The fouling of ultrafiltration membranes by natural organic matter after chemical coagulation treatment with different initial mixing conditions

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Abstract The flux decline in the UF membrane filtration of water pretreated by chemical coagulation using different initial mixing conditions were compared and the influence of natural organic matter (NOM) on the fouling of membranes was investigated. It was suggested that organic matter in the molecular weight ranges 300–2,000 and 20,000–40,000 Daltons were mainly responsible for the fouling. The fouling was greater for hydrophobic than hydrophilic membranes. ATR-FTIR analysis of the fouled hydrophobic membranes indicated that aliphatic amide and alcoholic compounds as well as polysaccharides contributed to significant membrane fouling. These adsorptive foulants are considered as neutral fractions present in hydrophobic and hydrophilic NOM components. In the case of similar hydrophilic fractions, water precoagulated with a high hydrophobic content resulted in greater flux decline, which was presumed to be due to the organic matter with neutral properties contained within the hydrophobic fraction. The relative concentrations of each NOM fraction in coagulated water are important. Mechanical mixing for chemical coagulation, with a backmixing-type, rather than pump diffusion mixing, with an in-line type, is likely to be more effective at reducing the fouling caused by NOM.

Keywords ATR-FTIR; coagulation; fouling; natural organic matter; ultrafiltration

Introduction Fouling is one of the main disadvantages in membrane filtration processes, which is defined as the loss of membrane permeability due to the accumulation of solutes onto the surface of the membrane and/or into its pores. Many studies have suggested that natural organic matter (NOM) is a most important foulant due to its possible interactions between membrane surfaces. Factors potentially affecting membrane fouling by NOM include properties of the feed constituents (molecular weight distribution, hydrophobicity and charge density) and the membrane (hydrophobicity, surface roughness, porosity), as well as the solution phase (pH, ionic strength, Ca^{2+} concentration; Cho and Amy, 1999; Lee et al., 2005). Although studies on the role of solution composition have been undertaken, there is little agreement on the role of the each NOM fraction. For instance, Fan et al. (2001) found that the major contribution to fouling was from the hydrophilic neutral fraction within bulk NOM. However, others have reported that the hydrophobic fraction, such as humic substances, is a major foulant controlling the rate and extent of fouling (Yuan and Zydney, 1999).

In any case, the removal of NOM before membrane filtration has became an important issue for the reduction of membrane fouling. The most common technique for treating water, including NOM, is coagulation/sedimentation with aluminium or ferric salts. According to Carroll et al. (2000), coagulation treatment improves the removal of NOM and reduces membrane fouling. In the study performed by Pikkarainen et al. (2004), the specific cake resistance decreased with increasing dosage of coagulants used for the
removal of NOM. The effectiveness of a coagulation process in removing NOM varies according to the nature of the NOM (its molecular weight, charge density, hydrophobicity; and so forth), and the physicochemical characteristics of the water and the operational conditions, such as the initial mixing intensity and duration (Letterman et al., 1999). Above all, the initial mixing conditions are critical in a coagulation process, since rapid and uniform dispersion of metal coagulants has advantages for the formation of charge-neutral products. In a previous study, differences in the removal of NOM have been found between pump diffusion and mechanical mixer of the in-line type and back-mixing-types, respectively, for chemical coagulation. It was reported that an in-line pump diffusion mixer is effective for the removal of the non-humic fraction within bulk NOM in comparison to a backmixing-type mixer (Kim et al., 2006).

If NOM components are selectively removed by chemical coagulation using different initial mixing conditions, membrane fouling might also be influenced by different NOM compositions, as mentioned above. In recent, related research, Park et al. (2002) and Oh and Lee (2005) filtered a large volume of coagulated water through a membrane filter under different initial mixing conditions. The results of these studies differed, with very little agreement on the consistency of in-line pump diffusion mixing being a good system for the reduction of flux decline compared to back-mixing. However, the water samples used in their studies contained both large particles, i.e. flocs, and dissolved organic matter, and little attention was given to the contribution of NOM toward membrane fouling. Therefore, the main purpose of this paper was to compare the membrane performance in the filtration of the pretreated water obtained using different initial mixers for the chemical coagulation, and investigate the influence of NOM characteristics on the fouling of membranes.

