



Ozonation as a pretreatment for nanofiltration: Effect of oxidation pathway on the permeate flux



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ABSTRACT

This study explored effects of feed water pre-ozonation via two distinct oxidation pathways (reactions with molecular O₃ or with radical species as primary oxidants) on the permeate flux during nanofiltration of synthetic humic acid solutions. Twenty treatment scenarios corresponding to different combinations of pre-ozonation pH, calcium concentration and ozone dosage were tested. Changes in the permeate flux of NF90 membranes were interpreted in terms of physicochemical characteristics of feed organics produced by different pre-treatments. The apparent trends in permeate flux depended mostly on calcium concentration and ozone dosage and not on the ozonation mechanism. However, feed waters pre-treated via different oxidation pathways differed significantly in terms of foulant charge, hydrophilicity and concentration, and produced fouling layers with different specific permeabilities. The reduction of NF90 membrane fouling was attributed in part to higher charge and hydrophilicity of ozonated foulants and, in the case of the oxidation by radical species, to partial mineralization of feed organics.

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1. Introduction

The increasing demand for safe and affordable water calls for cost-efficient and robust purification technologies capable of removing pathogenic microorganisms as well as chemical micropollutants, both naturally-occurring and anthropogenic. To respond to this challenge, water treatment plants have been installing additional treatment processes to implement a multiple barrier approach. Membrane separation and advanced oxidation processes as secondary or tertiary treatment options are examples of such additional barriers to contaminants. Nanofiltration (NF) can remove small molecular weight compounds and most micropollutants of concern. Membrane fouling, however, remains a problem that raises the cost of membrane operation and replacement. A robust and inexpensive pretreatment is one approach to mitigating membrane fouling. The NF plant located at Méry-sur-Oise (France) relies on water sources of variable quality and, therefore, needs a flexible yet reliable pretreatment strategy. The facility applies several pretreatment options including ozone-biological activated carbon process [1–3]. The pretreatment lightens the load of foulants on the NF membranes but does not eliminate fouling entirely [4–6]. Ozonation is also used as a pretreatment option at treatment

facilities that employ ultrafiltration, such as the Lake View water treatment plant in Mississauga, Canada [7]. Given the continued use of pre-ozonation in water treatment plants, the effect of this process on the performance of membranes installed downstream in the treatment train needs to be understood.

Many bench-scale and pilot studies have been performed to elucidate the impact of ozonation – alone or in combination with other pretreatment processes – on the flux performance of polymeric UF [8–14] and NF [13,15–22] membranes. Feed waters included natural surface water [8,13–15,19], wastewater treatment plant effluent [9–11,17], dairy wastewater [18], and landfill leachate [22] among others. In some cases, ozonation was found to be effective in reducing UF and NF membrane fouling [9–11,13,14,18,19] while in other studies no improvement in the permeate flux due to pre-ozonation was observed [8,15–17,21,22]. These differences were likely due to the complex dependence of fouling behavior on study-specific process parameters: feed water chemistry, O₃ dosage, additional pretreatment steps [12,23], membrane surface chemistry, presence of microorganisms and biopolymers in the feed, and membrane type (UF versus NF). Ozone dosage, for example, has a major effect on the concentration, charge, and hydrophilicity of ozonated molecules [24–26].

Recently Van Geluwe et al. [27] overviewed the state-of-the-art knowledge of the effects of ozonation on natural organic matter (NOM) and specifically addressed the implications of the ozone-induced changes in the physicochemical properties of

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NOM for membrane fouling. Despite the extensive research on the effects of ozone on NOM and the growing knowledge of how pre-ozonation impacts membrane filtration, there seems to be no systematic understanding of how fouling behavior of ozonated water differs depending on the ozonation mechanism. Even at neutral pH the balance can be shifted towards one of the pathways depending on the presence of initiators, promoters, and inhibitors of ozonation reactions. Another emerging group of membrane-based treatment processes where a particular oxidation pathway – indirect oxidation by radical species – dominates is catalytic oxidation in membrane reactors (e.g. photocatalysis and catalytic ozonation [28–31]).

The objective of our study is to explore whether different oxidation pathways (i.e. molecular O_3 versus $\cdot OH$ radicals as primary oxidants [24,25]) translate into differences in the fouling behavior of ozonated waters. Recognizing that the complexity of NOM may confound interpretation of fouling mechanisms, we choose Aldrich humic acid as a model organic macromolecule. We limit the scope of this work to NF and a synthetic feed solution of humic acid to analyze NF separation performance as a function of the ozonation pathway and calcium concentration in the feed for different O_3 dosages.

