The removal of disinfection by-product precursors from water with ceramic membranes

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ABSTRACT

The main objective of this work was to investigate the effectiveness of ceramic ultrafiltration (UF) membranes with different pore sizes in removing natural organic matter (NOM) from model solutions and drinking water sources. A lab-scale, cross-flow ceramic membrane test unit was used in all experiments. Two different single-channel tubular ceramic membrane modules were tested with average pore sizes of 4 and 10 nm. The impacts of membrane pore size and pressure on permeate flux and the removals of UV$_{280}$ absorbance, specific UV absorbance (SUVA$_{280}$), and dissolved organic carbon (DOC) were determined. Prior to experiments with model solutions and raw waters, clean water flux tests were conducted. UV$_{280}$ absorbance reductions ranged between 63 and 83% for all pressures and membranes tested in the raw water. More than 90% of UV$_{280}$ absorbance reduction was consistently achieved with both membranes in the model NOM solutions. Such high UV absorbance reductions are advantageous due to the fact that UV absorbing sites of NOM are known to be one of the major precursors to disinfection by-products (DBP) such as trihalomethanes and haloacetic acids. For both UF membranes, the ranges of DOC removals in the raw water and model NOM solutions were 55–73% and 79–91%, respectively. SUVA$_{280}$ value of the raw water decreased from 2 to about 1.5 L/mg-m by both membranes. For the model solutions, SUVA$_{280}$ values were consistently reduced to $\leq$ 1 L/mg-m levels after membrane treatment. As the SUVA$_{280}$ value of the NOM source increased, the extent of SUVA$_{280}$ reduction and DOC removal by the tested ceramic UF membranes also increased. The results overall indicated that ceramic UF membranes, especially the one with 4 nm average pore size, appear to be effective in removing organic matter and DBP precursors from drinking water sources with relatively high and sustainable permeate flux values.

Key words | ceramic membrane, DBPs, drinking water, NOM, ultrafiltration

INTRODUCTION

Natural organic matter (NOM) is a heterogeneous mixture of several organic materials including macromolecular humic substances, smaller molecular weight hydrophilic acids, proteins, lipids, carboxylic acids, amino acids, carbohydrates, and hydrocarbons (Malcolm 1985; Aiken & Leenheer 1993; McKnight & Aiken 1998; Kitis et al. 2006). NOM, which is present in all surface and groundwaters, is derived from various organic materials as a result of complex biotic and abiotic reactions. The presence of NOM causes a broad range of problems in drinking water treatment operations. However, one of the most pressing concerns from a public health point of view is the formation of suspected carcinogenic disinfection by-products (DBPs) as a result of reactions between NOM and oxidants/disinfectants such as chlorine (Bellar et al. 1974; Reckhow et al. 1990; Oxenford 1996; Kitis et al. 2006).

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A variety of processes have been tested and used for removing NOM or DBP precursors in water treatment, including coagulation, adsorption, ion exchange, and membrane processes.

Membrane filtration is an effective method to remove particles, microorganisms and organic matter from drinking waters. Compared to conventional treatment methods, membrane processes (i) can provide higher quality water, (ii) minimise disinfectant demand, (iii) are more compact, (iv) provide easier operational control and less maintenance, and (v) generate less sludge (Nakatsuka et al. 1996; Cleveland 1999; Karkik et al. 2005a). Ultrafiltration (UF) membranes are used in drinking water treatment for the removal of microbiological contaminants, high-molecular weight soluble species (e.g. NOM) and particles (Anselme & Jacobs 1996; Chen et al. 2006). Recent advances and cost declines in polymer technologies lead to significant increase in the applications of membrane processes for water and wastewater treatment. However, some limitations, such as the lack of durability against extreme pH and temperature levels, relatively premature degradation due to biological and chemical agents, and fouling, are considered to be the major disadvantages of polymeric membranes. In this context, research and applications on ceramic membranes are increasing rapidly. Ceramic membranes are used in a wider range of filtration processes than polymeric membranes because of their superior properties: mechanical strength; resistance to chemicals and extreme temperatures; the ability to withstand attacks from microorganisms; and their ease of cleaning. Ceramic membranes constructed from inorganic oxides such as alumina, silica, zirconia, and, more recently, stannic oxide are common (Manno et al. 1998; Santos et al. 2001; Narong & James 2008).

