Assessing nanofiltration fouling in drinking water treatment using fluorescence fingerprinting and LC-OCD analyses


ABSTRACT

The natural organic matter (NOM) components causing fouling of nanofiltration membranes used in drinking water applications consist in a complex mixture of humic and fulvic acids, proteins, and carbohydrates of various molecular size and functional groups. Understanding the characteristics of NOM fractions such as humic substances (HS) and biopolymers (proteins and polysaccharides) as foulants is of paramount importance to develop fouling control strategies. Fluorescence spectroscopy is becoming an increasingly popular method for characterizing NOM and shows good potential for online monitoring, as minimal sample pre-treatment and preparation is required, high instrumental sensitivity is available and the technique is non-destructive in nature. In this research an innovative approach involving both fluorescence and LC-OCD analyses is used to identify and to characterise organic membrane foulant.

Key words | drinking water treatment, fluorescence spectroscopy, LC-OCD, membrane foulants, nanofiltration

INTRODUCTION

The use of nanofiltration (NF) membranes to produce drinking water from surface water sources is increasing; however, membrane fouling is the main limitation to this technology. Fouling is caused by the deposition and accumulation of material on the surface of the membrane or within the internal structure of the membrane. Fouling increases the hydraulic resistance and operational costs.

Different types of fouling may occur during membrane processes; the main types are organic, inorganic, colloidal and particulate, and biofouling. In drinking water NF applications, natural organic matter (NOM) is a major membrane foulant. In general, NOM consists of a complex mixture of humic and fulvic acids, proteins, and carbohydrates of various molecular size and functional groups. The
nature of the NOM in water can vary significantly depending on the location, climate and hydrological conditions. Effluent organic matter from upstream municipal wastewater treatment plants can also be an important source of organic matter.

Understanding the characteristics of NOM fractions such as humic substances (HS) and biopolymers (proteins and polysaccharides) as foulants is of paramount importance to develop fouling control strategies. Reported methods for the characterization of NOM have mostly focused on traditional analyses such as light absorptivity, dissolved organic carbon (DOC) concentration and aromaticity due to the difficulty of detailed structural analysis (Her et al. 2003). More advanced methods for analysing the structural characteristics of NOM such as nuclear magnetic resonance (13C NMR) spectroscopy, infrared (IR) spectroscopy, differential thermal analysis, modulated differential scanning calorimetry, pyrolysis–gas chromatography/mass spectrometry and Fourier transform infrared spectroscopy (FTIR) have also been reported (Wilson et al. 1999; Smeulders et al. 2000; Lee et al. 2006; Gray et al. 2007). Most of these characterization methods, however, require concentration and/or fractionation of NOM to accommodate challenges associated with measuring the low NOM concentrations found in raw water (Croué 2004).

High performance size exclusion chromatography (HPSEC) can be used to determine the molecular size distribution of the dissolved NOM. Moreover, HPSEC coupled with UV and DOC detectors can be used to determine the specific nature of the NOM (Her et al. 2008). HPSEC has various advantages including small injection volumes and minimal sample pre-treatment but the analysis is expensive, requires sophisticated equipment and is not suitable for online application. In this context, fluorescence spectroscopy is becoming an increasingly popular method for characterizing NOM (Her et al. 2003) and shows good potential for online monitoring, as minimal sample pretreatment and preparation is required, high instrumental sensitivity is available and the technique is non-destructive in nature.

This paper demonstrates the feasibility of using fluorescence spectroscopy to detect the differences in permeates from two NF membranes that exhibited different fouling rates and how the differences in fluorescence spectra can be helpful in interpreting different rejection characteristics of NF membranes. LC-OCD analyses were used as an independent method to complement and validate the findings.

**METHODS**

**Water samples and NF set-up**

Grand River water (Southwestern Ontario, Canada) was used as feed water during this study. The river is impacted by urban runoff, agricultural activity and wastewater effluent. Characteristics of Grand River water (GRW) during the experimental period (August to September 2007) are presented in Table 1 (column 2).

