Evaluation of organic matter fouling potential by membrane fouling index

C. Park*, H. Kim**, S. Hong**, S. Lee* and S.-I. Choi***

*Center for Environmental Technology Research, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Republic of Korea (E-mail: chpark@kist.re.kr; yisanghyup@kist.re.kr)

**Department of Civil and Environmental Engineering, Korea University, Anam-dong, Seongbuk-gu, Seoul 136-713, Republic of Korea (E-mail: skhong21@korea.ac.kr)

***Department of Environmental Engineering, Korea University, Seochang-dong, Jochiwon-up, Yeongi-gun, Choongnam 339-800, Republic of Korea (E-mail: eechoi@korea.ac.kr)

Abstract The membrane fouling index, widely used in the reverse osmosis (RO) membrane industry, is developed mainly to assess the fouling potential of particulate matter. However, the fouling potential by organic matter should also be accurately evaluated as the productivity loss by organic fouling is often more severe than particle fouling, despite its low concentration in feed water. This study was performed to investigate the influence of organic characteristics and feed water solution chemistry on the membrane fouling index, such as the silt density index (SDI). The results showed that the feed solution chemistry (i.e. pH, ionic strength and hardness) affected the SDI values of organic rich feed water to some degree. In addition, Aldrich humic acid (AHA) exhibited higher fouling potential by SDI than Suwannee river humic acid (SRHA), emphasising the importance of organic properties. Lastly, it is shown that although SDI values measured were the same, the degree of NOM fouling was significantly different for the membranes with different surface properties.

Keywords Electrostatic repulsion; membrane fouling index; natural organic matter; organic fouling potential

Introduction

Membrane fouling (i.e. reversible and irreversible productivity loss), an inevitable phenomenon in membrane treatments (Song, 1998; Chen et al., 2004), is an important consideration in the design and operation of membrane systems. Usually, membrane modification (Belfer et al., 2004), chemical cleaning (Ang et al., 2006) or hydrodynamic adjustments (Williams and Wakeman, 2000) have to be employed to mitigate membrane fouling. Membrane filtration systems often have fouling problems, thus there is a pressing need for a fast and accurate method to measure and predict the fouling potential of the feed water (Vrijenhoek et al., 2001). Several parameters have been proposed for predicting a fouling potential and using it as a tool for assessing the adequacy of pretreatment. The existing silt density index (SDI) and modified fouling index (MFI) are the standardised parameters in reverse osmosis (RO)/nanofiltration (NF) membrane design procedure and are widely used; however, their limitations have been evidenced by several studies (Schippers and Verduyn, 1980; Boerlage et al., 2003). Both fouling indices using 0.45 μm microfiltration membrane were not able to take into account the influence of the particle and organic matters smaller than their membrane pore size responsible for fouling. In a recent study, the effect of fouling potential on the membrane fouling index were investigated using NF membranes which related to pore blocking and adsorption mechanisms (Khirani et al., 2006). Currently, no systematic study has been conducted to investigate the impact of organic matters on the membrane fouling index or to evaluate the real organic fouling potential in RO/NF membrane filtration experiments.
Natural organic matter (NOM) is considered to be a major contributor to membrane fouling in water separation applications, and NOM fouling has been previously observed to strongly correlate with membrane hydrophobicity, surface roughness, charge and molecular-weight cutoff (MWCO) (Hong and Elimelech, 1997). In this study, the impact of organic characteristics and solution chemistry on the membrane fouling index was conducted to predict the real organic fouling potential.

**Experimental methods**

**SDI and MFI experiments**

In order to evaluate the fouling potential of a feed through organic matter, the silt density index (SDI) was performed by a standard test method as instructed in ASTM-D4189. In this method, a dead-end filtration at 207 kPa (30 psi), through a 47 mm diameter (13.8 × 10⁻⁴ m²) microfiltration membrane (Millipore Corp., Bedford, MA) with an average pore size of 0.45 µm was conducted on the feed. A 47 mm diameter membrane was fixed by a silicone O-ring within an in-line filter holder (Millipore Corp., Bedford, MA) which pressures up to 5.5 bar (80 psi). The feed water was pumped to the membrane within the in-line filter holder at a constant pressure (30 psi) using a mini pressure regulator valve (14R113FC, Parker Hannifim Corp., MI). During each fouling index experiment, feed and permeate samples were collected and analysed for UV254, pH and turbidity using a UV absorbance at 254 nm (DR5000, HACH Company, CO), pH (Orion 520A+, Thermo Electron Corp., MA), and turbidity (2100P turbidimeter, HACH Company, CO) meter.