Although many studies have been conducted and published on the removal of NOM or DBP precursors from waters using polymeric membranes, there is limited information in the literature regarding NOM and DBP precursor removal performances of ceramic UF membranes. Furthermore, since the majority of existing full-scale membrane plants use polymeric membranes in drinking water treatment, full-scale data from ceramic membrane plants is also very limited. Thus, the main objective of this work was to investigate the effectiveness of ceramic UF membranes with different pore sizes in removing NOM from model solutions and drinking water sources. The impacts of membrane pore size and pressure on permeate flux and the removals of UV$_{280}$nm absorbance, specific UV absorbance (SUVA$_{280}$nm), and dissolved organic carbon (DOC) were determined. A total of three different model NOM solutions and a natural water were tested with a purpose of investigating the NOM removal performances of the ceramic UF membranes for a wide spectrum of NOM types having different DOC and SUVA$_{280}$ values. The selected raw water had a SUVA$_{280}$ value of about 2.0 L/mg-m, indicating that the NOM fractions in this water are predominantly hydrophilic in character and have relatively less aromaticity. On the other hand, the model solutions of the humic acid, fulvic acid and NOM isolates had much higher SUVA values, indicating the presence of more hydrophobic and aromatic NOM moieties. As widely discussed and accepted in the literature, a higher SUVA value is generally linked to the following NOM characteristics: higher degree of humification, more aromaticity, presence of higher molecular weight NOM fractions such as humic acids, and more hydrophobicity (Edzwald & Van Benschoten 1990; White et al. 1997; Kitis et al. 2001, 2002; Ates et al. 2007). Therefore, different NOM sources with a wide range of SUVA values were investigated in this work.

**MATERIALS AND METHODS**

**Membrane test unit**

A lab-scale, cross-flow ceramic membrane test unit (Figure 1) was used in all experiments. The unit includes a housing for a single tubular monolithic ceramic membrane module. During the membrane tests, feed tank temperature was kept constant (20 ± 2°C) by circulating water through the jacket around the feed tank outer walls using a water bath circulator (PolyScience, 9602). Permeate volume collected during the tests was calculated by measuring permeate weight using an electronic digital balance (accuracy of ±10 mg). The test system includes high-pressure pump (Hydra-Cell, D/G-03-B), variable frequency drive (ABB, ACS150) and 2.2 kW motor to adjust the pump speed and the feed flowrate, stainless steel feed tank (45 L max. solution volume), ceramic membrane module and its
housing, concentrate control valve, pressure gauges, stainless steel and/or teflon tubings resistant to high pressure. The membrane operating pressures were adjusted by the concentrate control valve.

**Water sources**

Membrane tests were conducted for different NOM sources: a natural raw water and model NOM solutions. Natural surface water (a reservoir) sample was obtained from the influent of a drinking water treatment plant in the City of Ankara, Turkey. Physicochemical characteristics of the filtered raw water are shown in Table 1. The raw water sample was filtered with 1-μm cartridge filter prior to membrane tests. Filtered samples were stored in high-density polyethylene bottles and kept at 4°C in the dark until use.

Three different model NOM solutions were prepared in distilled and deionised water (DDW) by dissolving Suwannee River Humic Acid Standard II (HA, Cat. No. 2S101H), Suwannee River Fulvic Acid Standard II (FA, Cat. No. 2S101F) and Nordic Lake Aquatic NOM (NOM Isolate, Cat. No. 1R108N). All these powder-form isolates were purchased from International Humic Substances Society (IHSS). The elemental compositions reported by IHSS are 52.63% C, 4.28% H, 42.04% O, and 1.17% N for HA; 52.54% C, 4.36% H, 42.98% O, and 0.67% N for FA; 53.17% C, 5.67% H, 1.10% N, and 41.4% ash for NOM isolate. The target DOC concentration in the prepared model NOM solutions was 3.5 mg/L. The DOC concentration of the DDW was less than 70 μg/L.

