Ozonation greatly improves ceramic membrane microfiltration efficiency during wastewater reuse: mechanisms and performance

Journal:	*Environmental Science: Water Research & Technology*
Manuscript ID	EW-ART-02-2022-000105.R2
Article Type:	Paper

Water Impact Statement

Reuse of impaired waters is a key strategy toward water sustainability worldwide. Wastewater reuse with high pressure polymeric membranes is costly energy-wise and prone to fouling. Ceramic membranes are showing real promise as an alternative and when combined with ozone carried onto the membrane surface, we show the promise of almost limitless filtration without the need for extensive cleaning regimes.

Ozonation greatly improves ceramic membrane microfiltration efficiency during wastewater reuse: mechanisms and performance

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Abstract

This study investigated the benefits of using in-situ ozonation to extend ceramic membrane filtration and mitigate fouling during treatment for wastewater reuse. Pre-ozonation has been proven to diminish ceramic membrane fouling, but in-situ ozonation can further sustain ceramic membrane flux. In this study, ceramic membrane filtration cycle times were compared for raw secondary effluent (SE), pre-ozonated SE, and in-situ ozonated SE and data were analyzed with respect to changes in organic matter composition. Operational parameters were chosen to simulate typical full-scale operation. Results show that while pre-ozonation ($mgO_3/mgDOC=1$) can extend filtration cycle time beyond non-ozonated ceramic membrane filtration by approximately 5 times, in-situ ozonation, with a residual ozone concentration of only 0.5ppm on the ceramic membrane surface, extended filtration time by orders of magnitude longer. Like pre-ozonation, in-situ ozonation transformed large molecular weight compounds to lower molecular weights, and also reduced organic matter hydrophobicity, mitigating ceramic membrane fouling. However, in-situ ozonation also simultaneously provided an oxidative mechanism within the membrane during filtration that pre-ozonation did not. No evidence of a major role of hydroxyl radicals produced via catalytic ozonation with the ceramic membrane material was detected. This work demonstrates the extensive improvements possible for ceramic membrane microfiltration when coupled with in-situ ozonation, as part of an alternative water reuse treatment train.

Keywords: ozonation, ceramic membrane, hydroxyl radicals, fouling

1. Introduction

Ceramic membranes have gained increasing interest for wastewater reclamation in recent years. Although water reuse is not a new field of study, it has become difficult for traditional technologies to provide reliable water quality as well as to meet stringent regulations. Compared to polymeric membranes, they can withstand higher temperature, chemical cleaning, and higher pressures[1]. However, like all other membrane processes, one main drawback is fouling, which remains an obstacle for long term operations.

Foulants can typically be divided into four categories, including 1) particles which typically form cake layers on the membrane surface, or get transported into the membrane and block the pores; 2) organic matters that adsorbs to the membrane surface; 3) inorganic components that precipitate on the membrane surface; and 4) microorganisms that result in biofouling[2]. Traditionally, membrane cleaning has been performed by physical backwash[3], chemical cleaning[4], and enhanced chemical backwash (ECB)[5]. Each of these cleaning processes have disadvantages. Physical backwash does not remove NOM adsorbed to the membrane surface nor stuck in the pores easily[4], and also cannot restore the initial flux of the membrane, with declining initial flux after each backwash due to irreversible fouling[6]. Sodium hypochlorite (NaOCl) and sodium hydroxide (NaOH) are two commonly used chemicals for chemical cleaning, but still not all organic matter is able to be removed from the membrane surface[7]. ECB is a more aggressive cleaning method, and not suitable for polymeric membranes since it cannot withstand aggressive chemicals without damaging the membrane integrity. ECB is beneficial in removing irreversible foulants, but can also have negative impacts on ceramic membranes by inducing the release of soluble microbial products (SMP) and extracellular polymeric substances (EPS)[8]. Ozone has also been used as a cleaning agent for ceramic membranes in recent studies[4,9–11].

Ozonation has been widely investigated as a pre-treatment for membrane processes[12–16]. These studies concluded that pre-ozonation can lead to significantly less fouling during membrane filtration due to the degradation of large molecular weight compounds. More recently, research has been focused on in-situ ozonation, allowing a dissolved ozone residual to contact the membrane surface[17–19]. This combined process is suitable for ceramic membrane filtration because ceramics have higher material integrity than polymeric membranes. One main benefit of the combined process over pre-ozonation is that residual ozone can react with foulant on/in the ceramic membrane surface/pores, further induce the degradation of organic matter, and increase permeability. Some studies have also suggested that ceramic membranes can induce the degradation of ozone through catalytic ozonation[20,21], producing hydroxyl radicals, which is a highly reactive and non-selective oxidant. However, other studies have suggested differently, indicating that ceramic membrane do not act as a catalyst for ozone degradation[22–24]. Nawrocki and Fijolek (2013) suggest that the discrepancies in these results stem from whether pH is controlled during the treatment process. Because ozone degrades faster at higher pH[25], it would be important to control pH during the filtration process to isolate any ceramic membrane catalytic effects. However, few studies have controlled pH during in-situ ozonation of wastewater and during catalytic ozonation on the membrane surface, while also evaluating the type of metal oxide that is most efficient at producing radicals.

A concern regarding ozonation in water treatment has been by-products such as NDMA and bromate, which are both potentially carcinogenic[26,27]. Bromate is formed when ozonating water containing bromide and NDMA is formed when water ozonated contains NDMA precursors such as dimethylamine (DMA) [27–29]. Bromate formation can be linearly correlated with higher ozone dose during treatment, and many methods have been established to minimize the formation of bromate during ozonation such as pH adjustment and addition of ammonia; however, when $\mathrm{mgO_3}$ $:\mathrm{mgDOC} \leq 0.4$, little bromate is formed [29]. Ibn Abdul Hamid et al. (2020) found that O_3 (10mg/L) coupled with ceramic membrane was able to reduce the formation of bromate by 50%. They hypothesized that the lower rate of bromate formation might be due to lower ozone exposure from the catalytic ozonation effect of ceramic membrane leading to the formation of hydroxyl radicals.