The first two time intervals are the times to collect an initial 500 mL (t₁) and final 500 mL (t₂). The third time interval (t₃) is 5, 10 or 15 min and is the time between the collection of the initial and final sample:

\[
\text{SDI} = \left( \frac{1 - (t_3/t_2)}{t} \right) \times 100
\]

The modified fouling index (MFI) was determined using the same equipment and procedure used for the SDI, except that the volume was recorded every 30 s over a 15 min filtration period (Schippers and Verdouw, 1980). The MFI is derived in equation (2) and is defined as the slope of an inverse flow rate (1/Q) vs. cumulative volume (V) curve:

\[
\frac{1}{Q} = a + \text{MFI} \times V
\]

**Natural organic matter (NOM)**

Commercial Aldrich humic acids (AHA) and Suwannee river humic acid (SRHA) were chosen as the model foulants for NOM in this study. Both of the NOMs were purchased from Aldrich Chemicals (St. Louis, MO) and International Humic Substances Society (Boulder, CO), and were used without further purification as the bound iron and ash contents were very low. Humics were received in a powder form and were dissolved in deionised (DI) water to make the stock solution (0.1 g/L). The pH, ionic strength (IS) and hardness concentration of feed waters and NOM solutions were adjusted with HCl and NaOH (0.1 M), NaCl (1.0 M) and CaCl₂ (0.01 M) stock solutions, respectively, as needed. The SUVA value related to the dissolved organic carbon (DOC) and UV absorbance at 254 nm was 9.83 and 3.98 of AHA and SRHA, respectively. NOM characteristics, including size (number-average ($M_n$) and weight-average ($M_w$)), structure (hydrophobic and hydrophilic content) and functionality (carboxylic and phenolic groups) are given in Table 1. Molecular weight distribution, number- and weight-average molecular weight and polydispersivity (= $M_w/M_n$) were analysed and calculated by an HPSEC method using a modified silica column and sodium polystyrene sulphonates (PSS)
(Chin et al., 1994). NOM isolation by XAD-8 and -4 resins were used to obtain hydrophobic NOM (XAD-8 adsorbable), transphilic NOM (XAD-4 adsorbable) and hydrophilic NOM (neither XAD-8 nor XAD-4 adsorbable) (Aiken et al., 1992). The charge density of NOM was measured by potentiometric titration (pH 3–8) with an autotitrator (702 SM Titroino, Metrohm, Switzerland) to measure carboxylic acidity, and twice the amount of NaOH titration from pH 8 to 10 was used as an estimate for phenolic acidity.

Membrane surface characterisation
Membrane samples were received as 1.8 inch spiral-wound type and stored in DI water at 4 °C. All membrane samples were cut and rinsed thoroughly with DI water prior to use. The average salt rejections of those membranes were rechecked according to the manufacturer’s experimental methods (determined at an applied pressure of 225 psi and 2,000 mg/L NaCl concentration). The primary membrane characteristics such as zeta potential, hydrophobicity and surface roughness are examined to investigate the membrane–solute interactions, as shown in Table 2. Membrane surface charge was evaluated by the zeta potential at the shear plane and was calculated from streaming potential measurements (ELS 8000, Otsuka Electronic, Japan). The pH of the electrolyte was adjusted in order to obtain zeta potential measurements between pH 2 and 10. The hydrophobicity of the membrane was determined by a contact angle measurement using a goniometer (TanTec, IL). The sessile drop method was used to determine contact angle by passing bubbles in aqueous conditions. The surface roughness was characterised by atomic force microscopy (AFM, XE-100, PSIA, Seoul, South Korea) in tapping mode operation, as presented in Figure 1.

Table 1 Both NOM characteristics in terms of size, structure and functionality

<table>
<thead>
<tr>
<th>NOM</th>
<th>Molecular weight (g/mol)</th>
<th>Structure (%)</th>
<th>Acidity (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Hydrophobic</td>
<td>Transphilic</td>
</tr>
<tr>
<td>AHA</td>
<td>$M_n = 2,400; M_w = 4,170$</td>
<td>39.1</td>
<td>12.3</td>
</tr>
<tr>
<td>SRHA</td>
<td>$M_n = 1,930; M_w = 3,250$</td>
<td>67.3</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Table 2 Characteristic of membranes used in RO bench-scale filtration testing

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Salt (NaCl) rejection (%)</th>
<th>Zeta potential (mV)</th>
<th>Contact angle (°)</th>
<th>Surface roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE</td>
<td>96.0</td>
<td>-63.11</td>
<td>37.7</td>
<td>78.64</td>
</tr>
<tr>
<td>FE</td>
<td>99.5</td>
<td>-17.43</td>
<td>36.5</td>
<td>87.62</td>
</tr>
</tbody>
</table>

Figure 1 AFM images of two different thin-film composite RO membrane surfaces.
Bench-scale membrane RO filtration unit
The NOM solutions were prepared and stored in a high-density polyethylene 20 L feed reservoir. The temperature of the solution was maintained at 20°C by a refrigerated recirculator (DH Water Master, Donghwa Cooling System). A crossflow flat filtration system includes a cross flow cell, a feed pump and a flowmeter. The effective membrane surface area was $1.5 \times 10^{-2}$ m$^2$ and the channel height was 0.25 cm. Initial operating conditions (e.g. filtrate flux and crossflow velocity) were set and maintained through the careful manipulation of feed, concentrate and bypass needle valves. Concentrate and filtrate flows were measured both by an in-line flow meter (Blue White Industries, Westminster, CA) and by the timed collection of filtrate in a graduated cylinder.

