

Fouling of microfiltration membranes by the fractional components of natural organic matter in surface water

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Abstract This paper examines the effect of the fractional components of natural organic matter (NOM) in surface water on the fouling of microfiltration membranes. The results are shown for the NOM derived from the Mt. Zero drinking water reservoir located in the state of Victoria, but they are representative of the other two water reservoirs investigated in the full study. The NOM was concentrated and isolated into four fractions according to hydrophobicity and charge using non-functionalised and anionic resins. Filtration experiments were conducted in a stirred cell using 0.22 μm hydrophobic and surface-modified hydrophilic polyvinylidene fluoride (PVDF) membranes to examine the fouling effects by the NOM fractions on membranes of different hydrophobicity. The fouling rate and extent of fouling were considerably less for the hydrophilic membrane compared to the hydrophobic membrane, which was due to the reduced organic interactions (i.e., hydrophobic adsorption, charge interaction) between the NOM and the hydrophilic membrane. However, for both the hydrophilic and hydrophobic membranes, the order of the fouling potential of the four fractions was the same, namely hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. The explanation for the high fouling potential of the hydrophilic neutral fraction was attributed to the calcium and carbohydrates (mainly polysaccharides) in the NOM, which were found to concentrate in the hydrophilic neutral fraction. Fourier transform infrared spectroscopy (FTIR) spectra for the fouled hydrophobic PVDF and polypropylene membranes revealed some visible changes in the regions of Ar-O-Ar, C-C, C-N stretching and C-H rocking vibrations, indicating polysaccharides and aromatics being the important foulants on the hydrophobic membranes. The mechanism by which the hydrophilic neutral fraction caused severe membrane fouling was a combination of adsorption of polysaccharides on the membrane structure due to hydrophobic bonding of the non-polar segments of the polysaccharides, and electrostatic attraction interactions between the polysaccharide-Ca²⁺ complexes and the negatively charged membrane.

Keywords Drinking water; fractional component; fouling; microfiltration; natural organic matter

Introduction

Membrane microfiltration (MF) is a low pressure process primarily used for the removal of turbidity and chlorine-resistant pathogens such as *Cryptosporidium* and *Giardia* from water. In Australia, microfiltration plants for town drinking water treatment include small-scale plants (i.e., 6 ML/day) and a full-scale plant with a capacity of 126–150 ML/day at Bendigo, Victoria (Swinton, 2000). The membranes used in these treatment plants are typically 0.2 μm hydrophobic polypropylene hollow-fibre membranes.

A critical factor limiting the use of microfiltration for drinking water treatment is the fouling of membranes by natural organic matter (NOM) which is ubiquitous in aquatic systems (Kaiya *et al.*, 1996). Significant flux reductions were observed in the constant-pressure microfiltration of aqueous solutions of NOM using 0.22 μm membranes although only a small amount of NOM (< 10%, measured as organic carbon) was retained by the membranes (Fan, 2001). The fouling was primarily attributed to the plugging/adsorption of the colloidal/dissolved natural organics within the pore structure.

In our recent study of the influence of NOM characteristics on the fouling of a 0.22 μm hydrophobic polyvinylidene fluoride (PVDF) membrane using three surface water NOMs,

the low-aromatic hydrophilic neutral fraction of NOM was shown to be the main determinant of the rate and flux decline (Fan *et al.*, 2001). The hydrophobic acids (mainly humic substances) fraction of NOM also caused significant flux decline. The cause of the high fouling potential of the hydrophilic neutral compounds was partly attributed to the high molecular size (weight) (>30 kDa), while the chemical aspect of the high binding capacity of this fraction on the membranes was not well defined (Fan *et al.*, 2001). This paper continues the study of the interactions of the fractional components of NOM with membranes of different hydrophobicity by investigating the chemical components involved in the fouling mechanism.