2. Experimental

2.1. Model feed solution

Humic acid (HA) sodium salt was purchased from Sigma–Aldrich and used as received. Aldrich HA has been used extensively in membrane filtration studies as a surrogate for NOM (e.g. Suwannee River NOM [32]). Deionized (DI) water was supplied by a commercial ultrapure water system (Lab Five, USFilter) equipped with a terminal 0.2 μm microfilter (PolyCap, Whatman Plc); the resistivity of water was greater than 16 $M\Omega$ cm. The stock solution of 1 g(HA)/L concentration was prepared by dissolving HA in DI water. The concentration of HA was monitored using total organic carbon (TOC) analysis. The stock solution was mixed using a magnetic bar with a rotation speed of ~ 300 rpm for 72 h and stored at 4 °C before diluting it to 6.05 ± 0.01 mg(TOC)/L. The dissolved organic carbon content of the stock solution was measured to be 5.80 ± 0.04 mg/L (after filtration through 0.45 μm syringe filter, Millipore). Calcium chloride (ACS grade, Sigma) was added to select samples. Ozonation was performed on the diluted (6.05 ± 0.01 mg(TOC)/L), unfiltered stock. Initial conductivity of the ozonated feed solutions was in the 65–70 $\mu S/cm$ range for calcium-free samples and in the 300–315 $\mu S/cm$ range for samples with $[Ca^{2+}] = 1$ mM; these conductivity values corresponded to ionic strengths within 1.04–1.12 mM and 4.80–5.04 mM ranges, respectively.

2.2. Preozonation-nanofiltration experiments

The ozone batch reactor and nanofiltration system are schematically illustrated in Fig. 1. Ozonation of the samples was performed in a 500 mL batch reactor. Ozone gas was produced by passing oxygen gas through an ozone generator (OZ2PCS-V; Ozotech, Inc.) with an ozone output of 0.26–0.6 g/h created by 4–9 kV corona discharge. Detailed information on the ozonation system and ozonation reactor performance has been reported elsewhere [13].

Nanofiltration was carried out using a crossflow filtration membrane cell (CF042 (modified); Sterlitech Corp.) with a membrane area of 20.2 cm^2 and a hydraulic diameter of the feed channel of 5.6 mm. Filtration was performed in a recycling mode when both retentate and permeate were returned into the feed tank. Retentate flow rate was monitored by an inline flowmeter (Alicat

Scientific Corp.). Transmembrane pressure and crossflow velocity were maintained constant at 6.89 bar (100 psi) and 5.8 cm/s, respectively, using a bypass valve (Swagelok) and a backpressure regulator (Swagelok). The permeate flux was measured continually by collecting the filtered water on a digital balance (AV8101C, Ohaus) interfaced with a computer via an RS-232 port. All experiments were conducted at the temperature of (23 ± 0.5) °C.

Separate dead-end filtration tests were conducted to apply pore blocking laws. These tests were performed using an unstirred dead-end filtration cell (HP 4750, Sterlitech Corp.; 14.6 cm^2 membrane area). In each experiment, 200 mL of the aqueous solution of non-ozonated or ozonated humic acid solution were filtered until the permeate volume reached ~ 100 mL. The experiments were conducted at the temperature of (20 ± 0.5) °C. The transmembrane pressure was maintained at constant level within the 7.58–10.30 bar (110–150 psi) range. The values of permeate mass were recorded with a time interval of 10 s using a mass balance.

Properties of the NF90 membrane (Dow Water & Process Solutions) are given in Table 1. Prior to each experiment, membranes were soaked overnight in DI water and compacted by filtering DI water at the transmembrane pressure of 6.89 bar for 12 h.

2.3. Pre-ozonation – nanofiltration experimental protocol

The experimental protocol is graphically illustrated in Fig. 2. To selectively enable a specific ozonation mechanism, the initial pH of the feed solution was adjusted to either (2.8–2.9), or 7.0, or (11.0–11.4). The reaction with molecular ozone (O_3) is dominant at the low pH while the oxidation by radical species dominates at high pH [24,26]. No buffers were used to eliminate the possible confounding effect of buffer constituents on the fouling behavior of feed waters. After adjusting pH of the samples treated by O_3 , their conductivity was determined to be ~ 870 , 305, and 1200 $\mu S/cm$ for samples ozonated at pH 2.8, 7.0, and 11.4, respectively. These conductivities corresponded to ionic strengths of 13.9, 4.9, and 19.2 mM. We assumed that this variability in ionic strength did not affect ozone solubility significantly. We note that pH values lower than 2.8 and higher than 11.4 were not chosen to avoid higher ionic strength solutions and possible interferences with ozonation. Adjusting pH to values lower than 2 or higher than 12 would have required addition of a larger amount of acid or base and would have increased conductivity and ionic strength.

Ozone dosages were varied from 0 to 2.5 mg(O_3)/mg(TOC), which corresponded to ozonation times in the 0–50 min range at the gas flow rate of 1 L/min. Given ~ 6 mg(TOC)/L in the feed, the applied dose was in the 0–15 mg(O_3)/L range. Ozonation led to a pH decrease (see Fig. 2) that was dependent on the initial pH: pH did not change substantially when the initial pH was low (2.8) or high (11.4) but decreased by at least 1.8 when the initial pH was 7.0.

Residual ozone was removed by mixing hermetically sealed samples for 1 h using a magnetic stirrer. It was important to remove ozone from the samples to prevent oxidative damage to the aromatic polyamide skin of the NF90 membrane. The indigo method [33] was used to measure the residual ozone and ascertain that it was removed to levels below the detection limit (5 $\mu g/L$).

After ozonation and prior to nanofiltration experiments, the pH of each sample was adjusted to 7.2. The ionic strength was also adjusted to 10 mM in all samples by adding NaCl. With sample-to-sample differences in pH and ionic strength values factored out, the relative behavior of NF flux as a function of pretreatment conditions could be interpreted in terms of differences in the concentration and physicochemical properties of HA ozonated via distinct pathways.

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