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The effects of combined ozonation and filtration on disinfection by-product formation

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Abstract

The effects of combined ozonation and membrane filtration on the removal of the natural organic matter (NOM) and the formation of disinfection by-products (DBPs) were investigated. Ozonation/filtration resulted in a reduction of up to 50% in the dissolved organic carbon (DOC) concentration. Furthermore, humic substances were converted to non-humic substances, with changes in the humic and non-humic substance concentrations of up to −50% and +20%, respectively. Ozonation/filtration resulted in the formation of partially oxidized compounds from NOM that were less reactive with chlorine, decreasing the concentration of simulated distribution system total trihalomethanes (SDS TTHMs) and simulated distribution system halo acetic acids (SDS HAAs) by up to 80% and 65%, respectively. Reducing the molecular weight cut-off (MWCO) of the membranes resulted in reductions in the concentrations of SDS TTHMs and SDS HAAs. Using a membrane with a 5 kD MWCO, the minimum gaseous ozone concentration required to bring about effective NOM degradation and meet regulatory requirements for chlorinated DBPs was 2.5 g/m^3.

Keywords: Ceramic membranes; Nanofiltration; Ultrafiltration; Ozonation; Disinfection by-products (DBPs); Water quality; Natural organic matter (NOM)

1. Introduction

Natural organic matter (NOM) is composed of a heterogeneous mixture of organic compounds that can be of human origin or the result of natural processes. NOM can be broadly divided into two fractions: humic substances (HS), which are composed of fulvic and humic acids, and non-humic substances (non-HS), which include carbohydrates, lipids, and amino acids.

In water treatment systems, the presence of NOM is a cause of concern because of its reaction with disinfectants. Chlorination of drinking water results in the formation of disinfection by-products (DBPs), such as trihalomethanes (THMs), some of which are known carcinogens (Morris et al., 1992; Mughal, 1992; Kool et al., 1985). While HS have been recognized as the primary precursors of chlorination byproducts (Ichihashi et al., 1999; Manahan, 1993; Reckhow et al., 1990; Collins et al., 1986), non-HS also result in the formation of many regulated or potentially regulated DBPs. The non-humic fraction of the NOM is generally more biodegradable and, as such, supports bacterial regrowth in water distribution systems (Yavich, 1998; Mogren et al., 1990).

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The use of ozonation in water treatment processes results in a decrease in the formation of THMs and halo acetic acids (HAAs) upon subsequent chlorination (Zhang et al., 2001; Richardson et al., 1999). Increases in ozone dosages result in a concomitant decrease in the concentrations of THMs and HAAs formed from subsequent chlorination (Lee, 2001; Cipparone et al., 1997; Amy et al., 1988). Ozonation results in the formation of more polar compounds and an increase in the biodegradability of the chemicals found in the water as compared to that generated with chlorination (Koechling et al., 1996; Owen et al., 1995; Amy et al., 1992). The reactions that occur during ozonation produce by-products, including aldehydes (formaldehyde, glyoxal, and methylglyoxal), ketones, gyloxylic acid, and pyruvic acid (Paode et al., 1997; Weinberg and Glaze, 1996). Some of these by-products are of particular concern due to their mutagenicity and carcinogenicity (Bull and McCabe, 1984). Also, as they are easily biodegradable, they can serve as substrates for microbial regrowth in the distribution system. The ozonation by-products can be easily removed by biofiltration (Yavich and Masten, 2003; Griffini et al., 1999).

Membrane filtration is an effective method to remove particles, microorganisms and organic matter from drinking waters. Compared with conventional treatment methods, membrane processes (i) can provide better quality water, (ii) minimize disinfectant demand, (iii) are more compact, (iv) provide easier operational control and less maintenance, and (v) generate less sludge (US EPA, 2001; Cleveland, 1999; Nakatsuka et al., 1996).

One of the major challenges associated with the operation of membrane filtration plants is the decrease in the permeate flux due to membrane fouling (Seidel and Elimelech, 2002; US EPA, 2001; Crozes et al., 1997). The deposition of NOM on the filter surface is a primary cause of membrane fouling (Lee et al., 2001; Nilson and Di Giano, 1996; Ravindran et al., 1993). Fouling not only reduces the efficiency of the membrane, but the characteristics of the foulants also control the rejection of other substances by the membrane (Schafer et al., 2000). The application of ozonation prior to membrane filtration reduces membrane fouling and enhances permeate flux (Karnik et al., 2005; Schlichter et al., 2003, 2004; Hashino et al., 2000; Hyung et al., 2000; Kim et al., 1999). The use of ozonation in combination with membrane processes has not been extensively investigated; however, the limited research in this area has shown that ceramic membranes in combination with ozonation achieved a high permeate flux without membrane damage (Schlichter et al., 2004; Chen, 2003; Kim et al., 1999; Kim and Somiya, 2001; Moulin et al., 1991; Bablon et al., 1991).

In this study, we have investigated the quality of water after combined ozonation–membrane filtration. The permeate collected was used to determine the effect of treatment on the UV absorbance measured at 254 nm (UV-254), DOC, HS, and non-HS. The concentrations of SDS TTHMs, SDS HAAs, aldehydes, ketones, and ketoacids were also evaluated. The effect of gaseous ozone concentration on the water quality of the permeate was investigated.

2. Materials and methods

2.1. Ozonation/membrane filtration

A schematic representation of the ozonation/membrane system is shown in Fig. 1. Tubular ceramic membranes (clover-leaf design (containing three channels), CéRAM Inside, Tami North America, St. Laurent, Qué., Canada) with molecular weight cut-offs of 15, 5, and 1 kD were used. The external diameter of each titania membrane was 10 mm and the active membrane length was 25 cm. The membrane had a total filtering area of 41.2 cm^2. A stainless steel filter holder, Teflon® tubing and stainless steel or Teflon® joints and valves were used throughout the system. Other components included: 3.5- and 1.5-L water-jacked glass reservoirs made of Pyrex glass, and a simple Y inline mixer (Ozone Service, Burton, B.C., Canada). Ozone gas was added into the water stream through the simple Y inline mixer just before entering the membrane module.