**Ceramic membrane tests**

Two different single-channel tubular ceramic membrane modules (γ-Al₂O₃, Media and Process Technology, Inc., USA) were tested with average pore sizes of 4 and 10 nm. The outer and inner diameters of the modules were 5.7 and 3.5 mm, respectively. The active length was 23.5 cm. The modules had a total filtration area of 29.5 cm². The membranes can be operated in the pH range from 3 to 11 for long-term operations. Prior to experiments with model solutions and raw waters, clean water flux tests were conducted for each module. The tested membrane pressures were 4, 8 and 12 bar. Each membrane test was conducted at a cross-flow velocity of about 3.3 m/s. Total recycle mode (the concentrate and permeate were returned back to the feed tank) was employed in all membrane tests. All tests were performed at feedwater temperatures of 20 ± 2°C. The duration of each membrane test was 10 h. Samples from feed tank and permeate were taken each hour for DOC, UV₂₈₀ absorbance, total dissolved solids (TDS), conductivity, and pH measurements. Buffering for pH was not employed in raw water tests. The differences in permeate and feedwater pH values of the raw water were generally less than ±0.4. Such differences were maximum.
Prior to the 10 h of membrane tests during which samples were taken for water quality measurements, the test unit was operated at least 3 h with the same feedwater for the conditioning of the new membranes. This pre-operation was also conducted for all flux measurement tests. Flowrates of concentrate and permeate streams, membrane unit and pump outlet pressures were also recorded each hour.

Analytical measurements

Conductivity and TDS were measured using a conductivity meter (WTW Inolab Cond. Level 1). pH was measured using WTW 340i pH meter. Turbidity was measured using WTW Turb 550 turbidimeter. Concentrations of sulfate and total iron were measured spectrophotometrically using HACH DR2500 spectrophotometer. A UV-visible spectrophotometer (UV-1700, Shimadzu) was used to measure the UV absorbances in water samples. Measurements were performed at a wavelength of 280 nm instead of 254 nm since sodium azide was added (50 mg/L) to the samples to prevent any potential microbial degradation of NOM before experiments. Sodium azide absorbs UV light at 254 nm but not at 280 nm. DOC analysis was performed by the high temperature combustion method using a high-sensitivity TOC Analyser (TOC-VM, Shimadzu). The minimum detection limit of the TOC analyser was about 50 μg/L. During the storage of water samples, concentrations and UV absorbances were within analytical measurement errors, i.e. ± 0.05 mg/L and ± 0.0007 for DOC and UV_{280} absorbance, respectively, which ensured the stability of NOM in waters until use. SUVA_{280} values were calculated by the formula: UV_{280 nm} absorbance/DOC £ 100. All chemicals were reagent grade. DDW was used for stock solution preparations and dilutions. Analytical measurements were conducted in triplicate.

RESULTS AND DISCUSSION

Flux tests

Clean water flux (CWF) and raw water flux (RWF) values are shown in Figures 2 and 3 for UF modules with 4 and 10 nm average pore size, respectively. As expected, for both types of membranes, CWF values increased with increasing membrane pressure. In the raw water with the 4-nm pore size membrane, permeate flux values were 15–18, 35–39 and 48–60 L/m^2-h at pressures of 4, 8 and 12 bar, respectively. Such flux values were 78–84, 119–148 and 127–170 L/m^2-h with the 10-nm pore size membrane. At constant pressure, flux obtained by the 10-nm pore size membrane was always larger than that of the 4-nm pore size membrane. Similarly, for ceramic UF membranes, it was found that permeability tended to rise as the pore size was increased (Karnik et al. 2005b,c). Karnik et al. (2005c) reported that the permeability of the 5 kD membrane was

### Table 1

The characteristics of the filtered raw water and model NOM solutions (average values of triplicate measurements)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Raw water</th>
<th>Model NOM solutions</th>
<th>FA</th>
<th>NOM isolate</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg/L)</td>
<td>4.0</td>
<td>3.1</td>
<td>3.4</td>
<td>3.8</td>
</tr>
<tr>
<td>UV_{280 nm} Abs.</td>
<td>0.081</td>
<td>0.139</td>
<td>0.121</td>
<td>0.125</td>
</tr>
<tr>
<td>SUVA_{280 nm} (L/mg-m)</td>
<td>2.0</td>
<td>4.5</td>
<td>3.6</td>
<td>3.3</td>
</tr>
<tr>
<td>pH</td>
<td>7.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>213</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total hardness (mg/L as CaCO_3)</td>
<td>125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO_3)</td>
<td>120</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfate (mg/L)</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total iron (mg/L)</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>2.44</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HA: Suwannee River Humic Acid Standard II; FA: Suwannee River Fulvic Acid Standard II; NOM Isolate: Nordic Lake Aquatic NOM.
three times greater than that of the 1 kD membrane. The specific fluxes for 15, 5 and 1 kD ceramic membranes were 60, 20 and 8 L/m²-bar, respectively (Karnik et al. 2005b).