Despite the dissimilar inferences on whether ceramic membranes are catalysts for ozone degradation, ozone helps reduce membrane fouling and improve permeability. Zhang et al. (2013) concluded that in-situ ozonation was able to double the filtration time of ultrafiltration but did not eliminate irreversible fouling. Song et al. (2020) suggested that pre-ozonation was better at mitigating membrane fouling but in-situ ozonation provided better backwash efficiency since the fouling layers are loosened. Because ozone is a strong oxidant, some have suggested that in-situ ozonation assisted in cleaning of the ceramic membrane since they observed that in-situ ozonation after in-line coagulation was able to maintain a stable transmembrane pressure[32]. Because in-situ ozonation is more resource intensive (injection streams, pressurized systems), it is important to determine how organic matter interacts with ozone inside the membrane and what dose of ozone can maximize filtration cycles. While some studies have demonstrated that pre-ozonation and in-situ ozonation at low concentration dosing can help reduce fouling during ceramic UF filtration, these were investigated using flat sheet ceramic UF membranes with synthetic wastewater [33–35] or were under low flow scenarios [36,37].

This study fills a unique gap in the literature in use of a microfiltration (MF) ceramic membrane to treat a complex wastewater matrix, comparing development of membrane fouling for both pre and in-situ ozonation in a realistic cylindrical membrane continuous flow scenario. It also compares the OH radical formation from different membrane materials. Experiments examined whether catalytic ozonation, producing OH radicals, occurs inside the ceramic membrane during wastewater treatment and the effects of low residual in-situ ozonation on the foulants inside the membrane during wastewater treatment. Understanding the transformation of foulants and its impact on ceramic membrane filtration cycles at the bench scale level will help with the implementation of in-situ ozonation for long term operation.

2. Materials and Methods

2.1 Membrane, reagents and test water

Two ceramic membranes were used for the study. An Al_2O_3 cylindrical membrane provided by Aqua-Aerobic Systems Inc. was the primary ceramic membrane system examined as this was a pilot version of a larger scale system developed for water treatment. For some specific studies on catalytic ozonation, a ZrO_2-TiO_2 disc membrane provided by Sterlitech Corporation was utilized to evaluate the potential production of OH radicals due to catalytic interaction of ozone with the membrane surface. Specifications provided by the respective manufacturer of each membrane are presented in Table 1.

This study evaluated secondary effluent from City of Boulder Water Resource Recovery Facility (WRRF) in Boulder, Colorado. The facility utilizes a multi-stage treatment process, including physical separation, microbiological nutrient removal and ultraviolet (UV) light disinfection, to treat an average of 12 million gallons of wastewater per day. All water was sampled before UV light disinfection, filtered through 0.45um polyethersulfone filters and stored at 4℃. Prior to all experiments, all water samples were adjusted to room temperature (25°C). Properties of the wastewater samples are shown in

Table 2. Para-chlorobenzoic acid (pCBA) and Indigo-trisulfonate were both purchased from Sigma Aldrich.

Table 1. Properties of the cylindrical ceramic membranes

Properties	Al_2O_3	ZrO_2-TiO_2
Manufacturer	Aqua-Aerobic Systems, Inc.	Sterlitech Corporation
Shape	Cylindrical	Disc
Dimensions (diameter x length) (mm)	30×100	4.7
Diameter of channels (mm)	2.5	n/a
Number of channels	55	n/a
Active membrane area (m^2)	0.04	0.0013
Nominal pore size (micron)	0.1	0.14
Flow direction	Inside out	n/a
Operation mode	Dead end	Dead end
Acceptable range of operating pH	3-12	0-14

Table 2. Properties of wastewater samples (n=4)

Properties	Values
pH	7.19 ± 0.06
UV_{254} (cm^{-1})	0.144 ± 0.006
DOC (mg/L)	7.63 ± 0.63
Alkalinity (mg-$CaCO_3$/L)	118

2.2 Experimental setup and procedure

Ceramic membrane microfiltration experiments were performed with the bench-scale cylindrical membrane set-up as shown in Figure 1. The ceramic membrane filtration system was a tubular membrane slightly modified to perform three different dead-end filtration experiments: 1) ceramic membrane filtration only; 2) pre-ozonation coupled with ceramic membrane filtration; 3) in-situ ozonation onto the ceramic membrane filtration. Prior to each experiment, the ceramic membrane was chemically cleaned following the procedure provided by by Aqua-Aerobic Systems Inc. To understand any possible catalytic ozonation resulting in OH radical production, the disc ceramic membrane filtration experiments were also set up as in Figure 1A, but only in-situ ozonation was performed. The disc ceramic membranes could not be backwashed, therefore, filtration cycles were not performed, and this system was only used to compare hydroxyl radical production from the zirconium and titanium embedded membrane to the Al_2O_3 ceramic membrane tubular system.

Stock aqueous ozone was generated by feeding pure oxygen (Airgas, USA) into a high output ozone generator (TG-40, Ozone Solutions, USA) and then feeding the gaseous ozone into a pressure vessel (10 psi) containing deionized water at 2 degrees Celsius. For pre-ozonation, ozone was mixed with secondary effluent at a ratio of mg-O_3/mg-DOC=1 for 10 minutes before filtration began, during which the entire ozone residual was degraded. For in-situ ozonation, ozone was continuously fed into the filtration system prior to ceramic membrane filtration, as presented in Figure 1, with a residual target of 0.5 mg/L detected directly before the membrane surface. For each filtration experiment, membrane flux was maintained at approximately $245 \frac{\mathrm{L}}{\mathrm{m^2 \cdot hr}}$.

Six different samples were collected throughout the experiments for comparison, 1) raw secondary effluent (Raw); 2) effluent from ceramic membrane filtration only (CMF); 3) ozonation alone (O_3); 4) effluent from pre-ozonation coupled with ceramic membrane filtration (O_3 + CMF); 5) In-situ ozonation prior to ceramic membrane filtration (In-situ (BF CMF)); 6) In-situ ozonation after ceramic membrane filtration (In-situ (AF CMF)).