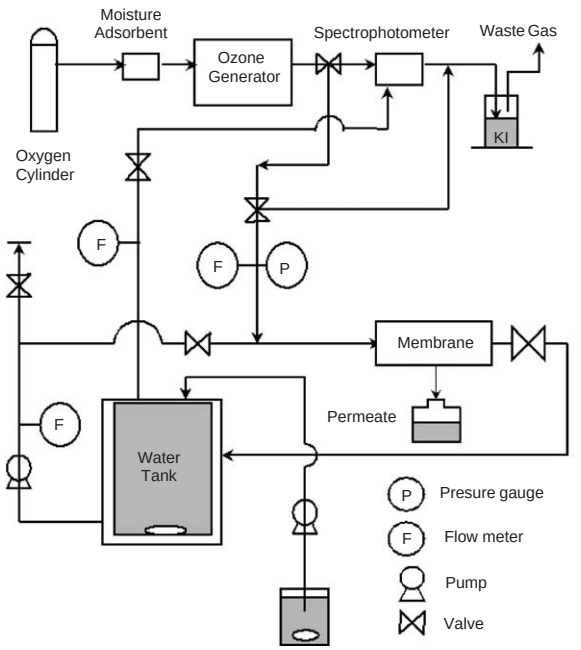

Fig. 1. Schematic representation of the ozone–membrane filtration system.

To generate ozone, pure oxygen gas (99.999%) from a pressurized cylinder was dried using a molecular sieve trap, and then fed to the ozone generator (Model OZ2PCS, Ozotech Inc., Yreka, CA). Varying the voltage applied to the ozone generator controlled the gaseous ozone concentration. The excess gas was vented after passing the gas through a 2% potassium iodide (KI) solution to destroy any residual ozone gas. The water level in the 3.5-L reservoir was maintained at a constant level during the experiments using a peristaltic pump (Masterflex Model 7520-35, Cole-Parmer Co., Chicago, IL) to transfer water from the 1.5-L reservoir into the 3.5-L reservoir. A constant water temperature of 20 °C was maintained using a recirculating water bath. The operating conditions used are given in Table 1. The gaseous ozone concentration was 2.5 g/m^3, unless otherwise stated.

The experiments were performed with membrane cross flow velocity of 0.6 m/s; the flow was turbulent with a Reynolds number of approximately 6000. Previous studies in our laboratory considered such important factors, as gas flow rate, water flow rate, and the characteristics of the source water, which influence the ozone transfer efficiency (Chen, 2003). The ozonation/membrane system used in this study can achieve high ozone mass transfer, and thus, requires a lower ozone dose, gas flow rate, and water flow rate than comparable systems (Chen, 2003). The volumetric mass transfer coefficient for ozone in the experimental setup was determined to be 0.138 min^{-1} (Chen, 2003).

Ceramic membranes with molecular weight cut-offs of 15, 5, and 1 kD were used. The specific flux for 15, 5 and 1 kD membranes were 60, 20 and 8 L/m^2-bar, respectively. The permeate flux recovery trends are discussed in detail in our earlier work (Karnik et al., 2005). The conductivity remained practically unchanged for the duration of the experiment (the change was <0.01 μS/cm).

Permeate samples were collected in bottles covered with Parafilm® and stored in an ice-bath for the duration of the experiment. The first 400 mL of permeate collected was labeled as P1 and the latter 1000 ml as P2. P1 and P2 samples were collected to study the effect of ozone contact time on the water quality.

Samples of the pre-filtered raw water (FRW), P1, P2 and from the 3.5-L water tank reservoir (WT) were analyzed for UV-254 absorbance, dissolved organic carbon (DOC), HS and non-HS, chlorine residual, SDS total trihalomethanes (SDS TTHMs), SDS halo acetic acids (SDS HAAs), aldehydes, ketones and ketoacids. The effect of gaseous ozone concentration on water quality was investigated using a membrane with a molecular weight cut-off (MWCO) of 15 kD. The gaseous ozone concentration was varied between 1.5 and 10 g/m^3.

To study the effect of pH on the process, the pH of Lake Lansing water (initial pH 8.2) sample was adjusted to 7.0 by the addition of hydrochloric acid (concentrated, ACS reagent grade). We chose a pH of 7 because earlier studies revealed no difference in the permeate flux recovery at pH 6 and pH 7 (Karnik et al., 2005). The membranes used in these experiments had MWCOs of 5 and 15 kD.

Table 1
Operating conditions for the ozone–membrane filtration system

Water recirculation rate	2.75 LPM
Water temperature	20 °C
Ozone gas flow rate	100 mL/min
TMP	0.2 bar

2.2. Water source

Experiments were carried out on samples taken from Lake Lansing (Haslett, MI). The typical characteristics of the water from Lake Lansing, a borderline eutrophic lake, are given in Table 2. The samples were collected at the boat ramp at the Lake Lansing Park-South, Haslett, MI in five-gallon polyethylene carboys and stored at 4 °C. The maximum storage period was 7 days. Water samples were pre-filtered through a 0.45-μm mixed cellulose ester (Millipore-HA) filter before testing.

2.3. Membrane cleaning and preparation

Prior to each experiment, the membrane was thoroughly cleaned using a procedure based on that developed by Xing et al. (2003). Membranes were soaked in a sodium hydroxide solution (15 g/L) at

Table 2
Typical characteristics of Lake Lansing water (Haslett, MI)[a]

Parameters	Lake Lansing
TOC (mg/L)	8.6–11.6
pH	7.7–8.6
Alkalinity (mg/L as $CaCO_3$)	145–157
UV-254 (abs.)	0.160–0.180
SDS THMs[b] (μg/L)	240
SDS HAAs[b] (μg/L)	75
BDOC (mg/L)	1.0–4.1
Nitrate (mg/L)	0.44
Total phosphate (mg/L)	0.06
Hardness (mg/L as $CaCO_3$)	190–198

[a]All data reported are obtained from the Lake Lansing Watershed Advisory Committee Report (1998) except for SDS THMs and SDS HAAs, which were measured as part of this study.