GRW was first filtered through a roughing filter to lower the turbidity level of raw water prior to biofiltration. The roughing filter was constructed of PVC piping and the diameter of the column was designed to provide a d_column/d_media of 10. The column was 1.5 m in height with a diameter of 0.2 m. The column was filled with three layers of gravel with decreasing media sizes from bottom to top. The roughing filter was operated in an upflow mode at a rate of 1.1 m/h using a constant head tank. The biofilter was operated in a downflow mode fed by the roughing filter effluent at a flow rate of 5 m/h. It consisted of a dual media filter (anthracite and sand) over a gravel support layer. The empty bed contact time of the filter was 14 minutes. The biofilter underwent an acclimation period of two months prior to the experiments described here.

Nanofiltration experiments were performed with a bench scale module (GE SEPA™ CFII) using flat sheet membranes as illustrated in Figure 1. Two different flat sheet NF membranes (XN45 and TS80) from TriSep Corporation (California, USA) were used for this study. The active layer of both NF membranes is made of polyamide and the molecular weight cut off (MWCO) provided by the manufacturer was 200 Da for both membranes. The hydrophobicity is determined by contact angle measurement and a large contact angle is representative of a hydrophobic surface. The contact angle of both TS80 and XN45 is 57 ± 1. The average roughness of the active layer is 8.8 and 21 nm for TS80 and XN45,
respectively. The nominal surface area of both membranes was 0.0140 m². The NF experiments with the XN45 and TS80 membranes were operated at a constant pressure of 8.2 and 12.4 bar, respectively. The pure water permeability of XN45 and TS80 were 10.4 and 10.0 LMH/bar, respectively. The initial recovery was 2% for both membranes. The initial permeate flux of XN45 and TS80 membranes was 85.7 LMH and 124.2 LMH. Prior to the experiments, the virgin membranes were compacted using deionized (DI) water until stable permeate flow was achieved. Following the compaction period the DI water was drained from the feed tank and 20 l of feed water (biofilter effluent) was introduced into the tank. Throughout the experiments the temperature was kept constant at 25°C through the use of a chiller. The experiments were performed in a recycle mode; both concentrate and permeate were returned to the feed tank. The duration of the experiment varied between 72 and 144 h.

### Analytical methods

The concentration of total organic carbon (TOC) and dissolved organic carbon (DOC) were measured using an OI-Analytical TOC analyser (Model 1010, College Station, TX) with a wet-oxidation method as described in Standard Methods (2005) 5310D. Turbidity of the water samples was measured using a turbidity meter (Hach 2100P) following the Standard Method (2005) 2130. Conductivity was measured using a conductivity meter (Hach 44600) following the Standard Method (2005) 2510. Size exclusion

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**Table 1** | Characteristics of Grand River water for the period August to September 2007

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Grand River water</th>
<th>Biofilter effluent</th>
<th>XN45 permeate</th>
<th>TS80 permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>17–22</td>
<td>20</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>pH</td>
<td>7.50–8.00</td>
<td>8.48</td>
<td>7.72</td>
<td>8.5</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>2.78–27.2</td>
<td>0.53</td>
<td>0.45</td>
<td>0.11</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>6.8–8.1</td>
<td>7.3</td>
<td>1.3</td>
<td>0.3</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>6.3–8.0</td>
<td>6.7</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>SUVA (L/mg-M)</td>
<td>2.4–4.0</td>
<td>3.0</td>
<td>0.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>540–588</td>
<td>607</td>
<td>491</td>
<td>94</td>
</tr>
<tr>
<td>Ca²⁺ (mg/L)</td>
<td>54–62</td>
<td>60</td>
<td>46</td>
<td>12</td>
</tr>
<tr>
<td>Mg²⁺ (mg/L)</td>
<td>19–23</td>
<td>18</td>
<td>16</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 1** | Schematic of the nanofiltration experimental set-up.
chromatography with continuous organic carbon detection (LC-OCD) was performed with a DOC-Labor Dr. Huber (Karlsruhe/Germany) system (Huber & Frimmel 1992). The system uses a Toyopearl HW-50S SEC column (Tosoh Bioscience, Tokyo/Japan).