Materials and methods
Membranes and filtration apparatus
Two types of UF membrane, hydrophobic (UF-HPO; polyethersulfone) and hydrophilic (UF-HPI; regenerated cellulose), supplied by Millipore, were used to compare the flux decline in relation to their properties. The molecular weight cut-off (MWCO) pore size of both these membranes was 100 kDa. Flux decline tests were performed using a dead-end stirred-cell filtration unit (Model 8200, Amicon) connected to a feed reservoir and nitrogen gas bomb. The raw and treated waters were filtered with a 0.45 μm filter before UF membrane filtration. The water quality is shown in Table 1. The permeate discharges from the bottom of the cell, under constant pressure (14 psi) and temperature, as well as the flux were checked at 15 second intervals.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw water</th>
<th>CRM</th>
<th>PDFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg/L)</td>
<td>2.53</td>
<td>2.04</td>
<td>1.88</td>
</tr>
<tr>
<td>UV254 (cm−1)</td>
<td>0.0281</td>
<td>0.0172</td>
<td>0.0186</td>
</tr>
<tr>
<td>SUVA (L/mg/m)</td>
<td>1.11</td>
<td>0.84</td>
<td>0.99</td>
</tr>
<tr>
<td>pH</td>
<td>7.9</td>
<td>7.8</td>
<td>7.8</td>
</tr>
<tr>
<td>Conductivity (μS/cm)</td>
<td>171</td>
<td>179</td>
<td>176</td>
</tr>
<tr>
<td>Ca2+ (mg/L)</td>
<td>0.05</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>0.018</td>
<td>BDL*</td>
<td>BDL*</td>
</tr>
<tr>
<td>Mn (mg/L)</td>
<td>BDL*</td>
<td>BDL*</td>
<td>BDL*</td>
</tr>
<tr>
<td>Si (mg/L)</td>
<td>2.22</td>
<td>1.85</td>
<td>1.93</td>
</tr>
</tbody>
</table>

*Below detection limit: 0.003 mg/L
*Filtered with a 0.45 μm MF filter before analysis
Initial mixing conditions for chemical coagulation

Pump diffusion flash mixing. Pump diffusion flash mixing (PDFM) is an effective in-line mixing method for the quick dispersion of a hydrolyzing coagulant, which also has the potential to solve problems, such as the noise, high energy consumption and high maintenance cost, associated with the use of mechanical mixers. A pilot plant, designed to treat 1,000 m$^3$/day, was built in the a water treatment plant, optimized for energy efficiency and mixing intensity, and operated for the study of the feasibility of introducing PDFM, with in-line mixing, as shown in Figure 1. The plant employs conventional water treatment, consisting of coagulation/sedimentation, sand filtration and chlorination, and uses Han River water as a water source. The Han River water was prechlorinated to satisfy the CT value for viruses within the aqueduct.

Conventional rapid mixing. A scaled-down mechanical mixing basin was used for comparison with PDFM for chemical coagulation; this mixing type is defined as conventional rapid mixing (CRM) in this study. CRM consists of a square baffled container constructed from polymethylmethacrylate, with a six flat-bladed stainless steel turbine impeller, one-third the standard geometry, similar to that of the turbine impeller used in a real plant. The typical residence time ($t$) and velocity gradient value ($G$) for mechanical mixing were applied for adequate CRM operation. The operational conditions for PDFM and CRM for coagulation treatment are shown in Table 2. Commercially available liquid poly-aluminium chloride (PACl; 17% as Al$_2$O$_3$) solution was used as the coagulant in all experiments, with the optimal coagulant dose for PDFM and CRM operation decided using the jar-test.

NOM characterization

NOM fractionation. NOM can be isolated into three fractions using Supelite DAX-8 and Amberlite XAD-4 resins. The hydrophobic (HPO) and transphilic fractions (TPI) are DAX-8 and XAD-4 absorbable, respectively. The effluent collected is termed as the hydrophilic fraction (HPI). The pH of the raw and treated waters was adjusted to 2 by the addition of hydrochloric acid, following filtration through a 0.45 µm membrane filter. The sample solution was then isolated into three fractions by sequentially passing through DAX-8 and XAD-4 resins.

Molecular weight distribution. Molecular weight separation was performed by high performance size exclusion chromatography (HPSEC), using a HW-50S column. A high performance liquid chromatograph (LC-20AD, Shimadzu, Japan) was used, with UV detection (SPD-20AD, Shimadzu, Japan) at 254 nm and an on-line dissolved organic carbon (DOC) detector (Modified Sievers Total Organic Carbon Analyzer 800 Turbo).

Figure 1 Schematic diagram of the PDFM system
Polyethylene glycols (PEG) were used to calibrate the relationship between the molecular weight and the retention time.

ATR-FTIR spectroscopy. An infrared spectrometer (Infinity Gold 60AR, Thermo Mattson, USA), fitted with a single reflection horizontal ATR (PIKE Technologies, USA), was used to identify the functional groups of the clean and fouled membranes. After the membranes were washed to remove any cake layer on their surfaces filtration, they were then placed in sterilized Petri dishes and stored in a desiccator for 48 hours. Infrared spectra of various membranes were obtained by scanning with an attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrometer.