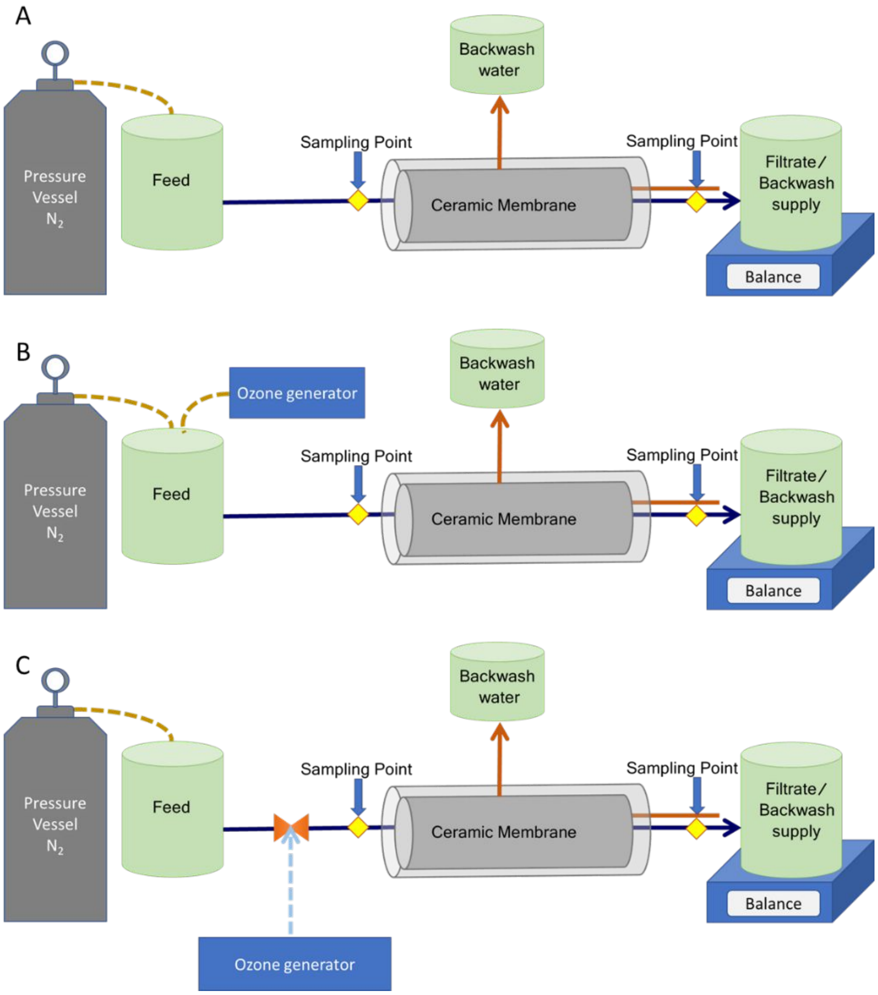

Figure 1. Schematic of bench-scale tubular ceramic membrane microfiltration system setup. A) raw (non-ozonated) filtration; B) Pre-ozonated filtration; C) In-situ ozonation.

2.3 Analytical methods

Organic carbon was measured using a Sievers M5310C TOC analyzer; alkalinity was measured using a HACH Digital Titrator; and pH was measured using a Fisher Scientific AB15 pH meter.

The concentration of stock and residual dissolved ozone was verified using the indigo method[38]. The absorbance of the samples was measured using a UV-vis spectrophotometer (HACH DR6000, Colorado, USA) at 600nm.

Three-dimensional excitation-emission matrices (EEMs) were collected using a spectrofluorometer (John Yvon Horiba FluoroMax-4, NJ). Fluorescence intensity was measured during emission scans from 300 nm to 700 nm every 2 nm at set excitation wavelengths in 10 nm increments from 240 nm to 500 nm. A 5 nm bandpass for excitation and emission wavelengths and 0.25s integration time were used.

Size characterization of the natural organic matter (NOM) was performed using size-exclusion chromatography (SEC) with UV and DOC quantification by an Agilent 1200 LC system (Palo Alto, CA) with a Toyopearl HW-50 S $250 \times 20\ \mathrm{mm}^2$ column (Grace, Rottenburg, Germany), with an injection volume of 2.0 mL. DOC eluting from the SEC column was measured with a Sievers M9 Portable TOC analyzer (General Electric, CO) with $1.5\mu\mathrm{L/min}$ acid and oxidizer flow rates. A diode array from Agilent was used as a detector (model 1200 Palo Alto, CA) monitoring at 254 nm. The mobile phase consisted of phosphate buffer (0.0024 M NaH_2PO_4, 0.0016 M Na_2HPO_4) and 0.025 M Na_2SO_4 adjusted to pH of 6.8 ± 0.1. The flow rate was held at 1.0 mL/min which corresponded to a pressure of 13 bar. Samples were prepared by adjusting the ionic strength to 1M with concentrated mobile phase eluent.

pCBA was selected as a probe compound to indirectly measure the concentration of hydroxyl radicals due its fast reaction rate with hydroxyl radicals compared to ozone $\left(\mathrm{k}_{\mathrm{O_3/pCBA}} < 0.15\mathrm{M}^{-1}\mathrm{s}^{-1}, \mathrm{k}_{\mathrm{OH/pCBA}} = 5 \times 10^9\mathrm{M}^{-1}\mathrm{s}^{-1}\right)$[39]. pCBA concentration was determined using an Agilent 1200 Series high performance liquid chromatography (HPLC) with a UV detector using 234nm for absorbance detection and a reverse phase C-18 column (all from Agilent, Santa Clara, CA, USA). pCBA was eluented with 60% methanol and 40% 10mM phosphoric acid, respectively.

3. Results and Discussion

3.1 Effects of ozonation and ceramic membrane filtration on wastewater characteristics

3.1.1 TOC, UV_{254}, and pH

Table 3 presents the changes of TOC, UV_{254}, and pH after various treatment methods. TOC concentration was reduced by 9%, 21%, and 30% by Al_2O_3 membrane filtration alone, pre-ozonation alone, and pre-ozonation coupled with Al_2O_3 membrane filtration, respectively. Absorbance at UV_{254} was reduced by 6%, 58%, and 63% by Al_2O_3 membrane filtration alone, pre-ozonation alone, and pre-ozonation coupled with Al_2O_3 membrane filtration, respectively. The similar reduction rate of TOC and UV_{254} after Al_2O_3 membrane filtration indicates that, as expected, the ceramic membrane did not alter the structure of the organic matter (OM). On the other hand, pre-ozonation minimally reduced TOC concentration (~21%), but UV_{254} was significantly reduced, indicating that OM was transformed during the process. UV_{254} is a surrogate for aromatic carbon content[40], therefore, the results from pre-ozonation alone primarily indicates a loss of aromatic carbon content, rather than a loss of overall TOC. Owen et al. also demonstrated that ozonation of OM will convert humic substances into non-humic substances, as well as increase the polarity of OM[41].

