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Combination of nanofiltration and ozonation for the remediation of real municipal wastewater effluents: Acute and chronic toxicity assessment

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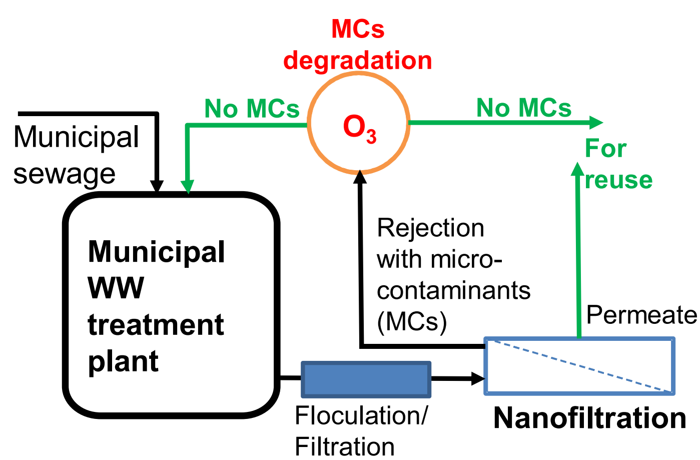
HIGHLIGHTS

- Microcontaminants eliminated (>99%) by ozonation but acute toxicity increased.
- Acute toxicity was related to micro-contaminant byproducts or other water components.
- *D. magna* adaptation and reduction of chronic toxicity in *S. capricornutum* was observed.
- Ozonation and membrane technologies could be combined to treat microcontaminants.

GRAPHICAL ABSTRACT



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ABSTRACT

The purpose of this work was to study the ozonation of nanofiltration (NF) retentates of real municipal wastewater treatment plant (MWTP) effluents for removal of microcontaminants (MCs) and toxicity. MCs present in these effluents were monitored using LC–MS/MS. Acute and chronic toxicity was addressed with *Daphnia magna*, *Vibrio fischeri* and *Selenastrum capricornutum*. Up to 40 MCs were found, most of them in concentrations over 100 ng/L. 90% degradation of the sum of MCs was the critical point of comparison. When the NF membrane system was applied to MWTP effluents, treatment of NF rejection needed 2.75–4.5 g O_3/m^3,4.5 g O_3/m^3, which is less than 50% of the ozone needed for direct treatment of MWTP effluent. Treatment time (lower than 11 min) was not influenced by MCs concentration, at least in the range tested (25–190 μg/L). It has been demonstrated that consumption of ozone increased with organic load and inorganic content of different real effluents. MCs were eliminated by ozonation but acute toxicity (against *V. fischeri* and *D. magna*) increased. Chronic toxicity results were different and contrary in *D. magna* and *S. capricornutum*, due to the generation of new transformation products more toxic to *D. magna* than the parent contaminants. *S. capricornutum* inhibition percentage decreased in all cases after ozonation treatment. According to these results, before ozonation is implemented in MWTPs

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for the removal of MCs, the transformation products must first be examined and the treatment time or ozone doses should be extended to complete degradation if necessary.

1. Introduction

Today it is known worldwide that conventional biological treatment systems cannot remove organic compounds in low concentrations (micro-contaminants, MCs) [1–3], and these MCs must be removed prior to discharge or reuse of the wastewater [4]. However, the presence of MCs in the environment is increasing, and more specifically, human and veterinary pharmaceuticals and personal care products, because of their growing use by the population [2,5]. A wide variety of studies on the effects of accumulated MCs on health and the environment can be found in the literature [6–13]. There is clear evidence linking reproductive and neuroendocrine defects in animals and humans with the detection of such contaminants [6–9]. In recent years, the relationship between exposure to endocrine disruptors and changes in metabolism, development, growth and reproduction of organisms (fish, algae, amphibians, etc.) has also been demonstrated [10,11], and some organophosphorus compounds with hormonal activity may be involved in an increasing incidence of certain metabolic disorders such as obesity and Type 2 Diabetes [12]. In addition, laboratory studies have shown the combined effects of these pollutants, so even if they are present in very low concentrations, deleterious effects may be observed when combined [13]. Therefore, the treatment of municipal effluents should also focus on the destruction of extremely low concentrations of potentially toxic organic compounds using several tertiary treatments: chemical oxidation, physical-based systems, and Advanced Oxidation Processes (AOPs) or their combination.

