Comparison of ceramic and polymeric membranes for natural organic matter (NOM) removal

Sangyoup Lee, Jaeweon Cho*

Department of Environmental Science and Engineering, Kwangju Institute of Science and Technology (K-JIST), Gwangju 500-712, Korea
Tel. +82 (62) 970-2443; Fax +82 (62) 970-2434; email: jwcho@kjist.ac.kr

Received 30 August 2002; accepted 25 June 2003

Abstract

Ceramic membranes were compared with polymeric membranes with respect to natural organic matter (NOM) removal using two removal mechanisms (i.e., size exclusion and charge repulsion). NOM properties including molecular weight and molecular structure, at different charge densities, were examined, along with membrane characteristics, including molecular weight cut-off (MWCO) and surface charge. Integrated analyses of both NOM and membrane characteristics provided information for membrane evaluation of different membrane materials and configurations (i.e., tubular vs. flat sheet type). A ceramic tight-ultrafiltration (UF) membrane showed the same potential as a similar nanofiltration (NF) polymeric membrane, in terms of the minimization of haloacetic acid (HAA) formation. Moreover, a ceramic UF membrane with a MWCO of 8000 Daltons showed almost the same behavior as an equitable polymeric UF membrane with a MWCO of 8000 Daltons in terms of NOM removal.

Keywords: Ceramic membrane; Size exclusion; Charge repulsion; Natural organic matter; Haloacetic acids

1. Introduction

Polymeric nanofiltration (NF) and ultrafiltration (UF) membranes has been widely examined for the removal of NOM from drinking water sources, to minimize the formation of chlorine disinfection by-products (DBPs). Previous studies have shown that electrostatic interactions and solute transport properties, such as mass transfer coefficient influence membrane performance [1–3]. Cho et al. [3] revealed that even a loose UF membrane (e.g. with a molecular weight cutoff (MWCO) value of approximately 8,000) could be used to remove macromolecular NOM with much lower molecular weights (MW) (ca. 2,000), with a negatively charged UF membrane surface. The concept of effective MWCO has been introduced in several previous papers to explain the enhanced NOM removal behavior of negatively-charged mem-

*Corresponding author.
Filtration using ceramic membranes is rarely used in drinking water compared to polymeric membranes, though a titanium dioxide NF membrane was tested to effectively reject mono- and di-valent anions by charge interaction between the negative-charged membrane surface and the anions [5]. However, practically no study has been undertaken on ceramic membrane filtration for NOM removal.

It is well known that ceramic membranes (such as the titanium dioxide membrane) are very resistant to severe chemical environments and are superior physically to the polymeric membrane, and thus they can be used for longer periods. There are two reasons why ceramic membranes have not been used for the removal of NOM in water treatment areas; (1) the performance of these membranes has not been rigorously investigated, with respect to NOM removal, as compared to the polymeric membranes, and (2) the membrane application systems for NOM removal are still being developed to replace or enhance conventional treatment processes, which mainly use polymeric NF, UF, and MF membranes. Given this situation, we undertook to evaluate the performance of ceramic membranes for the removal of NOM, and compared the results to those obtained for polymeric membranes with similar MWCO values with respect to size exclusion and charge interaction mechanisms. To examine these mechanisms, both the NOMs and the membranes were thoroughly examined. NOM was characterized in terms of size, structure (hydrophobic vs. hydrophilic), and functionality (i.e., charge density), whereas, membrane properties influencing NOM removal were categorized in terms of molecular weight cutoff (MWCO) and membrane surface charge.

It has been hypothesized that a ceramic membrane having a similar MWCO as a polymeric membrane, has a similar ability to remove NOM as a polymeric membrane. However, charge interactions [2,3] and transport characteristics [6] may alter the NOM removal characteristics anticipated on the basis that size exclusion criteria are exclusively considered. The goals of this paper were to initiate the use of ceramic membranes for the removal of NOM during water treatment and to identify the relative strengths of ceramic membranes, with respect to NOM removal, vs. polymeric membranes.

2. Experimental

2.1. Membranes

Two ceramic and two polymeric membranes were tested and compared with respect to the removal of NOM and HAA formation potential (HAAFP). The properties of the membranes are shown in Table 1. All bench-scale tests were performed using different membranes.