During in-situ ozonation treatment, TOC was reduced by 26% before Al_2O_3 membrane filtration and 24% after Al_2O_3 membrane filtration, indicating virtually no change in the TOC concentration due to filtration. UV_{254} absorbance was reduced by approximately 60% and did not vary much before and after Al_2O_3 membrane filtration either. Alresheedi et al. (2019) demonstrated that O_3 can be used as a cleaning agent for ceramic membranes with high efficiency, therefore, the slight increase in TOC after in-situ ozonation may be due to ozone dislodging OM adsorbed to the ceramic membrane surface, or oxidized OM that was blocking the pores. While UV_{254} absorbance did not change significantly for in-situ ozonation before and after Al_2O_3 membrane filtration, UV_{254} for in-situ ozonation prior to Al_2O_3 membrane filtration was reduced more than pre-ozonation alone. This might have been due to the higher initial dose of ozone for in-situ ozonation. For different system setups, the initial ozone exposure would vary depending on the distance from which ozone is injected upstream of the ceramic filtration to maintain approximately 0.5ppm on the ceramic membrane surface.

Regardless of treatment methods, pH did not vary significantly($\pm \mathbf{0.08\ units}$). This is likely due to the high alkalinity of the source water. Alkalinity has multiple implications regarding ceramic membrane filtration. First, bicarbonate and carbonate scavenges OH· at a relatively fast reaction rate ($\mathbf{k_{HCO_3^-/OH\cdot} = 8.5 \times 10^6 M^{-1} s^{-1}, k_{CO_3^{2-}/OH\cdot} = 3.9 \times 10^8 M^{-1} s^{-1}}$)[42], which will reduce the amount of available hydroxyl radicals for OM oxidation. Second, ozone decomposition is highly affected by pH, alkalinity, and DOM concentration[25]**.** High alkalinity will slow down ozone degradation, and scavenge hydroxyl radicals to diminish the availability of hydroxyl radicals to oxidize OM. These two factors will also play a significant role in catalytic ozonation on the membrane discussed in section 3.2.

Table 3. Variations of TOC, UV_{254}, and pH after various treatment processes. For pre-ozonation, mgO_3:mgDOC=1; for in-situ ozonation, target residual ozone on ceramic membrane surface was ~ 0.5ppm

Treatment Method	**TOC (ppm)**	**UV_{254} (cm^{-1})**	**pH**
Secondary Effluent	7.63 ± 0.63	0.144 ± 0.006	7.19
Non-ozonated filtration	6.99 ± 1.45	0.098 ± 0.034	7.28
O_3 Only	6.05 ± 0.68	0.061 ± 0.003	7.32
O_3 + CMF	5.33 ± 0.66	0.053 ± 0.005	7.27
In-situ (BF CMF)	5.66 ± 0.66	0.055 ± 0.003	7.38
In-situ (AF CMF)	5.82 ± 0.59	0.057 ± 0.005	7.40

3.1.2 Fluorescence

Fluorescence is a widely used technique to assess characteristics of organic matter in wastewater. Specific fluorescence peak intensity for peaks A, B, C, and T were assessed after various treatments. The excitation and emission region, center points, and type of organic for each peak is defined in Table 4.

Table 4. Peak region and center points for each peak[43]

Peak	**Range**	**Center Points (Ex, Em) nm**	**Type**
A	Ex: 240-270nm Em: 380-470nm	(260,426)	Humic-like
B	Ex: 260-290nm Em: 300-320nm	(280,310)	Tyrosin-like
C	Ex: 300-340nm Em: 400-480nm	(320,440)	Humic-like

T	Ex: 260-290nm Em: 326-350nm	(280,338)	Tryptophan

Comparing Al_2O_3 ceramic membrane filtered only samples to raw samples, Peaks A, B, C, and T were reduced by 0%, 2%, 2%, and 10%, respectively, compared to the raw samples, indicating that ceramic membrane filtration alone did not change the composition of the wastewater. This change is unsurprising since Al_2O_3 ceramic membrane filtration alone only minimally reduces TOC, and mostly removed large organic molecules (similar to a study by Song et al., (2010)), which are mainly protein-like substances in our sample. When ozonation alone was applied to the wastewater, Peaks A, B, C, and T were reduced by 63%, 50%, 71%, and 33%, respectively, compared to the raw samples. This is consistent with previous studies that concluded advanced treatment (i.e., filtration, chlorination, reverse osmosis, etc.) are better at removing compounds that fluoresce in region Em>380nm[45]. Peaks A and C were reduced the most, likely due to humic-like substances containing electron-rich moieties that react rapidly with ozone and hydroxyl radicals[46]. When pre-ozonation was coupled with Al_2O_3 ceramic membrane filtration, Peaks A, B, C, and T were reduced by 71%, 65%, 73%, and 75%, respectively. There was slight increase in removal of Peaks A and C, but much more significant improvement of removal for Peaks B and T. Peaks B and T reflect protein-like substances, which tend to be large molecular weight compounds, and may be retained on the membrane surface and the main reason for membrane fouling[12,47]. Peaks A and C are smaller molecular weight compounds and will likely pass through the ceramic membrane.

During in-situ ozonation prior to ceramic membrane filtration, Peaks A, B, C, and T were reduced by 62%, 58%, 69%, and 57%, respectively. These results are also consistent with pre-ozonation, where Peaks A and C had a higher reduction rate than Peaks B and T. Peak T had considerable reduction during in-situ ozonation, compared to pre-ozonation alone, while the other three peaks remained relatively similar. This may have been a result of better mixing mechanisms utilized during in-situ ozonation. During in-situ ozonation, wastewater and ozone was mixed in small volumes, providing better diffusion. The fluorescence intensity for in-situ ozonation after ceramic membrane filtration increased slightly. Peaks A, B, C, and T for in-situ ozonation after ceramic membrane filtration increased by 7%, 4%, 7%, and 3%, respectively. This is expected after the in-situ filtration process due to the release of organic matter that was previously deposited in the membrane during filtration. Further analysis would be needed to determine which type of foulant, humic or protein, ozone/hydroxyl radical oxidizes more quickly in the ceramic membrane.