[b]SDS THM and SDS HAA were measured using Standard Method 5710 and US EPA Method 552.2, respectively.

85 °C for 30 min; following this, the membrane was rinsed with double deionized (DDI) water. The membrane was then soaked in a nitric acid solution (0.1 M) at 50 °C for another 30 min followed by thorough rinsing with DDI water. Finally, the membrane was steam sterilized at 121 °C for 30 min. The effectiveness of the cleaning procedure was verified by measuring the permeate flux through the membranes using DDI water to ensure that the initial membrane flux was the same in all experiments.

2.4. Analytical methods

2.4.1. Gas-phase ozone analysis

The absorbance of ozone in the gas phase was measured at 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) using a 2-mm path length quartz flow-through cell. An extinction coefficient of 3000 $M^{-1} cm^{-1}$ (Hoigné, 1988) was used to calculate the ozone concentration.

2.4.2. UV-254 absorbance

The UV absorbance of the water samples was measured at a wavelength of 254 nm with a Milton Roy Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) using a 1 cm quartz cell.

2.4.3. Dissolved organic carbon (DOC)

DOC was analyzed using an OI Analytical Model 1010 analyzer. The TOC analyzer uses the UV/persulfate method (Standard Method, 1998). To ensure the reliability of the method, standards having TOC concentrations of 2.5, 5, 7, 10 mg/L (OI Analytical) were run and samples were analyzed in triplicate. A blank was also run with every set of samples.

2.4.4. Humic substances (HS) and non-humic substances (non-HS)

The HS in the samples were isolated from the water samples by adsorption on XAD-8 resin according to Method 5510C (Clesceri et al., 1998). A 100 mL sample was acidified with concentrated phosphoric acid and eluted through a 10 mm diameter (ID) × 15 cm long column at a flow rate of 2 mL/min. The effluent from the column was collected and then analyzed for TOC, which represented the non-humic fraction of the dissolved organic matter in the water sample. The resin-packed column was then back eluted with 100 mL of 0.1 N sodium hydroxide at a flow rate of 2 mL/min. The eluent was collected and acidified with concentrated phosphoric acid to a pH less than 4, purged with high-purity helium for 3 min to remove inorganic carbon, and analyzed for TOC. The organic content of the eluent represented the concentration of HS.

2.4.5. Chlorine residual

Chlorine residual was measured using the iodometric method, Method 4500B (Clesceri et al., 1998).

2.4.6. SDS total trihalomethanes (SDS TTHMs) and SDS halo acetic acids (SDS HAAs)

Water samples were dosed with a chlorine concentration that ensured a residual chlorine concentration in the range of 0.5–2 mg/L after 48 h incubation at room temperature according to the procedures in Standard Method 2350 (Clesceri et al., 1998). The THM compounds, chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$), were extracted from the water samples using hexane and analyzed by gas chromatography (Method 5710, Clesceri et al., 1998). A Perkin Elmer Autosystem gas chromatograph (Perkin Elmer Instruments, Shelton, CT) equipped with an electron capture detector (ECD), an auto-sampler, and a 30 m × 0.25 mm ID, 1 μm DB-5ms column (J&W Scientific, Folsom, CA) was used for the analysis. The oven temperature was ramped from 50 to 150 °C at a rate of 10 °C/min. The flow rate of the carrier gas (N_2) was 12.0 mL/min. The injector and detector temperatures were 275 and 350 °C, respectively.

SDS HAAs were produced by chlorination as described above. The concentrations of monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), trichloroacetic acid (TCAA), and dibromoacetic acid (DBAA) were determined using US EPA Method 552.2. A Perkin Elmer Autosystem gas chromatograph (Perkin Elmer Instruments, Shelton, CT) equipped with an ECD, an autosampler, and a 30 m × 0.32 mm ID, 3 μm DB-1 column (J&W Scientific, Folsom, CA) was used for the analysis. The oven temperature was programmed to hold for 15 min at 32 °C, then increased to 75 °C at a rate of 5 °C/min and held 5 min, then increased to 100 °C at a rate of 5 °C/min. The carrier gas flow (nitrogen) was 10 mL/min with the injector and detector temperatures at 200 and 260 °C, respectively.

2.4.7. Aldehydes, ketones and ketoacids

USEPA Method 556 (Munch et al., 1998) was used to monitor for formaldehyde, propionaldehyde, glyoxal, methyl glyoxal, acetone, and 2-butanone, ketomalonic acid, pyruvicacid and gyloxylic acid. A Perkin Elmer Autosystem gas chromatograph (Perkin Elmer Instruments, Shelton, CT) equipped with an ECD, an autosampler, and a 30 m × 0.25 mm ID, 0.5 μm DB-5ms column (J&W Scientific, Folsom, CA) was used in the analysis. The oven temperature was programmed to hold for 1 min at 50 °C, then increased to 220 °C at a rate of 4 °C/min followed by an increase to 250 °C at a rate of 20 °C/min with a 5 min hold time. The carrier gas flow

was 1.0 mL/min and the injector and detector temperatures were 180 and 300 °C, respectively.

3. Results and discussion

All data are reported as a percent decrease as compared to the concentrations present in the raw feed water. The results found for the feed water are given in Table 3.