Analytical methods. The DOC was determined using a total organic carbon (TOC) analyzer (TOC-V CPN, Shimadzu, Japan), after filtration of the samples through a 0.45 μm membrane filter. A UV-visible spectrophotometer (Cary 50 Probe, Varian, USA) was used to determine the absorbance at 254 nm (UV254). Turbidity was measured using a turbidimeter (2100P, Hach, USA). The concentrations of calcium, iron, manganese and silicon were measured using inductively coupled plasma spectrometry (ICPS-7500 spectrometer, Shimadzu, Japan).

Results and discussion

Comparison of PDFM and CRM on NOM removal

The DOC, specific ultraviolet absorbance (SUVA) and zeta potential, as well as the turbidity remaining in solution after coagulation/sedimentation under different mixing conditions, are shown in Figure 2. In the case of PDFM, the residual DOC was relatively low compared to that of CRM, while the SUVA, which has been used as an indicator of humic content in water environmental systems, was reduced to a lesser extent than in the case of CRM. The SUVA value was calculated from the UV254 divided by the DOC of the water sample, with the UV254 mainly caused by electro-rich sites, such as aromatic functional and double-bonded carbon groups in the NOM molecules. In general, the non-humic fraction of bulk NOM has less electron-rich sites than the humic fraction, implying that the non-humic fraction in bulk NOM is more effectively removed by PDFM than CRM. This assumption was identified by isolation of NOM components from raw and treated waters, as shown in Figure 2b. Figure 2b shows the variation in the distribution of hydrophilic, transphilic and hydrophobic fractions during water treatment, as determined in relation to the DOC concentration. The relative concentration of the hydrophilic fraction increased with the removal of the hydrophobic and transphilic fractions via CRM. In the case of PDFM, with the transphilic fraction mainly removed, the relative concentrations of the hydrophobic and hydrophilic fractions were increased. From the result of NOM isolation, the transphilic fraction was more effectively removed by PDFM, while the hydrophobic fraction was effectively reduced by CRM. However, no significant difference in the removal of the hydrophilic fraction was observed between the different mixing conditions.

Table 2 Operation conditions for CRM and PDFM

<table>
<thead>
<tr>
<th>Mixing type</th>
<th>PACI dosage (v/v)</th>
<th>G (s⁻¹)ᵃ</th>
<th>t (s)ᵇ</th>
<th>G (s⁻¹)ᵃ</th>
<th>t (min)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRM</td>
<td>15 ppm</td>
<td>320</td>
<td>30</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>PDFM</td>
<td>15 ppm</td>
<td>680</td>
<td>1</td>
<td>25</td>
<td>30</td>
</tr>
</tbody>
</table>

ᵃVelocity gradient;ᵇResidence time; "3.1 mg/L as Al₂O₃
During the early dissociation of aluminium salts, the soluble hydrolysis species will bind to sites, e.g. COO$^-$, on the NOM via charge neutralization. During the initial mixing stage, the rapid and uniform dispersion of coagulant could influence the charge neutralization mechanism. Amirtharajah (1981) suggested that the smaller eddies formed at higher $G$ values might be more successful at transporting preformed aluminium hydrolysis species to the surface of the particles responsible for turbidity, with the rapid-mix $G$ value being important in charge neutralization. Consequently, the coagulation mechanism in the case of CRM was dominated by conventional entrapment, i.e. sweep coagulation, while PDFM was more likely influenced by charge neutralization due to the quick dispersion of aluminium salts prior to the formation of the aluminium hydroxide precipitate. It was suggested that due to the different reactivities of NOM fractions toward cationic aluminium hydrolysis products, the transphilic fraction was more effectively removed by PDFM than CRM.

**NOM fouling of UF membranes**

The ratio of permeate to the initial flux ($J/J_o$) is shown in Figure 3 as a function of the delivered DOC (cumulative feed-water DOC mass per unit area of membrane surface = feed water DOC (mg/L) × cumulative volume (L)/membrane surface (m$^2$)) for the filtrations of raw and treated waters using UF-HPO/HPI membranes. The rate of flux decline for the UF-HPO was considerably greater than that for the UF-HPI. In general, NOM components smaller than the membrane pores can be adsorbed onto surfaces, which increases the flux decline, while larger components can block the pore entrances, which contributes to cake formation. Therefore, it is important to know the composition and size distribution of NOM components. Cho et al. (1998) reported that negatively-charged membranes can be easily fouled by the hydrophilic neutral fraction. Fan et al. (2001) also proposed a mechanism for membrane fouling by the hydrophilic neutral NOM fraction, which involved a combination of
adsorption of small molecules onto the membrane pore wall, with pore blockage by colloidal organics within the membrane pore structure. They also identified the potential foulants in order: hydrophilic neutrals > hydrophobic acids > transphilic acids.