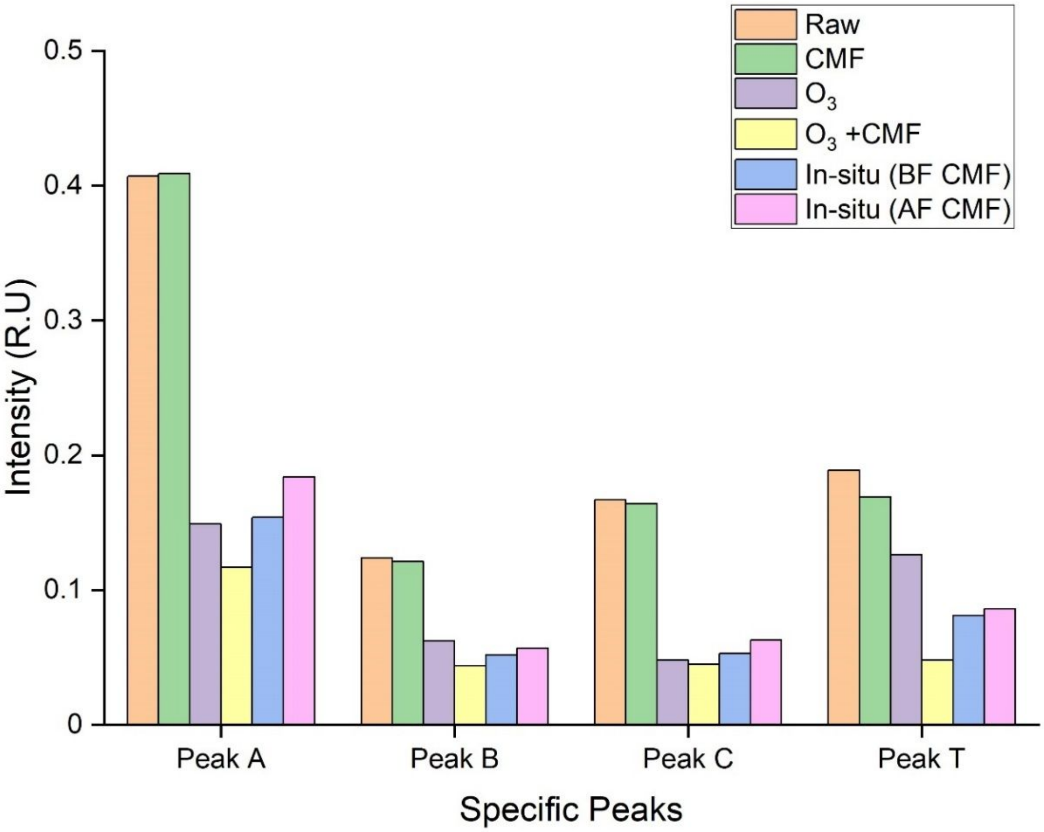

Figure 2. Fluorescence intensities at specific peaks for water samples after various treatment methods. Peak A, B, C, and T refers to humic-like, tyrosine-like, humic-like, and tryptophan-like substances.

3.1.3 Size Exclusion Chromatography

SEC was utilized to characterize the molecular weight distribution of organic matter in the water samples, comparing various treatment methods to the raw secondary effluent. Organic matter that eluted early (elution volume of 25mL) tends to be larger molecular weight compounds (i.e., biopolymers), and organic matter eluted later tends to be smaller molecular weight compounds (i.e., humic acids, building blocks etc.). All water samples show a multimodal distribution, but distinctive changes after different treatment processes.

Figure 3A presents the changes in TOC after Al_2O_3 membrane filtration alone, pre-ozonation coupled with Al_2O_3 membrane filtration, and in-situ ozonation, and Figure 3B presents the changes in UV_{254} after each of the aforementioned treatment processes. As shown in Figure 3A, Al_2O_3 membrane filtration alone slightly reduced large OM, but overall did not change the distribution of OM compared to the raw secondary effluent. UV_{254} for Al_2O_3 membrane filtration alone also displayed similar distribution with the raw secondary effluent, indicating it did not alter the molecular structure of the OM. When Al_2O_3 membrane filtration is coupled with pre-ozonation, a change in molecular weight distribution is observed. As shown in Figure 3A, the peak for pre-ozonation coupled with Al_2O_3 membrane filtration was not only reduced compared to raw secondary effluent at early elution volumes, but it also shifted slightly to the right, indicating a change in molecular size and structure, which is also evident by the change of UV_{254} shown in Figure 3B. There is also a significant reduction of TOC at elution volume of 50mL. Previous studies concluded that ozone reactions with OM chromophores were non-size specific, however, hydroxyl radicals favoured larger molecular weight compounds, likely due to its faster reaction rate with larger molecular weight compounds[48].

Figure 3C and D demonstrate the TOC and UV_{254} variations between pre-ozonation alone and in-situ ozonation prior to Al_2O_3 membrane filtration. In-situ ozonation reduced more TOC and UV_{254} compared to pre-ozonation alone, likely due to the higher ozone exposure given the place where ozone was spiked. Applied dose of ozone to achieve a residual of 0.5ppm will vary depending on the ozone exposure period before ceramic filtration. If ozone is injected closer to the ceramic membrane, the change in TOC and reduction of UV_{254} would be less significant, and vice versa if the ozone injection is further upstream. However, to maintain an ozone dose of approximately 0.5ppm on the ceramic membrane surface, injecting ozone further upstream would require a higher initial dose, which will require a higher cost.

Figure 3E and F demonstrate the TOC and UV_{254} variations between in-situ ozonation sampled prior to and after Al_2O_3 membrane filtration. Neither TOC nor UV_{254} signal distribution varied significantly, indicating minimal reaction between ozone/hydroxyl radicals and OM in the bulk water occurred during the filtration process. However, TOC and UV_{254} distributions are slightly higher for in-situ ozonation after Al_2O_3 membrane filtration, indicating some organic foulants might have been dislodged from the ceramic membrane pores. Because UV_{254} signal after Al_2O_3

membrane filtration also increased, it is likely that foulants dislodged from the membrane pores contained aromatic compounds[40].