3.1. Effect of ozonation, ultrafiltration, and ozonation–ultrafiltration on water quality

A study was conducted to compare the improvements in water quality results achieved using ultrafiltration (UF), ozonation, and ozonation–UF. The apparatus illustrated in Fig. 1 was used for all three experiments. In the case of the ozonation experiment, the membrane filter element was removed and the permeate collection ports were sealed. In the ozonation experiment, samples were collected from the 3.5 L reservoir after the same time as that used for sampling in the ozonation–UF experiment. As shown in Table 4, UF was the least effective of the three processes for the removal of DOC, HS, NHS, SDS TTHMs, and SDS HAAs. The quality of the treated water was further improved when ozonation and UF were combined. Not only was the removal of UV-254, DOC, HS, NHS, SDS TTHMs, and SDS HAAs enhanced over either of the processes used alone, but the combined process resulted in the production of lower concentrations of aldehydes, ketones, and ketoacids than ozonation alone. This suggests a synergy between ozonation and membrane filtration in providing high-quality water.

The effects of ozonation time on the removal efficiencies can be observed by comparing the results for permeate 1 and 2. The longer ozone contact time did not result in a large increase in the removal efficiency for UV-254 (65.2% vs. 70.1%), suggesting that most of the UV-254 absorbing material were degraded in the time necessary to collect the first 400 mL of sample (i.e., within 4–5 h). On the contrary, the removal efficiencies of DOC, SDS TTHMs, and SDS HAAs for permeate 2 were roughly twice that for permeate 1, indicating that the reaction of ozone with TTHM and HAA precursors is slower than that for ozone with the UV-absorbing material.

3.2. Effect of membrane MWCO on the water quality

As shown in Figs. 2 and 3, there is a little difference in the DOC levels in the P1 samples for all three membranes. However, for the P2 samples, there is a statistically significant ($p<0.05$) decrease in the DOC levels when the MWCO of the membrane was decreased

Table 3
Initial concentrations of filtered raw water from Lake Lansing

Experiment[c]	Effect of MWCO[a], natural pH 7.9–8.2			Effect of ozone dose[b], natural pH 7.9–8.2			Effect of pH[b], pH adjusted to 7.0	
	15 kD	5 kD	1 kD	10	2.5	1.5	15 kD	5 kD
UV-254 (abs)	0.174±0.001	0.174±0.001	0.174±0.001	0.174±0.003	0.174±0.003	0.174±0.003	0.171±0.005	0.171±0.056
DOC (mg/L)	10.6±1.9	10.6±1.9	10.6±1.9	10.9±0.2	10.9±0.2	10.9±0.2	11.9±0.49	11.9±0.49
HS (mg/L)	4.75±0.45	4.75±0.46	4.75±0.47	5.0±0.84	5.0±0.84	5.0±0.84	6.1±0.5	6.1±0.49
NHS (mg/L)	4.36±0.19	4.36±0.19	4.36±0.19	2.99±0.20	2.99±0.20	2.99±0.20	3.94±0.77	3.94±0.79
SDS TTHMs (μg/L)	195.3±12.5	195.3±12.5	195.3±12.5	242.3±20.0	242.3±20.0	242.3±20.0	230±9.1	230±9.1
SDS HAAs (μg/L)	81.1±4.23	81.1±4.2	81.2±4.2	82.3±4.2	82.3±4.25	82.3±4.25	87.7±1.6	87.7±1.6
Aldehydes–ketones (μg/L)	24.8±2.8	24.8±2.8	24.8±2.8	24.0±2.7	24±2.7	24±2.7	6.2±1.1	6.2±1.1
Ketoacids (μg/L)	1.7±2.5	1.7±2.5	1.7±2.5	0.67±0.48	0.67±0.48	0.67±0.48	1.83±0.86	1.83±0.86

The values are reported in actual concentration values ± standard deviation.
[a] $n = 9$, triplicate experiments with each analysis run in triplicate.
[b] $n = 6$, duplicate experiments with each analysis run in triplicate.
[c] These entries provide a cross reference to the relevant experiments described in this study.

Table 4
Comparison of performance parameters ozonation alone, UF alone, and combined ozonation/UF

Experiment[a]	FRW, initial values	Permeate 1 (% reduction)			Permeate 2 (% reduction)		
		UF	Ozonation	Ozonation + UF	UF	Ozonation	Ozonation + UF
UV-254 (abs)	0.174 ± 0.001	48.1 ± 2.8	65.2 ± 3.2	78.8 ± 1.4	48.2 ± 1.2	70.1 ± 2.9	83.9 ± 4.6
DOC (mg/L)	10.6 ± 1.9	12.3 ± 2.9	21.2 ± 0.6	26.6 ± 0.2	17.3 ± 1.0	42.1 ± 1.2	37.1 ± 7.9
HS (mg/L)	4.75 ± 0.45	5.4 ± 2.1	37.3 ± 6.1	48.0 ± 0.2	13.2 ± 3.0	50.2 ± 3.8	59.8 ± 12.0
NHS (mg/L) (% Increase)	−4.4 ± 0.19	−2.1 ± 0.6	−14.2 ± 0.6	−17.0 ± 0.1	−4.2 ± 2.0	−16.2 ± 2.0	−23.4 ± 7.7
SDS TTHMs (μg/L)	195.3 ± 12.5	4.2 ± 1.1	15.0 ± 1.3	16.5 ± 1.4	10.1 ± 2.1	35.4 ± 1.2	44.7 ± 3.3
SDS HAAs (μg/L)	81.2 ± 4.2	3.4 ± 0.4	10.2 ± 0.5	24.7 ± 3.7	13.2 ± 0.4	19.2 ± 2.6	34.7 ± 1.9
[b]Aldehydes-Ketones (μg/L)	24.8 ± 2.8	20.3 ± 0.3	201.3 ± 8.3	173.8 ± 4.0	19.2 ± 3.0	501.2 ± 10.2	386.1 ± 0.3
[b]Ketoacids (μg/L)	1.8 ± 2.5	1.5 ± 0.3	224.3 ± 15.4	156.2 ± 3.8	1.0 ± 0.1	890.0 ± 14.2	746.5 ± 0.1

[a]Experimental setup: Fig. 1, experimental conditions: Table 1. The membrane had a MWCO of 15 kD.
[b]The concentrations of aldehydes, ketones and ketoacids increase in P1 and P2. Also, the P1 and P2 values are the actual concentrations of these compounds.