Table 1
Summary of tested membranes

<table>
<thead>
<tr>
<th>Code</th>
<th>Material</th>
<th>Manufacturers provided MWCO</th>
<th>MWCO, as determined by the FR-PEG method*</th>
<th>Clean-water permeability (L/d-m²-kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESNA</td>
<td>Polyamide thin-film-composite (TFC)</td>
<td>250</td>
<td>230</td>
<td>2.70</td>
</tr>
<tr>
<td>CeRAM25 (T-1000)</td>
<td>TiO₂</td>
<td>1,000</td>
<td>1040</td>
<td>5.30</td>
</tr>
<tr>
<td>GM</td>
<td>Polyamide TFC</td>
<td>8,000</td>
<td>7830</td>
<td>6.80</td>
</tr>
<tr>
<td>CeRAM28 (T-8000)</td>
<td>TiO₂</td>
<td>8,000</td>
<td>7660</td>
<td>9.40</td>
</tr>
</tbody>
</table>

*The MWCO values were determined using the fractional rejection of polyethylene glycols, as described by Lee et al. [9].
performed under the same hydrodynamic operating conditions, as defined by the $f/k$ ratio (where $k$ (cm/s) is the mass transfer coefficient describing diffusional back-transport away from the membrane surface, and $f$ (cm/s) represents the initial pure water permeate flux [6]. Otherwise, the flat-sheet type of polymeric and tubular type of ceramic membranes may have been exposed to different conditions, though the same solute and MWCO were applied. The filtration unit and the mass transport behaviors inside the concentration boundary layer are depicted in Fig. 1. Fig. 1b implies that NOM mass balance is satisfied for the concentration boundary layer with NOM mass intrusion from the bulk material into the concentration boundary layer (i.e., $f \cdot C_0$), back-diffusional NOM transport [i.e., $k \cdot \delta (x) \cdot (\partial C/\partial y)$], and NOM transport into permeate side (i.e., $f \cdot C_p$). The filtration unit accommodated a flat-sheet polymeric membrane (with an active surface area of 58.9 cm², a flow channel thickness of 0.04 cm, an equivalent hydraulic diameter of 0.08 cm, a cross-flow velocity of 3.09 cm/s, and a corresponding Reynolds number of approx. 100) and a tubular ceramic membrane (with an active surface area of 95.2 cm², a channel diameter of 0.36 cm, a cross-flow velocity of 10.1 cm/s, and a corresponding Reynolds number of approx. 110). Clean water permeability increased with MWCO value, and a T-8000 membrane with a MWCO of 8000 Daltons exhibited greater water permeability than a GM membrane with the same MWCO value. The mass transfer coefficients ($k$) of the polymeric and ceramic membranes were calculated using the following Eqs. (1) [7] and (2) [8], respectively.

$$k = 1.62 \left( \frac{V_w D^2}{d_s L} \right)^{0.33}$$  (1)

where $k$ is the mass transfer coefficient (estimated using the average molecular weight of the bulk (not isolated) NOM in the feed), $D$ is the diffusion coefficient of the NOM solute, $V_w$ is the cross flow velocity parallel to the membrane surface, $d_s$ is the equivalent hydraulic diameter, and $L$ is the membrane channel length. The diffusion coefficient was estimated using the Stokes-Einstein equation [7].

$$Sh = 1.62 \left( \frac{Re Sc}{d_s L} \right)^{0.33}$$  (2)

where $Sh$ is the Sherwood number, $Re$ is the Reynolds number, and $Sc$ is the Schmidt number.

The materials and MWCO values of each membrane were provided by the respective manufacturers. Polymeric ESNA and GM membranes were purchased from Hydranautic (USA) and Desal, Osmonics (USA), respectively, and the ceramic membranes were purchased from TAMI industry (France). The nominal MWCO values (defined as the molecular weight which is 90% removed by a membrane) were also measured using a method, based upon the fractional rejection of polyethylene glycols (FR-PEG) by high performance liquid chromatography (HPLC, Waters) with a PEG separation column (Shodex, Ionpak KS-802, Japan) and a refractive index detector (Waters 410, Milford, USA) [9]. Zeta potential values of the membranes were measured using an electrophoresis based method [10] and a commercialized laser light scattering apparatus with a quartz cell (ELS8000, Otzca, Japan). Latex was used to provide standard particles for electrophoresis and a commercialized laser light scattering apparatus with a quartz cell (ELS8000, Otzca, Japan). The latex was coated with hydroxy propyl cellulose to prevent interaction with the quartz cells (i.e., to make the latex particles non-charged). The coated particles were added to a 10 mM NaCl solution, which was used as the measurement solution. Results are shown in Fig. 2. All of the membrane filtrations including clean-water permeability measurements were performed using a bench-scale membrane unit with two different holders for each membrane type under the same $f/k$ ratio of 5.0 (i.e., the same hydrodynamic operating condition). The $k$ value was calculated from Eq. (1) using an average molecular weight of bulk NOM included in the feed water for all of the filtrations with NOM solution and clean water. Thus, different NOM consti-
tuents (i.e., hydrophobic, transphilic, and hydrophilic) can exhibit different $k$ values depending on their molecular weights, even under the same $f/k$ ratio condition, accordingly providing different removal efficiencies. For clean-water filtration, the same $f/k$ ratio (recall that $k$ is a function of cross-flow velocity and NOM MW) was used as for NOM filtration to provide the membrane surface with an equivalent hydrodynamic condition, assuming that NOM is included. Thus, the last stage of the clean-water filtration and the initial stage of the NOM filtration have almost the same hydrodynamic conditions arising from the same $f/k$ ratio.
2.2. NOM source water characteristics and haloacetic acids