Experimental

The NOM was isolated from Mt. Zero reservoir at Horsham, Victoria, Australia. Raw water was collected at the intake to the water treatment plant at the reservoir. The physical and chemical properties of the raw water are summarised in Table 1. The NOM in raw water was concentrated by reverse osmosis to 250 mg/L of total organic carbon (TOC). Part of the water concentrate was filtered with a 0.45 µm cartridge hydrophilic membrane to remove particulates, and then fractionated according to published procedures (Aiken *et al.*, 1992; Bolto *et al.*, 1998) yielding the following four fractions:

- Hydrophobic acids (HA) – adsorbed by Supelite DAX-8 (Sigma-Aldrich).
- Transphilic acids (TA) – adsorbed by Amberlite XAD-4 (Rohm and Haas).
- Hydrophilic charged (Char) – adsorbed by Amberlite IRA-958 (Rohm and Haas).
- Hydrophilic neutral (Neut) – passed through all resin columns.

The major fraction of NOM was the hydrophobic acids (humic substances), while the hydrophilic neutral fraction accounted for only 9% of the DOC as shown in Table 2.

The NOM concentrates and fractions used in the preparation of the feed solutions were diluted to a TOC concentration of approximately 50 mg/L with Milli-Q water and filtered with a 0.45 µm hydrophilic membrane to remove any particulate material. The resulting solutions were then diluted to the desired dissolved organic carbon (DOC) concentration with Milli-Q water. The ionic strength and Ca²⁺ concentration in the feed solutions were adjusted to constant value to minimise their effect during the comparison of membrane performance.

The membranes used were 0.22 µm surface-modified hydrophilic (Millipore, GVWP) and hydrophobic PVDF membranes (Millipore, GVHP), and a polypropylene membrane

Table 1 Raw water quality parameters

Parameter	Mt. Zero
pH	6.7
DOC (mg L ⁻¹)	9.1
Conductivity (µs cm ⁻¹)	121
Turbidity (NTU)	7.6
Alkalinity (as CaCO ₃ , mg L ⁻¹)	9
UVA-254 (cm ⁻¹)	0.284

Table 2 Fractional components in Mt. Zero NOM

Fraction	Mt. Zero(%), based on DOC data
Hydrophobic acids	55
Transphilic acids	22
Hydrophilic charged compounds	14
Hydrophilic neutral compounds	9

Table 3 Characteristics of microfiltration membranes

Characteristics	GVWP	GVHP	WPP
Material	Modified PVDF	PVDF	Polypropylene
Surface property	Hydrophilic	Hydrophobic	Hydrophobic
Nominal pore size [μm]	0.22	0.22	0.2
Pure water flux (50 kPa, $22 \pm 2^\circ\text{C}$) [$\text{L m}^{-2} \text{hr}^{-1}$]	$2,230 \pm 80$	$2,280 \pm 100$	$2,210 \pm 150$
Mean thickness [μm]	125	125	150
Typical porosity (%)	70	75	N/A

(Whatman, WPP) with characteristics shown in Table 3. The experimental rig incorporated a stirred cell (Amicon, 8050, membrane effective area 13.4 cm^2) connected to a feed reservoir, and was operated at a constant pressure of 50 kPa regulated using nitrogen gas and a stirrer speed of 300 rpm (Fan *et al.*, 2001). All experiments were conducted at room temperature ($22 \pm 2^\circ\text{C}$). The permeate flux was determined using a top-loading electronic balance connected to a computer for continuous recording of data.

TOC and DOC were measured using a TOC analyser (I-O-Analytical, Model 1010). Calcium concentration was measured by inductively coupled plasma spectroscopy (Jobin-Yvon, JY24 ICP spectrometer). Total carbohydrates were determined using the phenol-sulphuric acid colorimetric method (Dubois *et al.*, 1956). A FTIR apparatus (Perkin-Elmer, Spectrum 2000) was used to analyse the surface of the clean and NOM-fouled membranes. The attenuated total reflection (ATR) method was used for recording the IR spectra of the membranes. The ATR accessory contained a ZnSe crystal at a nominal incident angle of 45° .