**Fluorescence analysis**

The fluorescence excitation/emission matrix (EEM) of each sample was collected using a Varian Cary Eclipse Fluorescence Spectrofluorometer (Palo Alto, CA) by scanning 301 individual emission spectra (300–600 nm) at sequential 10 nm increments of excitation wavelength between 250 and 380 nm. UV-grade polymethylmethacrylate cuvettes with four optical windows were used in the analyses. The instrument parameters (photomultiplier tube (PMT) voltage = 800 V, scan rate = 600 nm/min and excitation/emission slit width = 10 nm each) were maintained during the fluorescence signal acquisition. These parameter settings were identified as optimum instrument settings for obtaining reproducible fluorescence signals, especially for the low concentrations seen in NF permeates, in a separate study. To eliminate water Raman scattering and to reduce other background noise, fluorescence spectra for Milli-Q (Millipore) water, obtained under the same conditions, were subtracted from all fluorescence spectra. The temperature of all water samples was maintained at room temperature (25°C) during the analyses. Data processing was performed using Matlab 7.3.0 software (The Mathworks Inc., Natick, MA).

**RESULTS AND DISCUSSION**

The fluorescence EEM of untreated GRW water (RW) shows a peak (α) at Ex/Em = 320/415 nm (Figure 2a), which corresponds to the range reported for HS (Sierra et al. 2005). The presence of HS in GRW can also be independently confirmed by examining the LC-OCD spectra of the same water sample (Figure 2b). LC-OCD spectra of RW also reveal that HS is the most plentiful fraction of NOM in GRW. In addition to the primary peak (α), another secondary peak (β) which also corresponds to HS (Sierra et al. 2005) appears to be present in the form of a shoulder at Ex/Em = 270/450 nm (Figure 2a).

The fluorescence EEMs of GRW (RW), GRW water filtered through the roughing filter (RF), and biofilter effluent (BF) appear to have similar spectral characteristics (Figure 3). Nevertheless, differences in the fluorescence intensities at peak (α), peak (β) and the peak position (Ex/Em: 280/330 nm) corresponding to protein-like substances (Her et al. 2003) of RW, RF, and BF suggest some removal of NOM by the roughing filter and biofilter (Table 2).

The removal of HS, in these stages, is substantially less on a percentage basis than the removal of biopolymers. The above observations can be confirmed through the comparison of both LC-OCD spectra and fluorescence peak intensities of corresponding NOM components in RW, RF and BF (Figure 2b and Table 2).
The NF membranes XN45 and TS80 used in this study achieved significant levels of NOM removal, as would be expected. The fluorescence peak intensities of HS are reduced about tenfold or more, compared to the peak intensities of RW, depending on the type of NF membrane used. Fluorescence peak intensities that correspond to protein-like substances were, however, seen to be less affected on a percentage basis (Table 2). The peak (β) for HS, observed in the form of a shoulder in the EEMs of RW, RF, and BF, appears as a complete peak in the permeate streams (Figure 4c and d). The very weak, virtually nonexistent LC-OCD signals for the permeates of XN45 and TS80 NF membranes confirm the extent of NOM rejection (Figure 4a).

Even though both XN45 and TS80 membranes had similar MWCO and contact angle characteristics, the TS80 membrane demonstrated a substantially faster fouling rate with the same feed water. After 72 h of operation the XN45 and TS80 membranes had a flux equivalent to 72% and 5% of the initial flux, respectively. Higher levels of TOC and DOC, conductivity, calcium and magnesium concentrations observed for the XN45 permeate indicate different retention properties (Table 1). Different fouling rates therefore suggest different fouling mechanisms and/or different foulant material as well as potential differences in membrane properties.

Unlike the weak LC-OCD signals, fluorescence EEMs for the permeates of NF membranes, with very low levels of NOM (between 0.30 and 1.50 mg/L), contained many spectral details demonstrating the sensitivity of the technique at low concentrations. The LC-OCD signals of both XN45 and TS80 permeates do not show any significant sign of the presence of HS in the permeate (Figure 4a). The fluorescence EEMs of XN45 and TS80 permeates, on the other hand, display very different spectral characteristics. For example, the intensities of peak (α) and peak (β), which describe the extent of the presence of HS, are weaker in TS80 permeates compared to the XN45 permeates (Table 2). Especially, the fluorescence EEM peak (α) appears to be the major peak in XN45 permeate, whereas the same peak is significantly weaker in TS80 permeate (Figure 4c and d and Table 2). In addition, fluorescence peak (β) and the peak that corresponds to protein-like substances are more clearly noticeable in TS80 permeate than in XN45 permeate. These differences indicate that the composition of NOM in the permeate of the TS80 membrane is different than in the permeate of XN45. Therefore it is reasonable to assume that the different rejection properties of the two NF membranes, as indicated in Table 1, have likely contributed to the above differences in the permeates.