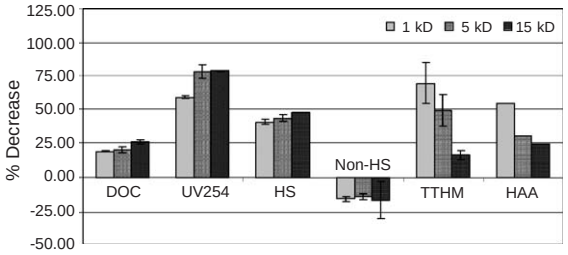

Fig. 2. Effect of molecular weight cut-off on permeate 1 (first 400 mL of the sample). Experimental setup: Fig. 1, operating conditions: Table 1. Ozone dose: 2.5 g/m^3, membrane size: 15, 5 and 1 kD. *All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%.

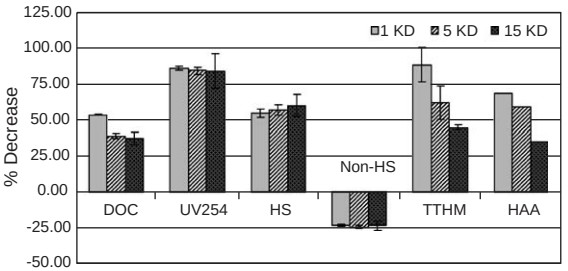

Fig. 3. Effect of molecular weight cut-off on permeate 2 (latter 1000 mL of the sample). Experimental setup: Fig. 1, operating conditions: Table 1. Ozone dose: 2.5 g/m^3, membrane size: 15, 5 and 1 kD. *All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%.

from 5 to 1 kD. One explanation for this result is that after extended ozonation a significant fraction of the DOC is in the molecular size range from 1 to 5 kD. Ozonation of NOM is known to result in a decrease in the molecular weight of the organic matter (Mellema, 1998), which would then result in these compounds passing through the coarser membranes, but not through the 1 kD membrane. An alternate explanation is that the 1 kD membrane is a more effective catalyst for the degradation of NOM than are the coarser membranes, presumably because the smaller pores have a greater surface area. If this is the case, then with the 1 kD membrane prolonged ozonation could result in the mineralization of a greater portion of the NOM to CO_2 and water.

As shown in Figs. 2 and 3, for the 5 and 15 kD membranes, the MWCO of the membranes did not have a statistically significant effect on the UV-254 of the P1 and P2 samples (>0.05). Also, as the results for the P1 and P2 samples were not very different, increasing the ozone contact time did not lead to a great increase in the removal of UV absorbing substances. Even after extensive ozonation, approximately 15% of the UV-254 absorbance of P2 samples remains in the samples, suggesting that while most of the UV absorbing substances react with ozone, there is a recalcitrant fraction that does not react with ozone.

The data presented in Table 4 show that the removal of UV-254 was much greater with ozonation than with UF. This suggests that the removal of the UV-254 absorbing compounds is predominately due to the reaction of ozone with these substances and not due to filtration. These results are consistent with previous research on the ozonation of Lake Lansing water. Yavich and Masten (2003) found that ozone reacts rapidly with aromatic fraction of the NOM, resulting in a significant decrease in UV-254 even at low ozone dosages. These workers also found that after this initial decrease increasing the ozone contact time did not lead to a further large decrease in the UV-254.

Only with the 1 kD membrane, did extended ozonation result in an increase in the removal of UV-254. The lower removal of UV-254 absorbance in P1 samples with the 1 kD membrane (as compared to that with the 5 and 15 kD membranes) cannot be explained by differences in the seasonal nature of the NOM, since replicate experiments (for the 1 kD membrane) were conducted in May and November, yielding consistent results. It is possible that with the 1 kD membrane there are catalytic reactions that produce UV absorbing compounds that pass through the membrane. It should also be noted that as the MWCO of the membranes is reduced, the permeate flux decreased, thus, the ozone contact time increased, as the time required to collect equal volumes of sample increases. While we plan to continue to investigate this phenomenon, one should note that this result does not negate our conclusions regarding the overall effectiveness of the hybrid process in reducing the concentrations of disinfection byproducts.

With all three membranes, ozonation/membrane filtration resulted in a reduction of approximately 45% in the HS concentration in the P1 samples and an approximately 55% reduction in the P2 samples (see Figs. 2 and 3). This reduction is, in part, due to the reaction of NOM with either ozone or .OH radicals, since an increase in the non-HS concentration after ozonation/filtration was observed. The increase in non-HS concentration could only be caused by the conversion of HS to non-HS. Filtration would not have resulted in such a conversion. This conclusion is substantiated by data shown in Table 4, which show that the percent removal of HS using UF is 5.4% and 13.2% for P1 and P2, respectively, while for the P1 and P2 samples, 37.3% and 50.2%, respectively, of the HS were removed by ozonation.

The concentrations of non-HS measured in P1 samples increased by approximately 10%, while that in P2 samples increased by approximately 20% (see Figs. 2 and 3), indicating that the reaction of HS to form non-HS continued throughout the course of the experiment. The enhanced reduction in the concentration of humic substance in the P2 samples compared to that in P1 samples provides further evidence of the importance of oxidation reactions. If the HS were removed purely by filtration, the level of removals would not likely change with ozonation time. These results are consistent with those of Mellema (1998), who found that ozonation resulted in a significant reduction in the concentration of HS with an apparent molecular weight of 3–7 kD (Mellema, 1998). For the UF experiment, the increase in HS removal from 5.4% to 13% in the P1 and P2 samples, respectively, suggests that there may be some formation of a fouling layer that results in improved removal of HS. If this is the case, then the presence of a fouling layer did not have a detrimental effect on permeate flux.