For the 10-nm pore size membrane, RWF values were similar at the pressures of 8 and 12 bar. A similar trend was also observed for the CWF values, suggesting that the permeability capacity of this 10-nm pore size membrane is reached at 8 bar pressure. RWF values generally slightly decreased during the 10 h of operation. RWF values found were about 15–25% lower than CWF values at all pressures with 4-nm pore size UF membrane. On the other hand, flux reductions due to raw water filtration approached 55% levels with the 10-nm pore size UF membrane. This indicates that the extent of fouling due to raw water filtration is higher with the 10-nm pore size membrane, which may be explained by the interactions among foulants (i.e. NOM) and membrane pores. While cake layer formation may dominate in the 4-nm pore size membrane, pore clogging may dominantly occur in the 10-nm pore size membrane. As the size of the foulants approaches the pore size of the membranes, internal pore clogging may cause irreversible fouling and thus reduce flux to a higher extent. On the other hand, the loosely bound cake layer in dynamic membrane conditions may cause only reversible fouling and affect flux to a smaller extent. Apparently, the NOM fractions and particles smaller than 1 μm in the filtered raw water (1-μm filtration) caused pore clogging in the 10-nm pore size UF membrane. Further tests will be conducted in the next phase of the project to determine the long term permeation performances of these membranes and the impacts of backwashing and cleaning on flux recoveries.

**NOM rejections**

Figure 4 shows the UV_{280} absorbance reductions in the raw water achieved by both UF membranes. In the raw water, UV_{280} abs. reductions ranged between 63 and 85% for all pressures and membranes tested. UF membrane with 4 nm pore size generally provided higher UV_{280} abs. reductions than those of 10 nm pore size membrane. Similarly, Karnik et al. (2005b) found that higher UV_{254} abs. reductions were obtained with the 5 kD membrane compared to 15 kD membrane. As a general trend, UV_{280} abs. reductions increased with increasing membrane pressures from 4 to 12 bar for both membranes.

Figure 5 shows the UV_{280} abs. reductions in model NOM solutions, which ranged between about 95 and 99%. Both membranes with 4 and 10 nm pore size were very effective in retaining NOM fractions which absorb UV light at 280 nm. Removal of UV absorbing fractions of NOM from waters is very important since the major NOM precursors to DBP formation (i.e. trihalomethanes and haloacetic acids) after chlorination are believed to be such NOM moieties. Overall, at constant membrane operational conditions, the extent of UV_{280} abs. removals was higher in the model NOM solutions than the raw water. As indicated before, the highest UV_{280} abs. reduction achieved in the raw water was 83%. The higher extent of UV_{280} abs. removals
in the model NOM solutions is due to the characteristics of NOM fractions. As indicated in Table 1, the SUVA values of all NOM isolates including humic and fulvic acids are much higher than that of the raw water. A higher SUVA value (i.e. > 3 L/mg-m) indicates that the NOM in a water has dominantly humic and fulvic acid moieties with higher molecular weight and larger molecular size (Kitis et al. 2001, 2002). Thus, the model NOM fractions were rejected to a higher extent by both UF membranes. This finding can be further supported by the fact that the humic acid, known to be more hydrophobic and have larger molecular size than fulvic acid, was retained slightly better than fulvic acid by both membranes. Overall, based on the different NOM sources studied it was found that there was a relation between SUVA and removals of UV\textsubscript{280} absorbing NOM moieties by ceramic UF membranes; e.g. as SUVA increased the extent of NOM retentions by the membranes also increased.

Figures 4 and 5 show UV\textsubscript{280} absorbance reduction in the raw water and model NOM solutions, respectively. The trends found for DOC removals were consistent with those of UV\textsubscript{280} absorbance reductions. A higher degree of DOC removals was achieved in the model NOM solutions. The range of DOC removals in the raw water was 55–75%. While maximum 65% DOC removal was achieved in the raw water at 8 bar pressure with the membrane having 10 nm pore size, at least 80% DOC removal was obtained in model solutions at the same conditions. Similar to the trends observed for UV absorbance, higher DOC removals were found with increasing SUVA values. For example, the raw water with the lowest SUVA value among all the four NOM sources exhibited the lowest DOC removals. The DOC concentrations achieved in the permeates of HA, FA and NOM isolate solutions were about 0.2, 0.4 and 0.6 mg/L, respectively, with the UF membrane having 10 nm pore size. These very low DOC concentrations (feed DOC concentrations were 3.1–3.8 mg/L) suggest that UF ceramic membranes even with 10 nm pore size are very effective in removing organic matter from waters. This point is further supported with the performance of these membranes in real raw waters. Higher DOC removals were found with the UF membrane having 4 nm average pore size compared to the one with
10 nm pore size. DOC removals were generally enhanced by increasing membrane pressure from 4 to 12 bar.