A drinking water source, Juam Lake surface water (JL-SW, source water of Gwangju City) was used to perform bench-scale membrane-filtration tests. The raw water was filtered through a 0.45 μm Nylon filter prior to the filtration experiments. The characteristics of JL-SW are listed in Table 2. The dissolved organic carbon (DOC) and UV absorbance at 254 nm (UVA) were measured using a TOC analyzer (Dorhman, DC-180, USA) and an UV spectrophotometer (UVmini-1240, Shimadzu, Japan). The specific UVA (SUVA), as defined as UVA/DOC, represents the relative aromatic character of the NOM constituent molecules. The molecular weights of the NOM components were measured by size exclusion chromatography (SEC) using a HPLC equipped with a proteinous silica column (Waters, USA). The molecular weight distributions of each NOM fraction are shown in Fig. 3. Details of this procedure have been described previously [4,11].

NOM was separated into three different fractions using the XAD-8/4 resins, namely, hydrophobic NOM (humic portion; mostly representing hydrophobic acids), transphilic NOM (mostly representing hydrophilic acids), and hydrophilic NOM (mostly representing hydrophilic neutrals and some NOM bases) [12–14]. Clean XAD-8/4 resins were transferred to a resin column, and rinsed with 0.1 N NaOH, pure water, 0.1 N HCl, and pure water. The rinsing procedure was repeated until the DOC of the XAD resin effluent was below 0.5 mg/L.

Table 2
Characteristics of the source water

<table>
<thead>
<tr>
<th>Source</th>
<th>Hardness (mg/L as CaCO₃)/Ca (mg/L)</th>
<th>DOC (mg/L)</th>
<th>UVA (cm⁻¹)</th>
<th>SUVA (L/mg-m)</th>
<th>Conductivity (s/cm)</th>
<th>pH</th>
<th>Humic content (% DOC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JL-SW</td>
<td>20.5/4.0</td>
<td>3.81</td>
<td>0.088</td>
<td>2.30</td>
<td>286</td>
<td>7.04</td>
<td>35.0</td>
</tr>
<tr>
<td>Weight-averaged molecular weight of fractionated NOMs</td>
<td>Raw</td>
<td>Hydrophobic NOM</td>
<td>Transphilic NOM</td>
<td>Hydrophilic NOM</td>
<td>Diffusivity (10⁻⁶ cm²/s)</td>
<td>1240</td>
<td>1246</td>
</tr>
</tbody>
</table>
was almost exactly the same as that of deionized pure water. Prior to being injected into the resin, the 0.45 μm filtered samples were acidified with 5 N HCl to lower the pH to 2. The acidified samples were then passed through the resins in order for the hydrophobic or transphilic components of NOM to be adsorbed onto the XAD-8 or XAD-4 resins, respectively; the XAD-8/4 effluent was designated as the hydrophilic NOM component. Adsorbed NOM fractions were eluted by allowing 0.1 N of NaOH to flow through each resin; the DOC and UVA of the eluted solutions were measured, along with those of the XAD-8/4 effluent, to determine the mass (as carbon) fractions of the different NOM components. Used resins were stored in methanol, and cleaned using a Soxhlet extraction based method with methanol followed by acetonitrile for 48 h each.

Each NOM fraction was filtered through different membrane types to examine the structure and charge density effects of the different membranes. The charge densities of the NOM acids (i.e., hydrophobic and transphilic NOM) were measured by potentiometric titration (for carboxylic acidity, pH: 3~8; for phenolic acidity, pH: 8~12) and expressed in units of meq/gC [12,15].