In the case of PDFM, in contrast to CRM, the treated water contained relatively low transphilic and high hydrophobic fractions, as shown in Figure 2b. The fouling effect was higher with PDFM than CRM for similar hydrophilic concentration and molecular weight distribution (Figures 2b and 4). It is reasonable to suppose that significant fouling occurred due to the hydrophobic as well as the hydrophilic fraction, whether the fouling is irreversible or not.

Therefore, CRM is more effective in respect to the reduction in fouling by NOM compared to PDFM. Although the relative contributions to fouling by residual NOM and flocs could be influenced by the morphological characteristics of the flocs, the relative concentrations of each fraction in the NOM components are also important in hybrid membrane systems that employ precoagulation treatment.

**Figure 3** Flux decline curves with different precoagulation treatments: (a) UF-HP; and (b) UF-HPO

**Figure 4** HPSEC-DOC chromatograms for raw and treated waters based on molecular weight
Characterization of NOM fouling and identification of foulants

Figure 4 shows the relative molecular weight distribution, as determined by the PEG standards. For further interpretation, the chromatograms were divided into four bands, based on previous research (Huber, 1998). Substances in bands (I) and (II) were assigned as polysaccharides and humic substances, and large molecules (or aggregates), respectively. Substances in band (III) were assigned as the building blocks of refractory organic substances, while the low molecular weight substances, e.g. carbohydrates, aldehydes or alcohols, were assigned to band (IV). Bands (I) and (II) were effectively reduced through coagulation treatment, irrespective of initial mixing conditions, which caused decreases in the flux decline. It is suggested that these bands included significant organic foulants.

The FT-IR spectra of a clean UF-HPO, as well as one fouled during filtration of the raw and treated waters, are shown in Figure 5. Interpretation of the absorption bands of the NOM was performed, as described by Aiken et al. (1985) and Stevenson (1994). The peak at 1,660 cm$^{-1}$ was attributed to the C=O stretching of amide groups (amide I band), and this stretching vibration was coupled with the N–H (amide II band) bonding vibration peak that appeared at 1,580 cm$^{-1}$. The bands at 1,070 and 1,010 cm$^{-1}$ were attributed to the C–O stretching of alcoholic compounds. The alcoholic C–O bonds may have originated from polysaccharide-like substances (Her et al., 2004). Also, bands in the 1,280–1,137 cm$^{-1}$ region were attributed to the C–O stretching of esters, ethers and phenols, and those at 800 and 630 cm$^{-1}$ to OH stretching vibration of carboxylic groups and deformation of COOH, respectively.

The areas of the peaks at 1,660, 1,070, 1,010, 800 and 630 cm$^{-1}$ in the spectrum of the clean membrane were increased by irreversible fouling, while those at 1,240 and 1,150 cm$^{-1}$ decreased, as shown in Figure 5. In summary, this indicates that aliphatics, such as short and/or long chain aliphatic amides and alcohols, rather than humic substances, including aromatic groups, caused the irreversible NOM fouling. The foulants are also considered neutral NOM components, based on the fractionation of NOM components (Świetlik et al., 2004). For the case of a similar molecular weight distribution, the peak area corresponding to alcoholic compounds with PDFM was relatively larger than for CRM for a similar hydrophilic fraction, suggesting that hydrophobic, e.g. $> C_5$ aliphatic amides and alcohols, as well as hydrophilic neutral fractions, e.g. short chain ($< C_5$) aliphatic amides and alcohols polysaccharides, in the bulk NOM were adsorbed onto the membrane surface or within the pores.

Conclusions

The fouling effect for a hydrophobic membrane was greater than that for a hydrophilic membrane with a similar pore size, due to fouling caused by adsorption. In the case of a
hydrophobic membrane, alcoholic compounds, aliphatic amides and polysaccharides were the main contributors to significant membrane fouling due to adsorption. These adsorptive foulants are considered as the neutral fraction present in hydrophobic and/or hydrophilic NOM components. The precoagulated water with a high hydrophobic fraction resulted in a greater flux decline, which was likely due to the organic matter with neutral properties contained within this fraction.

Although the morphological characteristics of flocs in coagulated water can alter the relative contributions to fouling due to residual NOM and flocs, the relative concentrations of each NOM fraction in the coagulated water are also important. For the case of UF membranes with treated water containing few large particles, i.e. flocs, following the coagulation/sedimentation process, mechanical mixing with the backmixing-type, compared to pump diffusion mixing with the in-line type, is more effective in the reduction of fouling. This is due to residual NOM when the coagulant dosage has been optimized for the removal of turbidity-causing materials.

References