Results and discussion
Effect of NOM characteristics on the membrane fouling index
The membrane fouling index was mainly used to evaluate the fouling potential of particles in feed water or pretreated water. In a typical membrane fouling index test, the mean diameter of membrane pores is selected in such a way that the majority of the particles to be separated are larger than the membrane pore size, thus particle cake formation on the membrane is the dominant fouling mechanism. However, other mechanisms such as pore blocking or pore adsorption should be considered when organic fouling is concerned. According to our previous research paper (Park et al., 2006), the results indicated that a linear relationship was found relating the fouling index values to particle concentration, however, fouling index values increased exponentially with increasing organic concentration. This observation resulted from membrane pores which are rapidly blocked by pore adsorption, causing more organics to be captured and accumulated on the membrane at high organic concentrations.

In order to further investigate the evaluation of organic fouling potential by the existing fouling index, the effects of organic characteristics and feed water chemistry on membrane fouling index were systematically investigated in this study. Specifically, the fouling potential of two commercially available humic acids which have different fundamental characteristics, i.e. average molecular weight and SUVA value, were evaluated.

The results of the fouling index tests clearly demonstrated that the characteristics of organic matter affected SDI values, as shown in Figure 2. Higher SDI values were observed with increasing NOM concentration. AHA with larger molecular weight and SUVA resulted in higher SDI values, compared to SRHA. These results were further supported by data obtained through molecular weight distribution. The AHA molecular weight distribution was mainly around 2,000 g/mol, however, these of SRHA varied widely from 2,000 to 4,000 g/mol. The effects of different SUVA values on NOM transport behaviours through the MF membrane pores were also evidenced by pore blocking and adsorption mechanisms. Specifically,
within the same concentration of organic adsorbed mass, the SDI values were significantly different between AHA and SRHA. This observation was explained by increasing the hydraulic resistance due to the large molecular weight of AHA.

Effect of feed water solution chemistry on membrane fouling index

The role of solution chemistry (pH, ionic strength and hardness) in the evaluation of membrane fouling index was systematically investigated in this study. The fouling index experiments were performed under fixed hydrodynamic conditions, so that only chemical factors influencing fouling behaviour were evaluated. Results for AHA and SRHA at three different pH values (2, 7 and 10) are presented in Figure 3(a). A more significant increase in SDI is observed at pH 2. This behaviour is attributed to the charge reduction of humic macromolecules at low pH. To investigate the influence of ionic strength on SDI, fouling index experiments were performed at three different ionic concentrations of an indifferent salt (0.005, 0.01 and 0.25 M NaCl). Figure 3(b) does not show clearly that NOM fouling becomes more severe as the ionic strength of the feed solution increases. The effect of divalent cations (Ca$^{2+}$) on SDI is illustrated in Figure 3(c) for AHA and SRHA. The results clearly demonstrate that SDI of AHA increases dramatically as calcium concentration increases. These results explained that the charge of the NOM is reduced significantly due to calcium complexation, subsequently, a more compact coiled NOM fouling layer forms. The effect of hardness concentration in SRHA was not significantly observed due to the relatively low molecular weight.

RO filtration of organic rich feed waters with the same SDI values

Bench-scale RO filtration experiments were investigated to the influence of organic characteristics such as AHA and SRHA on real organic fouling. Figure 4 represents that...
membrane fouling was more severe when containing the AHA despite the similar SDI values at pH 7.0.

This result was verified by the pictures of fouled membrane surfaces, as shown in Figure 5. AHA showed the darker colour of membrane surface due to accumulated organic matter.

In this study, two commercial polyamide thin-film-composite (TFC) RO membranes were utilised to evaluate the effect of membrane characteristics on NOM fouling. The commercial names of two RO membranes are BE and FE (Saehan, Ltd., Korea), respectively. The results are presented in Figure 6. In the presence of AHA 1.5 mg/L,
NOM fouling was differently observed for these two membranes despite the same concentrations, thus the same SDI values. It is speculated that a less negatively charged membrane (FE) experienced lower adsorption of organic matter due to less charge interaction between membrane surface and organic matter.

Conclusions
Primary inferences from this research are summarised as follows.

- Higher SDI values were observed with increasing organic concentration. AHA with larger molecular weight ($M_w$) and SUVA ($=\text{UV}_{254}/\text{TOC}$) resulted in higher SDI values, compared to SRHA.
- The feed water solution chemistry (i.e. pH, ionic strength and hardness) affects SDI values of organic rich feed waters to some degree. In particular, the SDI value increased with increasing calcium hardness concentration for AHA.
- Despite the same SDI values measured for organic-rich feed waters, the NOM fouling of RO membranes is greatly affected by membrane characteristics such as charge and organic properties, suggesting that SDI measurements are not able to accurately evaluate the true fouling potential by organic matter.

Acknowledgements
This research was financially supported by the Saehan Industries, Ltd., Project “Evaluation of Commercial Fouling Resistance Membrane and Elucidation of Fouling Mechanisms”.

References