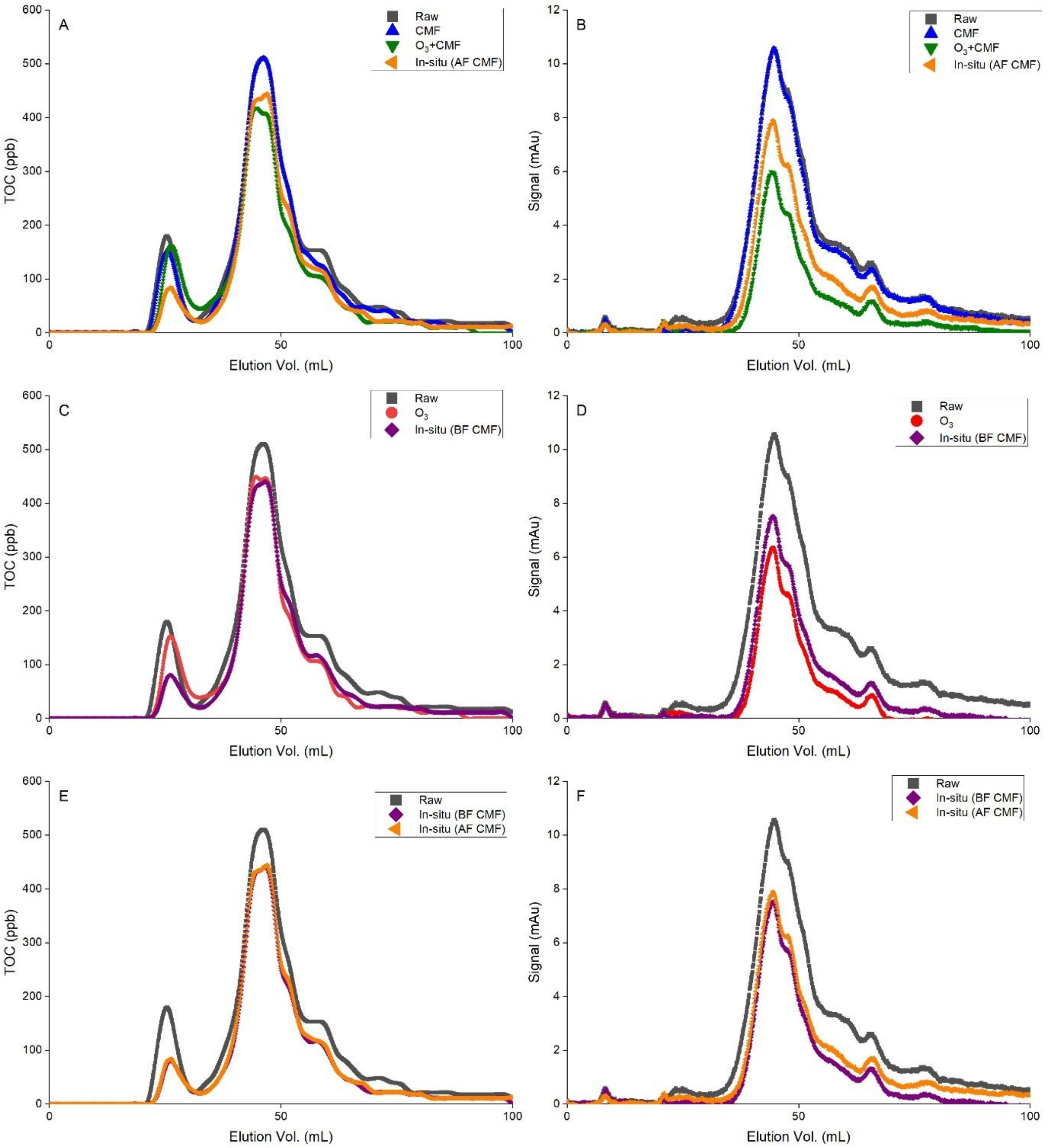

Figure 3. TOC and UV_{254} variations during size exclusion chromatography examinations following different treatment processes. A), C), and E) are TOC comparisons, and B), D), and F) are UV_{254} comparisons accordingly.

3.2 Steady-state hydroxyl radical concentration across the ceramic membranes

Catalytic ozonation was investigated across ceramic membrane filtration for two different membrane materials: Al_2O_3 and ZrO_2-TiO_2. Table 5 presents the average steady-state concentration of hydroxyl radicals, and the average percentage increase across its respective ceramic membranes. For Al_2O_3, the average steady-state concentration before ceramic membrane filtration is 8.35×10^{-13} M, and 8.47×10^{-13} M after ceramic membrane filtration, with an average of 1.4% increase in steady-state hydroxyl radical production. For ZrO_2-TiO_2, the average steady-state concentration before ceramic membrane filtration is 9.51×10^{-13} M, and 1.06×10^{-12} M after ceramic membrane filtration, with an average of 9.6% increase in steady-state hydroxyl radical production. Past studies have shown that ceramic membranes have catalytic ozonation effects that can increase ozone degradation and enhance hydroxyl radical production on the membrane surface[30,49–51]. This study demonstrated that neither Al_2O_3 nor ZrO_2-TiO_2 ceramic membranes have induced catalytic ozonation. For both Al_2O_3 and ZrO_2-TiO_2, steady-state hydroxyl radical concentration before and after ceramic membrane filtration was not statistically different ($p>0.05$). However, hydroxyl radical production on ZrO_2-TiO_2 membranes surface did show better results than Al_2O_3 membrane ($p<0.05$).

Ozone degradation depends greatly on pH, where higher pH accelerates ozone decomposition[25]. One of the major impurities of ceramic membranes is sodium[23], due to the use of sodium hydroxide as a leaching agent during production[52]. Commercially available aluminium oxide produced using this method often results in alkaline residues that will affect pH of the solution when introduced to the water sample. Previous research regarding catalytic ozonation either did not control pH or did not measure alkalinity of the water samples[21,50,53]. Water samples with low alkalinity, when coming in contact with the ceramic membrane with high concentration of sodium, would be prone to an increase in pH, resulting in the acceleration of ozone decomposition. For BLDRSE, the alkalinity for the water sample was approximately 118 mg-$CaCO_3$/L and did not change significantly after ceramic membrane filtration. The high alkalinity from the secondary effluent, BLDRSE, likely provided enough buffering capacity to avoid accelerated ozone degradation due to increased pH.

Commercially available ceramic membranes (i.e., Aqua-Aerobic System Inc, Tami Industries, etc.) contain impurities that may affect the ozone degradation processes when in contact with the water sample. Ozone molecules, being relatively non-polar compared to water molecules, are often out competed by water molecules to adsorb to alumina adsorption sites[54]. If ozone is out competed by water and cannot adsorb to alumina surface, there would be no catalytic ozonation reaction occurring on the surface of the ceramic membranes. It is also unsurprising that Al_2O_3 ceramic membrane produced little to no catalytic activity since it is mostly used as a supporting layer for other catalytic metals rather than being used as a catalytic material itself[22].

Another catalytic mechanism proposed by Legube and Karpel Vel Leitner, (1999) suggested that the ceramic membrane surface acts as an adsorption site for organic compounds to form chelates, which can be degraded by ozone or hydroxyl radical easier. This can lead to desorption of the oxidized organic compounds, providing new adsorption sites for further oxidation of organic compounds newly adsorbed to the surface of the ceramic membrane. This is highly dependent on the adsorption affinity to ceramic membranes and constituents that will compete for adsorption sites. Orthophosphate anions and carbonate can adsorb preferably to the ceramic membrane surface, decreasing the available sites for organic compounds and decreasing the potential membrane catalytic activity[51,56]. Considering the high alkalinity in the water samples, it is likely that carbonate ions interfered with the catalytic activity of ozonation.