Ozonation/filtration resulted in a significant reduction ($p<0.05$) in the SDS TTHMs and SDS HAA formed after chlorination (see Figs. 2 and 3), as compared to that removed by filtration alone (see Table 4). This reduction was seen in both the P1 and P2 samples. The reduction in SDS TTHMs found in the chlorinated P2 samples increased from 44% to 88% when the membrane pore size was decreased from 15 to 1 kD. The reduction in SDS TTHMs was significantly greater in the P2 than in the P1 samples ($p<0.05$). This decrease in the concentration of TTHM precursors with extended ozonation, along with the data comparing removal efficiencies for the hybrid system with ozonation alone and membrane filtration alone (see Table 4), is further confirmation of the importance of oxidation reactions in the removal of DBP precursors. This is consistent with the work of Lee (2001) and Chen (2003) who showed that ozonation resulted in a significant decrease in SDS TTHM formation after chlorination. Similar trends were observed for SDS HAAs, although the levels of reductions were less than that achieved for SDS TTHMs (38% compared to 68%), indicating that the precursors of TTHMs and HAAs react at different rates with ozone and/or OH radicals, resulting in different removal efficiencies. In both cases it appears that after ozonation a significant fraction of the TTHM and HAA precursors that remain are in molecular weight range from 1 to 15 kD.

As shown in Fig. 4 and Table 4, the concentrations of aldehydes, ketones and ketoacids increased after both ozonation and ozonation/membrane filtration and with ozone contact time (compare P1 and P2 results). The concentrations of these species found in the permeate after UF was less than 10% of that after ozonation or ozonation/filtration, indicating the importance of ozonation in forming these chemicals. The influence of ozone contact time on the concentrations of these chemicals is consistent with the work of Lee (2001) who found that the concentration of ketoacids in treated Lake Lansing water ranged from 42 to 370 μg/L for retention times of 4–25 min at an ozone dose of 1 mg/mg C, and that the concentrations increased with increasing retention time. Similar concentration ranges were reported by Chen (2003) who found that the concentration of ketoacids in treated Lake Lansing water ranged from 40 to 1200 μg/L for an ozone dose of 2.5 mg ozone/mg C. As shown in Fig. 4, the concentration of aldehydes, ketones and ketoacids decreased ten-fold when the membrane MWCO was decreased from 5 to 1 kD. This is quite surprising, since the molecular weights of these compounds measured are much smaller than 1 kD and would be expected to pass through the 1 kD membrane. Again, these results suggest that oxidation reactions play a significant role in determining the effectiveness of the ozone/membrane system and that the catalytic oxidation of compounds appears to be

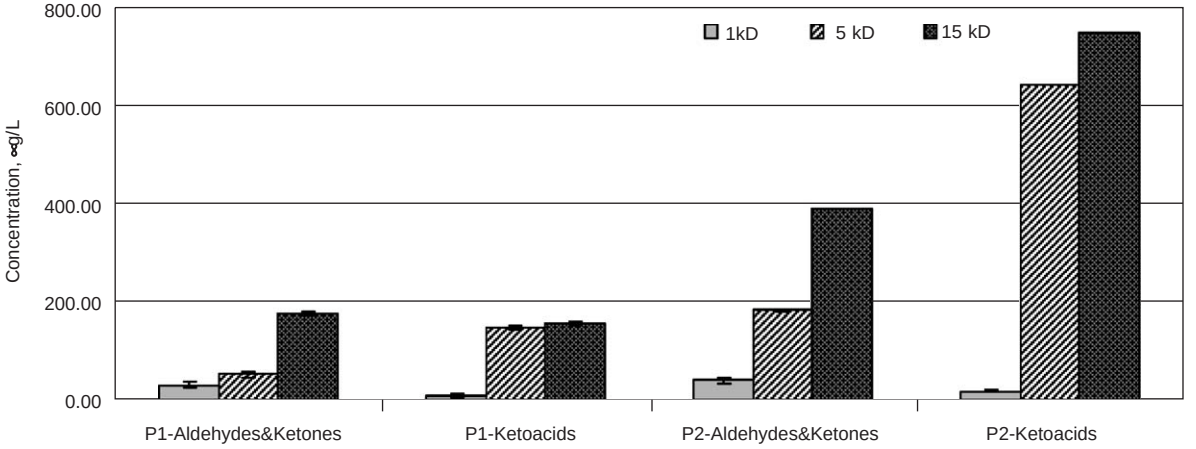

Fig. 4. Effect of molecular weight cut-off on ozonation by-products. Experimental setup: Fig. 1, operating conditions: Table 1. Ozone dose: 2.5 g/m^3, membrane size: 15, 5 and 1 kD. *All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%.

more effective on the 1 kD membrane than that on the 5 or 15 kD membrane.

3.3. The effect of gaseous ozone concentration on water quality

As shown in Figs. 5 and 6, with 15 kD MWCO membrane, variations in the gaseous ozone concentration (over the range from 1.5 to 10 g/m^3) had little effect on the extent DOC removal. An explanation for this behavior is that, at the dosages used in this experiment, only a small fraction of the DOC is mineralized (converted to CO_2 and water) and that ozone simply converts larger molecules into smaller ones, which then pass through the membrane. Chen (2003) and Mellema (1998) also found, that at ozone dosages in the range 1–4 mg/mg C, little of the organic carbon was mineralized. This was confirmed by the apparent molecular weight distribution of the organic carbon, which increased in lower molecular weight compounds (<1000 Da) at ozone doses of 2.0 and 7.0 mg/mg C (Mellema, 1998).