Source and treated samples were chlorinated using a concentrated HOCI solution at a chlorine concentration of 3 times the DOC concentration and 7 times the NH₄⁺ concentration (the formed HAA is defined as HAAFP). The chlorinated samples were stored in an incubator at 20°C for 72 h, HAA was extracted using the Modified EPA 552 micro-extraction method with a diazo methane addition, and HAA concentrations were measured using a GC (HP 5890 Series II Plus) with an autosampler (HP 6890 Series). Six HAA species (monochloro, dichloro, trichloro, monobromo, dibromo, bromochloro acetic acids) and nine HAA species (six species plus dibromochloro, dichlorobromo, and tribromo acetic acids) are denoted as HAAFP6 and HAAFP9, respectively.

3. Results and discussion

3.1. Effects of molecular structure on NOM removal

As hypothesized in the introduction, charge repulsion effects were evident in terms of NOM rejection by all of the membranes. Carboxylic acidity was significantly reduced by all of the membranes regardless of membrane material and MWCO value (see Fig. 4a). However, this was true for only carboxylic sourced acidity (see Fig. 4a and 4b). No significant change in phenolic acidity was observed; the raw NOM and the four different membranes permeates showed similar acidity values, as shown in Fig. 4b. This was because the pH of the solutions used for the membrane filtration was around 7.0, and the phenolic functional group is not ionized at this pH.

NOM removals for fractionated NOM by each membrane were evaluated in terms of DOC and UVA, and were expressed on the basis of mass balance calculation for the membrane feed and permeate NOM solutions (see Fig. 5). Both the ESNA and T-1000 membranes exhibited similar removal trends even with different MWCO values (250 vs. 1000 Daltons). The T-1000 membrane removed larger amounts of the hydrophobic and
transphilic NOM than expected, which was attributed to its higher membrane surface charge than ESNA (see Fig. 2). However, it was surprising to find that the hydrophilic NOM (with an average MW of 820 Daltons) was removed very efficiently (by approx. 70%) by the ceramic T-1000 membrane (with a nominal MWCO of 1000 Daltons). This was probably due to hydrodynamically-induced back diffusion from the membrane surface (i.e., the mass transfer coefficient, \( k \)); the lower the MW of a NOM, the higher its \( k \) value, which is resulted from a higher cross-flow velocity, as indicated by Eqs. (1) and (2) (because lower molecular weight exhibits a higher \( k \) value). This explanation of the back-diffusion transport of NOM is supported by the notion that the convective solute transport (toward the membrane surface) is balanced by both solute diffusion (away from the membrane surface) and the solute flux through the membrane pores into the membrane permeate at a steady state (see Fig. 1). Diffusive transport can be described by the expression \(-D (dC/dy)\) where \( D \) is the diffusion coefficient of a solute (\( k = D/\delta \), \( \delta = \) the thickness of the boundary layer), \( C \) is the NOM concentration, \( y \) is the distance measured from the membrane surface, and the minus sign means in a direction away from the membrane surface, and is equal to solute back-diffusion, thus providing higher solute removal than expected [6,7]. In summary, as cross-flow velocity increases with transmembrane pressure being maintained, both \( f/k \) ratio and concentration polarization can be reduced, producing a higher NOM removal efficiency. These results suggest that some tight UF membranes made of ceramic material and with a tubular configuration, may be
suitable alternatives to NF membranes for the effective removal of NOM, as they have much higher permeabilities, without significantly sacrificing NOM removal efficiency. The two UF membranes, which had different materials and configurations, showed similar removal characteristics in terms of raw NOM and different NOM fractions. Though the two UF membranes with MWCOs of 8000 Daltons exhibited different removal characteristics in terms of the transphilic and hydrophilic NOM, they proved to be similar in terms of raw NOM removal efficiencies with respect to both DOC and UVA.

3.2. Evaluation of size exclusion

The two membrane types (with four different membranes) were evaluated with respect to the MWs of the fractionated NOMs removed (see Fig. 6a), which can be described by Eq. (3). This information on MW removal by each membrane enables one to determine which membrane can effectively remove NOM through a size exclusion mechanism, and the molecular weight distributions of membrane feed and permeates (see Fig. 6b).

\[
\text{Percentage reduction in weight-averaged molecular weight} = \frac{M_w(\text{feed}) - M_w(\text{permeate})}{M_w(\text{feed})} 
\]

where \(M_w\) is the weight-average molecular weight, which is calculated by \(M_w = \Sigma (h_i M_i^2)/\Sigma (h_i M_i)\), here \(h_i\) is the height of the SEC curve of the sample and \(M_i\) is the molecular weight at a designated point (i.e., molecular weight) of the chromatography horizontal axis [11].