There is a growing trend of applying nanofiltration and reverse osmosis units (NF/RO) to municipal wastewater treatment plant (MWTP) effluents and other water matrices (groundwater, surface and drinking water), specifically for the removal of MCs (priority and emerging contaminants) [14–16]. But the membrane concentrate usually contains organic matter, MCs and residue from the biological wastewater treatment (e.g., soluble microbial products, partially biodegraded organics, and anti-scaling chemicals), and must in turn be treated to minimize its environmental impact. In this study, ozonation was proposed as a suitable treatment for NF/RO retentate, though key process integration parameters must be optimized. At high pH (pH > 7.5), ozonation is considered an AOP because hydroxyl radicals are formed during ozone decomposition in water [17]. Ozone molecules react selectively with compounds containing double chain bonds (C=C), certain functional groups (e.g., OH, CH_3, OCH_3) and N, P, O, and S anions, however, oxidation by $HO^•$ is non-selective. The direct reaction of ozone is known to occur under acidic conditions and in the presence of radical scavengers that inhibit the chain reaction responsible for ozone decomposition. Under alkaline conditions, or in the presence of solutes that promote the radical chain reaction and $HO^•$ formation, the indirect reaction predominates due to the extremely rapid and non-selective nature of $HO^•$ ($10^9\ M^{-1}\ s^{-1}$). However, some authors [18–20] have suggested that in the presence of certain types of radical scavengers found in real wastewater, such as carbonates and bicarbonates and high concentrations of salts, such as SO_4^{2-}, Cl^-, etc., oxidation by molecular ozone is the predominant mechanism, particularly at lower ozone doses.

Ozonation has been studied for treating municipal wastewater treatment plant (MWTP) effluents resulting in ozone consumption in the range of 9–30 mg/L [18,20]. Huber et al., 2005 treated effluents from Conventional Activated Sludge (CAS) and membrane bioreactors (MBR) by ozonation, and found that a high DOC load strongly affects ozonation MC-removal efficiency. Furthermore, ozone reaction with the organic matter dissolved in such effluents could produce toxic compounds, such as formaldehyde, ketones, phenols, nitromethanes, and carcinogenic substances, like bromates and *N*-nitrodimethylamine [21,22]. Current evaluation and determination of MC byproduct degradation by ozonation are also important considerations for environmental protection. These intermediates often differ from the parent compounds in their toxicity and potential for accumulation [23]. According to the literature, most research on the effects of pharmaceuticals or MCs on biological systems and tertiary treatments are based on model compound elimination [4]. Toxicity assessment of pharmaceutical mixtures is both an urgent need and a great challenge to progress in proactive environmental and health risk assessment. Variation in the mixtures, wastewater effluents and the high number of potentially adverse effects to human health and the environment make it difficult to design uniform guidelines [4]. Libralato et al. [24] suggested more or less user-friendly tools such as toxicity scores and indexes with a variety of statistical approaches. For waste discharged into the aquatic environment, Persoone et al. [25] suggested a wastewater classification system which classifies samples as Class I for TU < 0.4, Class II for 0.4 < TU < 1, Class III for 1 < TU < 10, Class IV for 10 < TU < 100 and Class V for TU > 100, where TUs are Toxicity Units representing $100/EC_{50}$. When it is impossible to determine the EC_{50} or TU, toxicity is represented by the percentage of inhibition and immobilization (percentage effect, PE). The hazard classification system for natural waters defines Class I for PE < 20%, Class II for 20 < PE < 50%, Class III for 50 < PE < 100%, Class IV when PE = 100% in at least one test and Class V when PE = 100% in all tests. In addition, all classes are accompanied by a concise judgment: Class I: no acute/chronic toxicity, Class II: slight acute/chronic toxicity, Class III: acute/chronic toxicity, Class IV: high acute/chronic toxicity and Class V: very high acute/chronic toxicity.

There are few studies in the literature that monitor MCs in real municipal wastewater effluents treated by ozonation. Nakada et al. [18] studied the removal efficiencies of 24 pharmaceutically active compounds (PhACs) during sand filtration and ozonation in an operating municipal sewage treatment plant, and concluded that a combination of technologies efficiently removed (>80%) all target compounds. Hollender et al. [26] assessed ozonation as a treatment step for the removal of 220 MCs from a secondary MWTP effluent, the formation of their toxic byproducts such as bromate and nitrosamines, and determined the energy requirements for this enhanced wastewater treatment [26]. Prieto-Rodríguez et al. [27] compared conventional ozonation and Advanced Oxidation Processes (AOPs) that can be powered by solar radiation. Sixty-six MCs were identified and monitored during ozonation. In addition, acute toxicity, measured with *Vibrio fischeri and* respirometry assays, was found to be negligible. It was concluded that chronic toxicity tests must be included in evaluation of the long-term effects on the environment and human health of MCs and their transformation products [27].

The purpose of this work was to study the ozonation of NF retentates of real MWTP effluents for removal of MCs and toxicity. MWTP effluent samples were collected downstream of the secondary