Increasing the gaseous ozone concentration from 1.5 to 2.5 g/m^3 resulted in an increase in the percent reduction of both UV-254 in the P1 samples, suggesting that, at the lower ozone gas concentration, the ozone dosage was not sufficient to remove the reactive UV-254 absorbing compounds.

As shown in Fig. 6, the levels of SDS TTHMs in P2 were reduced by about 50% by ozonation/membrane filtration. The levels of SDS HAAs decreased by approximately 35–45% compared to that in the filtered raw water. No statistically significant decreases were observed in the concentration of SDS TTHMs when the ozone concentration was increased from 1.5 to 10 g/m^3 ($p<0.05$). There was a smaller reduction in the overall

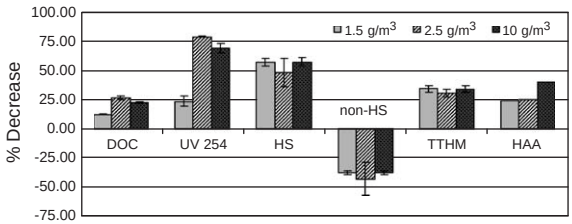

Fig. 5. Effect of gaseous ozone concentration on permeate 1 (first 400 mL of the sample). Experimental setup: Fig. 1, operating conditions: Table 1. Ozone concentration: 1.5, 2.5 and 10 g/m^3, membrane size: 15 kD. *All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%.

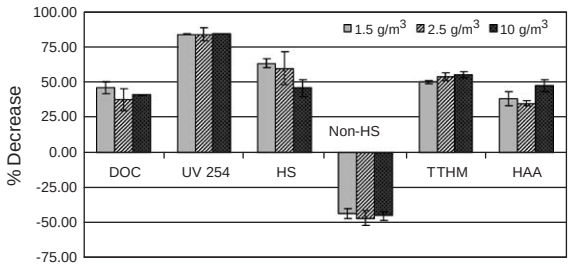

Fig. 6. Effect of gaseous ozone concentration on permeate 2 (latter 1000 mL of the sample). Experimental setup: Fig. 1, operating conditions: Table 1. Ozone dose: 1.5, 2.5 and 10 g/m^3. Membrane size: 15 kD. *All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%.

levels of the SDS HAAs compared to the SDS TTHMs in the P1 and P2 samples (Figs. 5 and 6). The results given here support the previously mentioned hypothesis that the precursors of TTHMs and HAAs have different

reaction rates with ozone. Chen (2003) also found that TTHMs and HAAs precursors had different reaction rates with ozone. He observed the concentrations of SDS TTHMs decreased by approximately 40–45% whereas, the concentrations of SDS HAAs decreased by around 30%. Ko et al. (2000) also reported that the TTHMs and HAAs produced following ozonation and chlorination had different formation rates.

The concentrations of aldehydes and ketones increased with increasing gaseous ozone concentrations. Also, the concentrations of these compounds in the P2 samples were greater than those in P1 samples, due to increased contact time with ozone. The concentration of ketoacids is almost twice that of the aldehydes and ketones (see Fig. 7). While the highest ketoacid concentrations were observed when the ozone gas concentration was 10 g/m^3, there was no significant difference (>0.05) in the ketoacids concentrations found at the two lower ozone gas concentrations (i.e., 1.5 and 2.5 g/m^3).

3.4. Effect of pH on the water quality

Membranes with molecular weight cut-offs of 5 and 15 kD were used to evaluate the performance of the system at pH 7.0 and pH 8.2 with an ozone dose of 2.5 g/m^3 (Fig. 8a–10b). The pH was measured during the course of the experiment and it did not change appreciably. The results show that decreasing the pH from 8.2 to pH 7.0 resulted in significant changes in the permeate characteristics. As shown in Fig. 8b, ozonation/filtration through the 15 kD membrane resulted in a reduction in the DOC concentration of around 35% at pH 8.2 and approximately 45% at pH 7.0 (in P2). With the membrane having a 5 kD molecular weight cut-off, the DOC removal for P2 was approximately 46% at pH 8.2 and $>95\%$ at pH 7.0 (Fig. 8b). Similar results were observed with the 5 kD membrane and for the P1 samples (Figs. 8a and 9a). Thus, DOC removal is

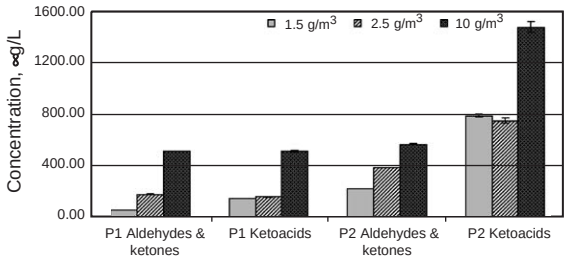

Fig. 7. Effect of gaseous ozone concentration on ozonation by-products. Experimental setup: Fig. 1, operating conditions: Table 1. Ozone concentration: 1.5, 2.5 and 10 g/m^3, membrane size: 15 kD. *All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%.

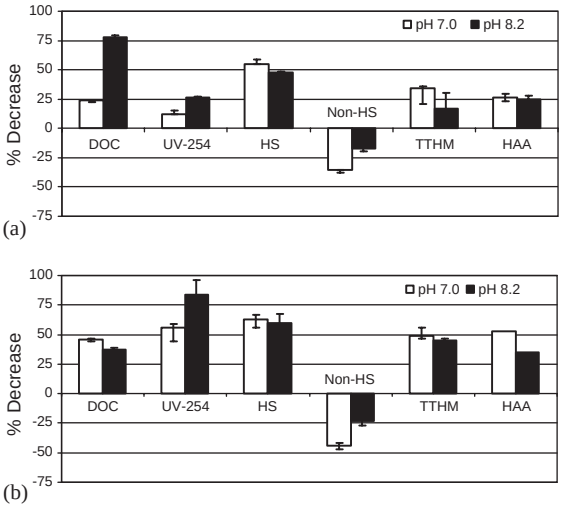

Fig. 8. Effects of pH on (a) permeate 1 and (b) permeate 2 of 15 kD molecular weight cut-off membrane. Experimental setup: Fig. 1, operating conditions: Table 1. Ozone dose: 2.5 g/m^3, membrane size: 15 kD, pH 7 and 8.2. *All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%.