Moreover, EEMs of XN45 and TS80 permeates indicate a red shift (i.e., a peak shift towards a lower wavelength) in the position of peak (α) suggesting the absence of a certain fraction of HS. The new positions of peak (α) (peak-α') are found at Ex/Em: 320/390 and Ex/Em: 320/380 for XN45 and TS80 permeates, respectively (Figure 4c and d and Table 2). This shift may have resulted from preferential rejection of a certain fraction of NOM.
Table 2 | Fluorescence intensities at reported peak positions for HS and protein-like substances

<table>
<thead>
<tr>
<th></th>
<th>Intensity (a.u)</th>
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<tr>
<td></td>
<td>Peak (a): Ex/Em: 320/415 (HS)</td>
<td>Peak (b): Ex/Em: 270/450 (HS)</td>
<td>Ex/Em: 280/330 (protein-like)</td>
</tr>
<tr>
<td>RW</td>
<td>904.0</td>
<td>694.6</td>
<td>201.9</td>
</tr>
<tr>
<td>RF-effluent</td>
<td>858.5</td>
<td>617.5</td>
<td>161.2</td>
</tr>
<tr>
<td>BF-effluent</td>
<td>849.4</td>
<td>606.3</td>
<td>152.6</td>
</tr>
<tr>
<td>NF-permeates XN45</td>
<td>88.5</td>
<td>54.7</td>
<td>44.2</td>
</tr>
<tr>
<td></td>
<td>(103.00 @ Ex/Em: 320/390)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF-permeates TS80</td>
<td>11.6</td>
<td>20.9</td>
<td>45.6</td>
</tr>
<tr>
<td></td>
<td>(22.17 @ Ex/Em: 320/380)</td>
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</table>

The values given within brackets (bold letters) are the intensities of peak (a).

Figure 4 | Fluorescence EEMs of the membrane feed (b) and the permeates of the NF membranes; XN45 (c) and TS80 (d) and the corresponding LC-OCD spectra (a).
fraction of HS by both NF membranes. The difference in the positions of peak ($\alpha'$) between the XN45 and TS80 permeates also correlates with the different rejection (or retention) properties of the two NF membranes. These different rejection properties of the membranes appear to have played significantly different roles in the fouling of XN45 and TS80 membranes as discussed above.

Subsequently, in five more NF experiments which were limited to XN45 membranes due to the rapid fouling rates of the TS80 membranes, permeates with similar characteristics were produced even with measurable variation in raw water quality over a 3 month period. The similarities in XN45 permeate quality were confirmed by three approaches (results not presented for reasons of space): (i) comparison of parameters such as TOC, conductivity, calcium and magnesium; (ii) absence of any significant LC-OCD spectra and (iii) almost identical fluorescence EEMs. These results suggest that the characterization of the permeates from the NF experiments as carried out in this study is reproducible and that fluorescence spectroscopy can be used to obtain reproducible information that may be useful for assessment of NF fouling. Note though that fluorescence EEM is limited to the detection of macromolecules containing a fluorophore (e.g., proteins and humic substances); whereas LC-OCD is capable of measuring organic based macromolecules such as polysaccharides in addition to proteins and humic substances. However, fluorescence EEM displayed a higher sensitivity than LC-OCD for the molecules it detected in this study.

CONCLUSIONS

This study demonstrated how fluorescence spectroscopy can be used to assess the NF fouling in drinking water treatment. The two NF membranes used in this study (XN45 and TS80) provided different levels of NOM removal. The LC-OCD spectra that were collected in parallel at different stages of the process also confirmed these findings. The fluorescence EEMs of XN45 and TS80 permeates indicated that the composition of NOM for the two NF membrane permeates is different. These differences, captured by fluorescence EEMs, appeared to have a correlation with the fouling behaviour observed. LC-OCD was however, comparatively less sensitive in capturing these differences. The LC-OCD chromatograms of both NF membranes showed essentially complete rejection of biopolymers and humic substances, which offered little help in understanding the reasons for the different fouling rates observed. Further work should be directed at relating the fluorescence EEMs of NOM to the rejection properties of the membranes for predicting and mitigating membrane fouling.

REFERENCES