SUVA\textsubscript{280} reductions in the raw water and model NOM solutions are shown in Figures 8 and 9 for UF membranes with 4 and 10 nm pore size, respectively. For both of the membranes, UF ceramic membrane separation significantly reduced the SUVA values in permeates compared to the feedwater, a trend consistent for all NOM sources. The reductions in SUVA values indicate that the UF membranes removed UV absorbing fractions of NOM to a greater extent than the DOC. In other words, UV absorbing NOM fractions were preferentially removed in all NOM fractions. As discussed before, this is advantageous since UV absorbing sites of NOM contribute significantly to DBP formation after chlorination. Consistent with the UV abs. and DOC data, UF membrane with 4 nm pore size was more effective for SUVA\textsubscript{280} reduction. Similarly, Syafei et al. (2008) found that 1 kDa membrane was more effective than 15 kDa membrane in reducing SUVA. SUVA\textsubscript{280} value of the raw water decreased from 2 to about 1.5 (L/mg-m) by both membranes. On the other hand, the extent of SUVA\textsubscript{280} reductions was higher in model NOMs; e.g. < 1 (L/mg-m) levels were consistently achieved. This further proved the previous finding that as the SUVA value of the NOM source increases the extent of SUVA reduction and NOM removal by ceramic UF membranes also increases.

**CONCLUSIONS**

Initial flux tests indicated that flux obtained by the ceramic UF membrane having 10 nm average pore size was always larger than that of 4-nm pore size membrane at constant pressure. However, the extent of fouling by the raw water filtration was higher with the 10-nm pore size membrane. It appears that, while cake layer formation may dominate in the 4-nm pore size membrane, pore clogging may occur in the 10-nm pore size membrane. Apparently, the NOM fractions and the particles less than 1 µm size in the filtered raw water caused some degree of pore clogging in the 10-nm pore size UF ceramic membrane. UV\textsubscript{280} absorbance reductions ranged between 65 and 85% for all pressures and membranes tested in the raw water. More than 90% of UV\textsubscript{280} absorbance reduction was consistently achieved with both membranes in the model NOM solutions. Such high UV absorbance reductions are advantageous.
since UV absorbing sites of NOM are known to be one of the major precursors to DBPs after chlorination, such as trihalomethanes and haloacetic acids. Ceramic UF membrane with 4 nm pore size provided higher UV\textsubscript{280} abs. reductions than those of 10-nm pore size membrane. UV\textsubscript{280} abs. reductions increased with increasing membrane pressures from 4 to 12 bar for both membranes. At constant membrane operational conditions, the UV\textsubscript{280} abs. reductions were higher in the model NOM solutions than the raw water.

DOC removals were generally enhanced by increasing membrane pressure from 4 to 12 bar. A higher degree of DOC removals was achieved in the model NOM solutions. While maximum 65% DOC removal was achieved in the raw water at 8 bar pressure with the membrane having 10 nm pore size, at least 80% DOC removal was obtained in model solutions in the same conditions. Higher DOC removals were found with increasing SUVA values. The DOC concentrations achieved in the permeates of HA, FA and NOM isolate solutions were about 0.2, 0.4 and 0.6 mg/L, respectively, with the UF membrane having 10 nm pore size. These very low DOC concentrations suggest that UF ceramic membranes even with 10 nm pore size are very effective in removing organic matter from waters. UF ceramic membrane separation significantly reduced the SUVA values in permeates compared to the feedwater. UF membranes removed UV absorbing fractions of NOM to a greater extent than the DOC. The extent of SUVA\textsubscript{280} reductions was higher in model NOMs; e.g. <1 (L/mg-m) levels were consistently achieved. There was a positive relation among SUVA and the removals of UV\textsubscript{280} absorbing NOM moieties by ceramic UF membranes. As the SUVA value of the NOM source increased the extent of SUVA reduction and DOC removal by the tested ceramic UF membranes also increased.

Overall, the results indicated that the tested ceramic UF membranes, especially the one with 4 nm average pore size, appear to be effective in removing organic matter and DBP precursors from drinking water sources with relatively high and sustainable permeate flux values. The durability and resistance to various means of degradation are the major advantages of ceramic membranes over polymeric ones. These issues are important especially in terms of long-term operations.

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