Table 5. Comparison of steady-state hydroxyl radical concentration across Al_2O_3 and ZrO_2-TiO_2 ceramic membranes

	Average Steady-state OH radical concentration [M]		
Membrane Material	Before Membrane	After Membrane	% Difference Range
Al_2O_3	$(8.35 \pm 2.71) \times 10^{-13}$	$(8.47 \pm 2.73) \times 10^{-13}$	$0\% - 3.9\%$
ZrO_2-TiO_2	$(1.11 \pm 0.0379) \times 10^{-12}$	$(1.21 \pm 0.129) \times 10^{-12}$	$3.7\% - 18.3\%$

3.3 Filtration cycle

When comparing ceramic membrane filtration coupled with either raw (non-ozonated) secondary effluent, pre-ozonated secondary effluent, or in-situ ozonated secondary effluent, raw secondary effluent filtration cycles simulated typical wastewater treatment plant filtration operational procedures, with a filtration time of approximately 30 minutes or reaching critical transmembrane pressure of 10 psi first, before backwash begun. Pre-ozonation and in-situ ozonation filtration were run until reaching a critical transmembrane pressure of 10 psi, as recommended by the ceramic membrane manufacturer.

As illustrated in Figure 4, transmembrane pressure for raw secondary effluent increased the fastest. After 3 filtration cycles (~90 minutes), the transmembrane pressure already approached the critical level of 10 psi. At the end of 6 filtration cycles, backwash alone was not able recover the membrane permeability to below 10 psi. Substantial foulants accumulated on the membrane surface, resulting in the 7th filtration cycle to end before 30 minutes, since the system was not able to maintain constant flow. For pre-ozonation, the transmembrane pressure increased at a much slower rate. Critical transmembrane pressure was not reached until approximately 168 minutes. Interestingly, in-situ ozonation did not ever reach critical transmembrane pressure during the experimental period. Based on the linear rate that the transmembrane pressure was increasing, filtration for in-situ ozonation would proceed for an estimated 300 hours (~18,000 minutes). This demonstrates that in addition to ozone oxidizing large organic matter compounds, it can also remove or degrade foulants that are adsorbed to the membrane surface or retained in the pores. Owen showed that scanning electron microscopy of a disc membrane demonstrated no signs of foulants when the membrane was directly exposed to ozone in solution[57].

The improvement in flux could be due to a number of reasons. As mentioned in the introduction, there are four processes that can result in fouling of the membrane, and this study focused on the organic matter that adsorbs on the membrane surface. Direct ozone reaction with OM is known to convert more hydrophobic OM into more hydrophilic OM[41]. Previous studies demonstrated that while little overall DOC was reduced by ozonation, hydrophobic DOC was reduced by 45-50%[44,58]. The hydrophilic products of these reactions are less adsorptive to the membrane surface, resulting in an increase in membrane flux after ozonation.

The change in molecular size distribution after ozonation also likely helped improve membrane flux. Large molecular weight compounds (i.e., protein, polysaccharide) tend to block membrane pores, and result in an increase in transmembrane pressure to maintain constant flow[59]. This hypothesis is consistent with SEC results, where large molecular weight compounds showed a slight decrease, and smaller molecular weight compounds showed no change. Overall TOC rejection by Al_2O_3 ceramic membrane was approximately 9%, which is consistent with other studies that show low percentage of TOC rejection, and large portions of OM passing through the membrane[3]. After pre-ozonation, we saw a distinctive reduction in molecular size of each group of compounds. This likely contributed to the prolonged filtration cycle for pre-ozonation. As for in-situ ozonation, large molecular weight compounds were further reduced, likely because of the higher applied dose of ozone, and ozone's preferential reaction with large molecular weight compounds. Further reduction of large molecular weight compounds will improve membrane flux, as was the case for the membrane flux for in-situ ozonation improving significantly relative to pre-ozonation.

Chemical cleaning is performed in many ways: 1) clean-in-place (CIP); 2) clean-out-of-place (COP); 3) chemical wash (CW); and 4) chemical enhanced backwash (CEB)[60]. A wide variety of chemicals are used for chemical cleaning, such as phosphoric, hydrochloric, and citric acids[60]. Ozone, a strong oxidant, has also been used for membrane cleaning in recent years where after 30 minutes of ozone cleaning, initial membrane flux was able to be re-established[9]. For our study, small amount of (~0.5ppm) of ozone residual was maintained on the surface of the ceramic membrane. The residual ozone likely oxidized both the cake layer retained on the membrane surface, and also the foulants in the membrane pores, dislodging them from the membrane surface/pores to pass through membrane, as evidenced by the slight increase in TOC and UV_{254} post-ceramic membrane filtration in the SEC results. Asif, Li, et al., (2021) reported similar results, where in-situ ozonation significantly reduced the concentration of TOC, and polysaccharide and protein fractions of SMP on the membrane surface. The small amount of ozone residual provided a cleaning mechanism to help alleviate membrane fouling considerably, as hypothesized in the oxidation schematic in Figure 5, and extended filtration cycle time by orders of magnitude.

