al., 2014). In particular, several studies have promoted ozone as an oxidant of choice for the degradation of a wide range of PhACs in various water matrixes (Benitez et al., 2009; Dodd et al., 2006; Huber et al., 2003; Ikehata et al., 2006; Snyder et al., 2006; Ternes et al., 2003; Wert et al., 2009). Nevertheless, a few studies have focused on the application of AOPs for the treatment of membrane concentrates from WWTPs (Dialynas et al., 2008; Justo et al., 2014; Westerhoff et al., 2009). AOPs are highly recommended as treatment for urban concentrates with high organic pollutant load but low salinity compared to the desalination plants concentrates (Perez-Gonzalez et al., 2012). The treatment of organic pollution of RO concentrates from a municipal wastewater reclamation plant (Singapore) by four AOPs (heterogeneous photocatalytic oxidation, sonolysis (US), ozonation and H_2O_2 oxidation) was studied by Zhou et al., 2011. The authors concluded that ozone treatment (1 L min^{-1} and 17.6 ± 8.3 mgO_3 h^{-1}) is the most effective treatment with a removal of 22% of the dissolved concentrates organic matter (COM). Concerning the ozone-based AOPs and specifically the peroxone process, it was observed that the overall •OH formation by this process is only 10% higher than that obtained during ozonation under similar O_3:DOC conditions (Wert et al., 2009). Furthermore, the authors stipulate that peroxone process might be less efficient for the oxidation of trace contaminants which react with molecular ozone due to a significant portion of their oxidation in competition with side reactions of ozone with H_2O_2. For the reasons previously exposed, ozonation is investigated as a potential pretreatment option for NF concentrates.

From bibliographic study, it appears that there is a lack of comprehensive study about oxidation mechanisms during ozonation of NF concentrates during wastewater treatment. Hence, the objective of this study is to investigate the ozonation of PhACs in real concentrate matrixes and the influence of NF recovery on their removal. Indeed, the degree of oxidation of organics is function of the rate constants with oxidative species (here, ozone and •OH) and the stability of ozone in water which determines the exposures to ozone and hydroxyl radicals. The stability of ozone largely depends on the water matrix, especially its pH and alkalinity, the nature and the content of its organic matter. In fact, specific organic compounds which expose electron-rich moieties (ERMs) promote the ozone decomposition and the •OH generation by direct reactions between ozone molecule and double bonds, activated aromatic systems, amines or sulfides (Buffle and Von Gunten, 2006; Nothe et al., 2009). Simultaneously, the dissolved organic matter indirectly affects the ozone stability through the scavenging of •OH radicals with others inorganic species as bicarbonates and nitrites. Thus, it appears that PhACs oxidation efficiencies should depend on organic and inorganic contents of the NF concentrates while the main parameter that impacts the concentrate composition is the recovery rate applied during the membrane operation. Although some studies have investigated the RO concentrates treatment by AOPs, the influence of the membrane operation is rarely mentioned. We can cite Miralles-Cuevas et al. (2014) who had studied RO retentates treatment with different AOPs under different concentration factors (Miralles-Cuevas et al., 2014). Hence, we propose to investigate the effect of recovery rates ranging from 50 to 90% (expressed as a volume reduction factor (VRF) from 2 to 10) on rejection of selected PhACs by NF and the further treatment of NF concentrate by ozonation. The four selected PhACs namely acetaminophen (ACT), carbamazepine (CBZ), atenolol (ATL) and diatrizoic acid (DTZ) were selected to be representative of various therapeutic classes of PhACs (analgesic, antiepileptic, β-blocker and X-ray contrast media) found in all aquatic compartments. Although the ACT and the ATL concentrations are reduced during conventional biologic wastewater treatment (activated sludge), microgram per liter order concentration still remains in urban effluent due to a large consumption (Kasprzyk-Hordern et al., 2008). In the environment, these molecules are eliminated mainly by biodegradation and photodegradation (De Laurentiis et al., 2014; Wang et al., 2012). CBZ and DTZ are not degraded in the water cycle because of their persistence under aerobic conditions (Paxeus, 2004; Ternes and Hirsch, 2000).

2. Experimental methods

2.1. PhACs selection and characterization

The chosen compounds represent a wide range of properties (i.e. molecular weight, hydrophobicity, size, shape and charge) that are anticipated to influence membrane rejection. These organics were specifically selected according to their widely spread second order reaction rate constants with ozone as reported in literature (Table S1). All the PhACs were purchased at Sigma-Aldrich and were of analytical grade. The molecular weight (M_W in g mol^{-1}), the octanol–water distribution coefficient (K_{OW}) were determined using ACD Lab Chemsketch software. The pKa values are obtained from PubChem database. A stock solution of PhACs was prepared from powdered substances in an ethanol (EtOH):ultrapure water (1:1) solution at a concentration of 1 g L^{-1} and conserved in the fridge at 4 °C for two months.

2.2. PhACs analysis

LC-MS/MS analysis was performed with a Waters 2695 pump, an autosampler with a 20 μL loop, a Waters 2695 separation module (HPLC), and a Waters Micromass (Wythenshawe, Manchester,UK) Quattro Micro mass spectrometer equipped with ESI in positive mode. A C18 column (HSS-T3:100 mm * 2.1 mm, 3.5 μm particles) was used. The detailed analytical method and the instrumental quantification limits were given in Azais et al., 2014.