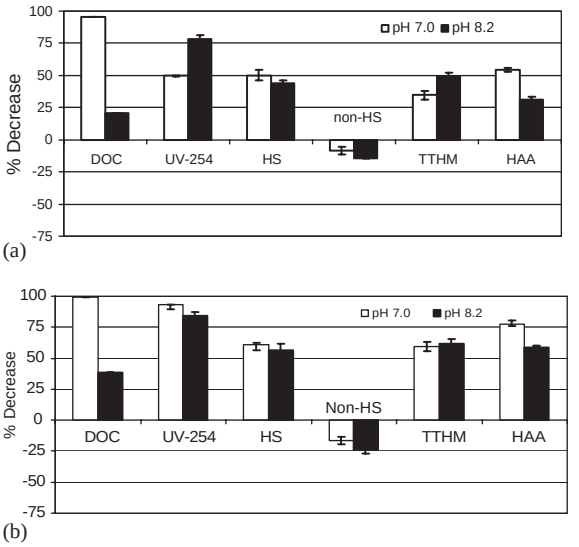

Fig. 9. Effects of pH on (a) permeate 1 and (b) permeate 2 of 5 kD molecular weight cut-off membrane. Experimental setup: Fig. 1, operating conditions: Table 1. Ozone dose: 2.5 g/m^3, membrane size: 5 kD, pH 7 and 8.2. *All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%.

favored at the lower pH, where ozone is more stable, and the dissolved ozone concentrations are higher (Karnik et al., 2005).

For the 5 kD MWCO membrane, the UV-254 absorbance of the permeate was similar at both pH 7.0

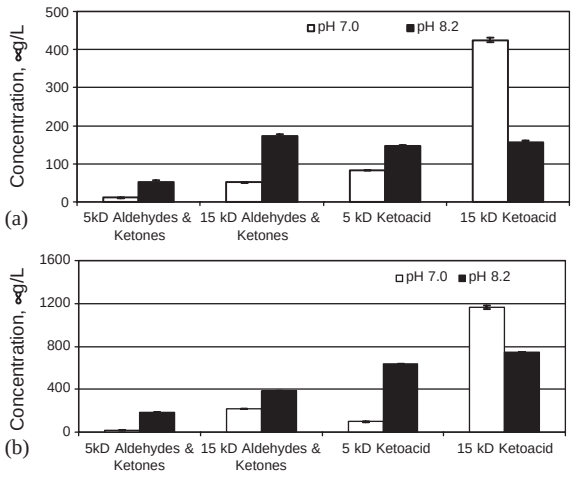

Fig. 10. Effects of pH on ozonation by-products in (a) permeate 1 and (b) permeate 2 of 15 and 5 kD molecular weight cut-off membrane. Experimental setup: Fig. 1, operating conditions: Table 1. Ozone dose: 2.5 g/m^3 , membrane size: 5 and 15 kD, pH 7 and 8.2. *All values are average of triplicates within experiments and duplicate experiments. The values have a maximum std. deviation of 5%.

and 8.2. For the 15 kD membrane, the reduction in the UV-254 absorbance was greater at the higher pH, suggesting that an OH radical mechanism may play a role in degrading UV absorbing substances under these conditions. Also, greater reductions in UV-254 were seen for the 5 kD membrane than for the 15 kD membrane. However, the direct comparison of the results for the two membrane sizes is difficult, since, due to the lower permeate flux for the 5 kD membrane, the contact time with ozone is longer than it is for the 15 kD membrane.

Neither varying the molecular weight cut-offs of the membrane nor the pH resulted in a statistically significant change in the reduction of HS. The greater extent of conversion of HS to non-HS substances could be attributed to the increased residual ozone concentration at circumneutral pH (Karnik et al., 2005).

Decreasing the pH resulted in a statistically significant ($p < 0.05$) decrease in the concentrations of SDS TTHMs and SDS HAAs found after chlorination in the permeate samples of both the 5 and 15 kD membranes (see Figs. 8a–9b). The higher of residual ozone concentration (Karnik et al., 2005) found at pH 7 is the likely cause for the lower concentrations of SDS TTHMs and SDS HAAs found at this pH.

For the aldehydes and ketones (shown in Figs. 10a and b), there is a reduction of at least 50% in the concentrations of these compounds at pH 7.0, compared to pH 8.2. With a 5 kD MWCO membrane, there is greater reduction in the concentrations of these compounds as compared to that obtained with the 15 kD MWCO membrane at pH 8.2 (see Figs. 10a and b). If the formation of these compounds is predominately due to a radical mechanism, then the lower concentrations of these compounds found at pH 7.0 may be explained by the slower formation of these compounds at the lower pH, where the radical concentration would be expected to be lower as ozone degradation is slower. Alternatively, it may also be explained by the catalytic degradation of these compounds at the membrane surface. Further studies are required to confirm the reaction mechanism. For the 15 kD MWCO membrane, a higher concentration of ketoacids is found at pH 7.0 than at pH 8.2. For the 5 kD MWCO membrane, the opposite is true. At this time we have no clear explanation for this behavior.

4. Conclusions

Use of the combined ozonation/filtration treatment system resulted in significant improvements in water quality compared to the filtered raw water and to that using either ozonation or membrane filtration alone. The levels of DOC, UV absorbing compounds, SDS TTHMs and SDS HAAs were reduced by ozonation/membrane filtration, as compared to either ozonation or filtration alone. The concentration of aldehydes, ketones and ketoacids after ozonation/filtration were significantly less than the concentrations of these compounds found after ozonation (at the same ozone dosage).

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