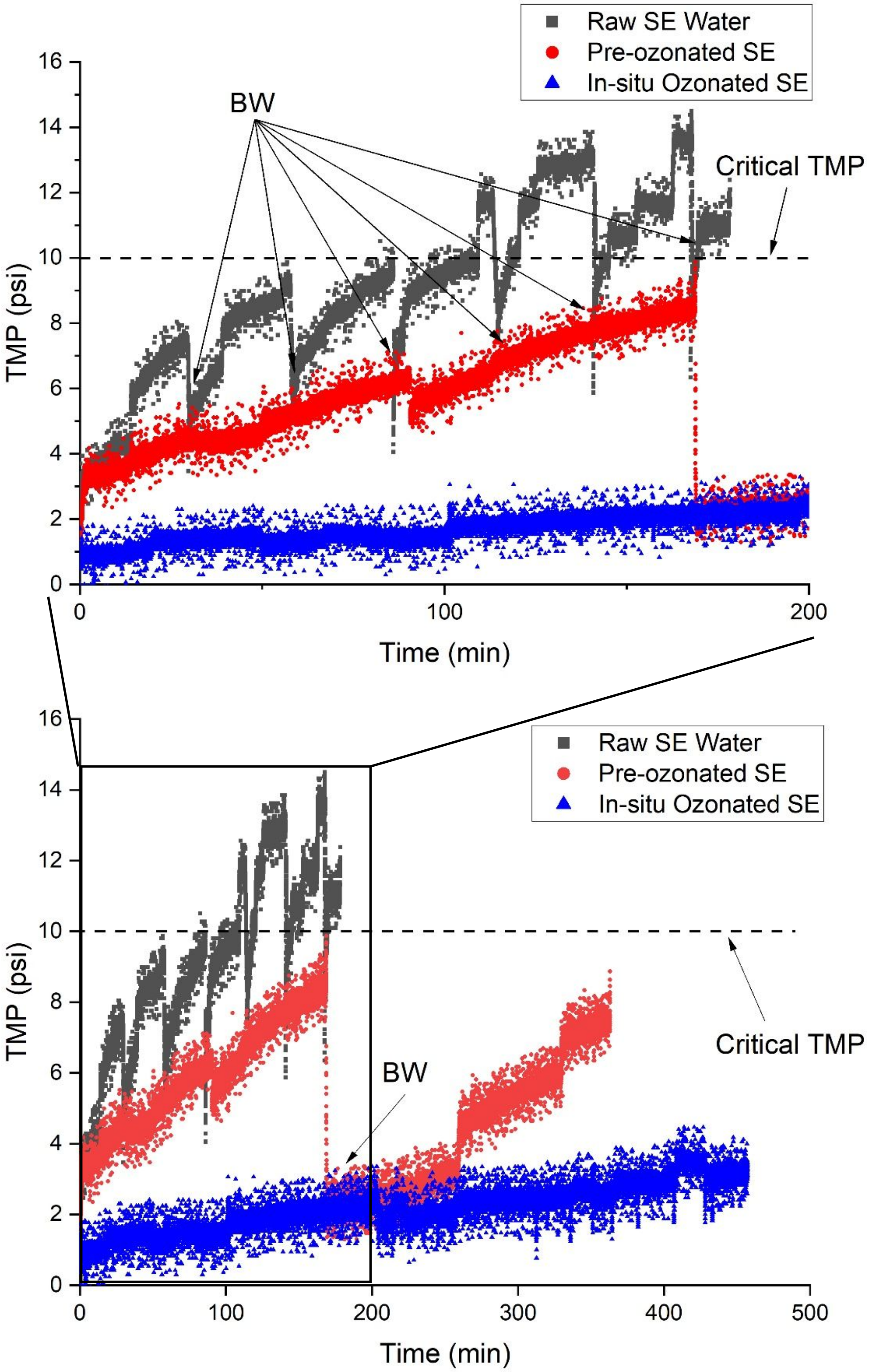
Raw SE Water
Pre-ozonated SE
In-situ Ozonated SE
BW
Critical TMP
TMP (psi)
0
2
4
6
8
10
12
14
16
Time (min)
0
100
200
Raw SE Water
Pre-ozonated SE
In-situ Ozonated SE
BW
Critical TMP
TMP (psi)
0
2
4
6
8
10
12
14
16
Time (min)
0
100
200
300
400
500

Figure 4. Filtration cycles using Al_2O_3 cylindrical membrane for raw SE, pre-ozonated SE, and in-situ ozonated SE. A) Filtration cycle for 200 mins; B) Filtration cycle for 500 mins. Initial TMP for all three filtration modes are between 0.5-1 psi as measured using ultrapure water.

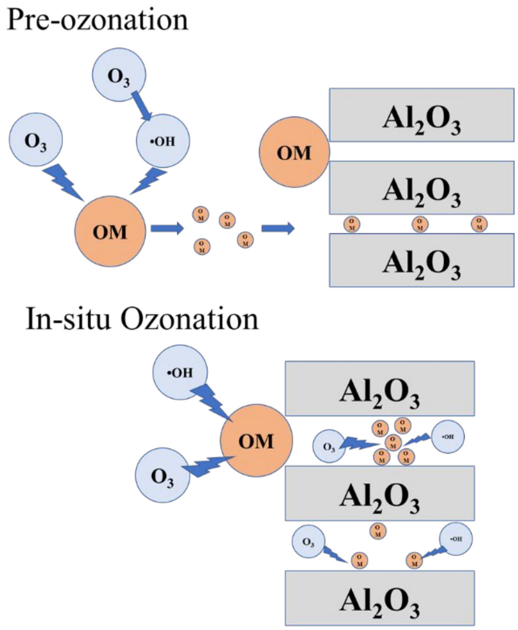

Figure 5: Hypothesized fouling mitigation mechanism of pre- and in-situ oxidation of organic matter foulants

Conclusion

While pre-ozonation was able to mitigate fouling for ceramic membrane filtration, in-situ ozonation not only mitigated fouling, but was also able to simultaneously clean the ceramic membrane, further extending its filtration cycle time.

Pre-ozonation of secondary effluent extended the filtration cycle time approximately 5 times compared to ceramic membrane filtration of raw secondary effluent. This is mainly due to the transformation of organic matter due to ozonation. Ozonation of organic matter did not reduce the concentration of organic matter but altered its composition. Large molecular weight compounds, which are a primary cause of fouling, were transformed into lower molecular weight compounds.

Hydrophobic organic matter was also transformed into more hydrophilic compounds, which result in less fouling.

As for in-situ ozonation, not only was organic matter transformed before entering the ceramic membrane, ozonation process occurring inside the ceramic membrane pores also assisted in extending the filtration cycle time. Similar to pre-ozonation, ozone transformed the size and hydrophobicity of the organic matter. However, the residual ozone likely reacted with foulants inside the membrane pores, further oxidizing the foulants to improve the ceramic membrane's permeability. TOC results showed that there is a slight increase in organic matter concentration, indicating some organic foulants in the ceramic membrane pores likely got dislodged.

This study also investigated catalytic ozonation on two ceramic membrane surfaces. Ozone degradation was not accelerated when contacted with the ceramic membranes tested. pCBA was used as a probe compound to indirectly measure hydroxyl radical concentration, and no statistical difference in hydroxyl radical steady-state concentration before and after ceramic membrane filtration resulted. While ozone decays into hydroxyl radicals faster at high pH, the high alkalinity in the water sample minimized any pH change when in contact with the ceramic membrane, and thus no pH-driven acceleration of ozone decay was noted.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was supported by the National Science Foundation (Washington, DC) supported I/UCRC, the Membrane Science, Engineering and Technology (MAST) Center (Boulder, CO). We would like to thank the MAST Center for providing funding, and excellent suggestions throughout the progress of this work.

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