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Research paper

Ozonation as a pretreatment process for nanofiltration brines: Monitoring of transformation products and toxicity evaluation

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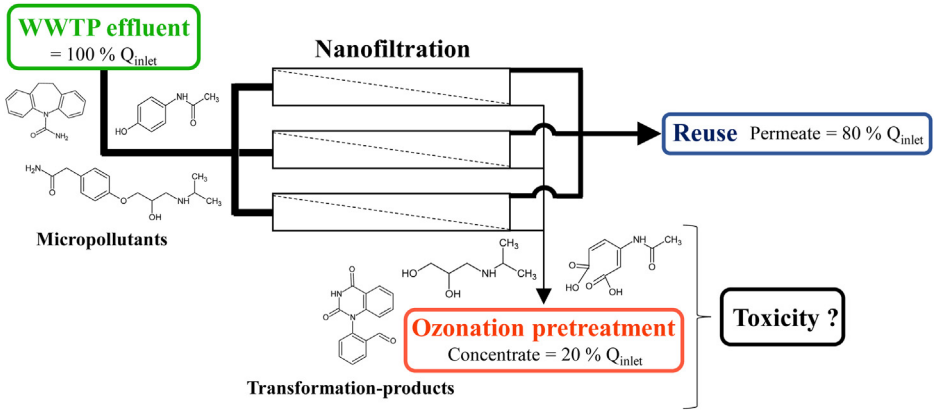
HIGHLIGHTS

- Tight nanofiltration membranes could reject ninety percents of pharmaceuticals in wastewater.
- Ozonation is effective to remove drugs in membrane concentrates.
- Transformation products; oxidation pathways and kinetics were determined along ozonation experiments.
- Quinazoline moities from carbamazepine oxidation are identified as potential toxics.

GRAPHICAL ABSTRACT



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ABSTRACT

Considerable interest has been given to using nanofiltration (NF) in lieu of reverse osmosis for water reclamation schemes due to lower energy consumption, higher flux rates while ensuring good micropollutants rejection. The application NF results in the generation of a large concentrated waste stream. Treatment of the concentrate is a major hurdle for the implementation of membrane technologies since the concentrate is usually unusable due to a large pollutants content. This work focuses on the application of ozonation as pretreatment of urban NF concentrates, the generation of transformation products and their relative toxicity. Three pharmaceutical micropollutants largely encountered in water cycle were selected as target molecules: acetaminophen, carbamazepine and atenolol. Through accurate-mass Q-TOF LC–MS/MS analyses, more than twenty ozonation products were detected, structure proposals and formation pathways were elaborated. Attempts were made to understand the correlation between the transformation products and acute toxicity on *Vibrio fischeri* strain. It is the first time that an integrated study reported on the ozonation of pharmaceuticals in urban membrane concentrates, in terms of transformation products, kinetics, degradation mechanisms, as well as toxicity assessment.

1. Introduction

Nanofiltration (NF) has been recognized as effective technology to remove micropollutants as pharmaceutically active compounds

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(PhACs) from wastewater treatment plants (WWTPs) effluents during advanced wastewater treatment for surface water augmentation and groundwater injection projects using reclaimed water [1]. However, the application of high pressure driven membranes suffer from significant drawbacks: *i*) a severe fouling tendency due to a strong rejection of the effluent organic matter (EfOM) and salts from pretreated effluent and *ii*) the need of further treatment of concentrates (brines) ranging usually between 15 and 50% of the feed volume [2]. Many fouling mitigation possibilities are proposed in literature as pretreatment methods (coagulation and flocculation, membrane filtration, oxidative and/or adsorption processes, etc.), optimization of membrane design and process conditions, addition of anti-scaling agents, cleaning and finally membrane surface modification to obtain fouling-resistant polymeric layer [3]. Concerning the disposal of the concentrates, the most widely used strategy is the direct discharge into sewers and the environment [4]. Membrane concentrates contain almost all the contaminants present in the original wastewater at elevated concentration levels with other chemicals as antiscalants, biocides and acids used during the membrane operation. These organics may be toxic and/or bioaccumulative, and so disposal of untreated concentrates presents a potential environmental risk [4]. As a consequence, further treatment of the concentrates is required. Advanced oxidation processes (AOPs) are highly recommended as pretreatment for urban concentrates with high organic load but low salinity compared to desalination plants concentrates [5]. Indeed, an oxidation step is usually performed to transform a large amount of the concentrate organic matter (COM) to reduce fouling of the downstream biological and desalting processes [6] or further membrane stages [7]. In this way, ozonation process have been demonstrated to be an effective membrane concentrates pretreatment process to mitigate the concentrations of the most reactive micropollutants toward molecular ozone and to improve the COM biodegradability [8]. However, a complete mineralization of the parent compounds is not achieved and little is known about the potential toxicity of the unknown transformation products (TPs) formed after the ozonation of highly contaminated waters as membrane concentrates. Indeed, to the best of authors' knowledge no article proposes today to investigate the formation of possibly toxic TPs in membrane brines while their treatment would become a widespread practice in the current worldwide environmentally conscious water policy. Hence, the objective of the present paper is to constitute a first integrated approach regarding the generation of persistent ozonation products during NF concentrates pretreatment focusing on: *i*) the elucidation of the transformation pathways through the identification of the intermediates formed using high resolution LC–MS/MS techniques and *ii*) the acute toxicity assessment along the treatment in order to identify potential environmental risks.