As expected from the MWCO values of each membrane, the percentage removal of each fraction was in the order ESNA > T-1000 > T-8000 > GM. All of the NOM fractions exhibited very similar removal values for the ESNA membrane, because the membrane MWCO was much lower than that of each NOM fraction. The tight UF (T-1000) membrane exhibited lower levels of MW removal with respect to NOM mass (with respect to DOC and UVA) removal (see Fig. 5; recall that the DOC removal was almost the same as the NF membrane) than the ESNA membrane, which suggests that T-1000 was not as effective in terms of size exclusion, due to the larger MWCO of the T-1000 membrane, but was very effective in terms of NOM mass removal due to charge repulsion and hydrodynamically-induced back diffusion (κ). This trend was also true for the other two UF membranes with MWCO values of 8000 Daltons. Similar trends of NOM removal were observed for the three UF membranes (T-1000, T-8000, and GM) regardless of membrane material (i.e., polymer or titanium dioxide); the transphilic NOM fraction was preferentially removed in terms of
MW than the other NOM fractions. As described earlier in this paper on the basis of charge repulsion, it can be envisioned that (1) transphilic NOM generally contains a higher charge density than hydrophobic NOM and/or (2) transphilic NOM with a larger MW could be preferentially rejected by the negatively-charged membrane surface than transphilic NOM with a smaller MW. However, the first of these hypotheses is invalid because the charge densities of the hydrophobic and transphilic NOMs were similar (i.e., 86.0 : 90.5 eq/g-C of carboxylic functional group), as determined by potentiometric titration. Thus, it seems that the transphilic NOMs with larger MW contain higher charge density than both the transphilic NOMs with lower MWs and the hydrophobic NOMs. The T-8000 and GM membranes with nominal MWCOs of 8000 Daltons showed similar trends in terms of the removal of fractionated NOM, which suggests that the membrane material does not influence NOM rejection with respect to NOM molecular size.

3.3. Haloacetic acids removals

The removal efficiency of haloacetic acid formation potential by a membrane indicates the ability of a membrane to reduce the DBPs concentration of treated water. Recall that natural organic matter itself is not a toxic material, but it can produce carcinogenic chlorinated compounds (i.e., DBPs) during chlorination. Thus, it is more important to remove DBPs precursors (i.e., HAAFP) as natural organic matter included in the source water, than to simply remove simply natural organic matter (i.e., in terms of DOC). The polymeric NF and the tight ceramic UF (T-1000) membranes showed similar efficiencies for DOC/UVA and HAAFP removals, regardless of significantly different MWCO values (250 vs. 8000 Daltons), as shown in Figs. 5 and 7, respectively. These results are very different from the DOC removal trends observed for T-1000 and ESNA membranes: approx. 45% by T-1000 vs. approx. 80% by ESNA. These results suggest that the tight ceramic UF membrane (T-1000), with a higher permeability than the NF membrane, is a good candidate for the removal of NOM, especially for the removal of haloacetic acids precursors.

Compared to NOM removal in terms of DOC and UVA, the two UF membranes (T-8000 and GM) with MWCOs of 8000 Daltons showed higher abilities to remove HAAFP, which is an encouraging result from the perspective of DBPs minimization (see Fig. 7). In particular, the T-8000 membrane exhibited fairly high HAAFP6 and HAAFP9 removals, of over 60%, compared to a DOC removal of approximate 40% by the same membrane. Overall, the study showed that the two ceramic membranes exhibited the ability to remove haloacetic acids precursors efficiently, versus the polymeric membranes of equivalent or significantly lower pore sizes.

4. Conclusions

This study shows that two ceramic tight-UF membranes with MWCO values of 1000 and 8000 are good candidates for the removal of DBPs precursors. Membrane performances were evaluated from the perspective of size exclusion and charge interaction (along with the NOM molecular structure effect). Moreover, the ceramic UF membrane proved to be very effective at removing HAAFP, compared with NOM with respect to DOC and UVA. It should be noted that
this work on ceramic UF membranes was intended to initiate the use of an inorganic ceramic membrane for water treatment (especially NOM removal) and to suggest some ways of replacing polymeric membranes in drinking water plants, by identifying the advantages offered by ceramic membranes. Some advantages of the ceramic membranes were identified: (1) these membranes exhibited the potential to more effectively remove DBP precursors (i.e., HAAFP) than natural organic matter in terms of DOC, versus the tested polymeric membranes, and in addition (2) the ceramic membranes also exhibited higher permeability than the equivalent polymeric membranes.

Acknowledgements

This work was supported by a grant (code 4-1-1) from Sustainable Water Resources Research Center of 21st Century Frontier Research Program through the Water Reuse Technology Center (WRTC) at K-JIST.

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