2. Material and methods

2.1. Pharmaceuticals selection and characterization

The chosen compounds namely acetaminophen (ACT), carbamazepine (CBZ) and atenolol (ATL) were selected to be representative of various therapeutic classes of PhACs (analgesic, antiepileptic and β-blocker) found in all aquatic compartments. They represent a range of properties (*i.e.* molecular weight, hydrophobicity, size, shape and charge) that are anticipated to influence NF membrane rejection [1]. Furthermore, these organics were specifically selected according to their widely spread second order reaction rate constants with ozone [8]. All the pharmaceuticals were purchased at Sigma-Aldrich and were of analytical grade. The molecular weight and the octanol–water distribution coefficient ($LogK_{OW}$) were determined using ACD Lab Chemsketch software. The pKa values are obtained from PubChem database. The pharmaceuticals stock solution 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. Individual stock solutions of ACT, CBZ and ATL were prepared at a concentration of $1\,g\,L^{-1}$ in pure EtOH.

2.2. Pharmaceuticals analysis

The analytical method for organics in aqueous matrices usually includes solid-phase extraction (SPE), in order to enrich the analytes, followed by liquid chromatography (LC) with tandem mass spectrometry (MS/MS) to quantify low analytes concentrations. However, SPE methods can suffer from poor recovery for polar pharmaceuticals as β-blockers even if polar solvents as methanol were used [9]. Hence, past studies have suggested using direct injection LC–MS/MS which avoids the time consuming nature of SPE, the need to measure recovery with a labelled internal standard and which increase the overall robustness of the analysis particularly when sequential SPE columns are used [10]. Hence, in this study, analyses were carried out without SPE pre-concentration (direct injection). LC–MS/MS analyses were performed with a Waters 2695 pump, a Waters 2695 separation module (HPLC) and a Waters Quattro micro Tandem Quadrupole system equipped with an electrospray ionization source (ESI) in positive mode. A HSS-T3 column ($100\,mm \times 2.1\,mm$, $3.5\,\mu m$ particles) was used. The detailed analytical method and the instrumental quantification limits based on a signal to noise of 3 and 10 were given elsewhere [1]. According to these values, the feed solution was spiked at $750\,\mu g\,L^{-1}$ so that rejection values greater than 98% could be determined taking into account the NF permeate concentrations.

2.3. Feed solution and nanofiltration procedure

The feed solution is a secondary effluent obtained from a municipal WWTP (30 000 population equivalent) located in the south of France. The treatment process incorporates a ZeeWeed 500 (GE Zenon) membrane bioreactor (MBR) with ultrafiltration hollow-fiber membranes (pore size of $0.04\,\mu m$). More details on the MBR process, samples collection, water analyses and physicochemical quality of the effluent are presented in Azaïs et *al.* [1]. Filtration experiments were carried out with an Osmonics Sepa CF II cell which uses flat sheet membrane coupons of $155\,cm^2$. A commercial NF membrane namely NF-90 (DOW FILMTEC™) was used. A detailed description of protocols used for membrane characterization and experimental values of NF-90 properties are available in a previous study [11]. The filtration runs were conducted with a transmembrane pressure (TMP) of 800 kPa, a cross-flow velocity (V_T) of $0.5\,m\,s^{-1}$ for a medium foulant spacer, 47 Mil (1.194 mm) and at 20 ± 0.5 °C. As previously mentioned, the secondary effluent was spiked with PhACs stock solution to a targeted concentration of $750\,\mu g\,L^{-1}$. Then, the solution was fed to the lab cross-flow filtration cell by a Hydra-Cell pump from a 50 L feed vessel. A stainless steel control valve on the brine outlet allows the control of the TMP which is monitored through two manometers located on the inlet and outlet of the filtration cell. The bench-scale membrane filtration system was operated with a complete return of concentrate to the feed tank which is stirred to ensure homogenization and discharge of permeate. The total tank volume gradually diminished to 10 L corresponding to a volumic reduction factor (VRF) of 5 (or also a conversion rate of 80%) typically encountered in full-scale facilities. Before ozonation experiments, residual concentrates were stored at 4 °C and transferred to the ozonation lab scale plant's reactor 24 h maximum after the end of the NF operation. Water characteristics of the initial effluent and the concentrate are presented in Table 1. The ratio between the biochemical oxygen