Results and discussion

Microfiltration of NOM fractions

The effect of the fractional components of NOM on fouling of the GVHP membrane is shown in Figure 1 where the relative flux, the ratio of the permeate flux at a given time (J) to the initial pure water flux (J_0), is plotted as a function of time. The concentration of each fraction was made to the same DOC value as in the original NOM. The unfractionated NOM caused a flux decline of 84% after 30 min filtration. Although the hydrophilic neutral fraction solution contained only 0.4 mg L^{-1} of DOC, it caused more severe flux decline (72%) than the other fractions even though they were at higher DOC concentration. This indicated that the hydrophilic neutral fraction was a strong fouling component in this surface water NOM. The fouling potential of the four fractions was then compared at the same concentration of 5 mg L^{-1} of DOC as shown in Figures 2 and 3 for the hydrophobic GVHP

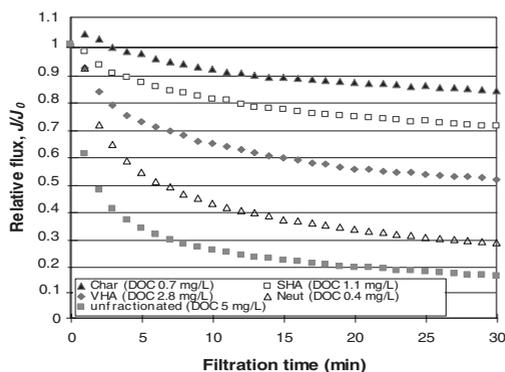


Figure 1 Relative flux versus time for the microfiltration of Mt. Zero NOM and its fractional components using GVHP membranes

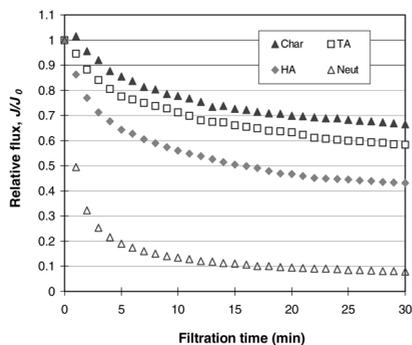


Figure 2 Relative flux versus time in the filtration of the four fractions of Mt. Zero NOM using GVHP membranes. DOC 5 mg L^{-1}

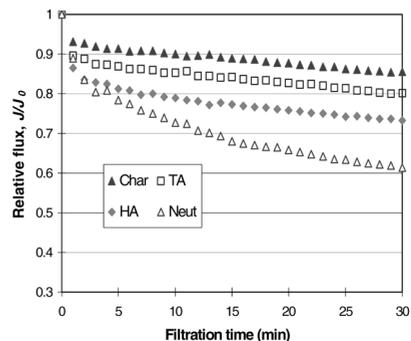


Figure 3 Relative flux versus time in the filtration of the four fractions of Mt. Zero NOM using GVWP membranes. DOC 5 mg L^{-1}

and hydrophilic GVWP membranes, respectively. The fouling rate and extent for each of the NOM fractions on the hydrophilic membrane were less compared to the hydrophobic membrane. This was mainly due to the reduced organic interactions (i.e., hydrophobic adsorption, electrostatic repulsion) between the NOM and the hydrophilic membranes (Fan, 2001).

The order of the fouling potential of the four fractions for both membranes was the same, namely hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. The hydrophilic neutral fraction caused significantly greater flux decline for both membranes (92% for GVHP, 40% for GVWP) than the other three fractions. This has been partly attributed to the high molecular weight fraction of the neutral compounds (> 30 kDa), which accounted for nearly 30% of the total neutral DOC (Fan *et al.*, 2001). The hydrophobic acids also caused significant flux decline, which was related to the higher content of large molecules in this fraction, and hydrophobic adsorption on the hydrophobic membrane (Jucker and Clark, 1994). The charged fraction had less effect on membrane fouling. This was attributed mainly to the electrostatic repulsion between the negatively charged membranes and the negatively charged NOM fraction. Moreover, it was less likely that there was any significant hydrophobic adsorption of the charged fraction on the hydrophobic membranes as this fraction was hydrophilic in character. An interesting phenomenon at the beginning of the filtration was the flux for the charged fraction exceeding the pure water flux for the GVHP membrane as observable in both Figures 1 and 2. This extended permeate flux at the beginning of the filtration was probably due to the increased membrane hydrophilicity resulting from the coating of hydrophilic charged compounds on the membrane structure.

Relationship of chemical components in neutral fraction to fouling

Chemical analysis of each fraction together with mass balance determination was used to identify the distribution of the DOC, carbohydrates and calcium between the various fractions. The objective was to identify which chemical components were related to the cause of the strong fouling by the hydrophilic neutral fraction. Carbohydrates and calcium were found to concentrate in the neutral fraction as illustrated in Figure 4. The percentage of carbohydrates in feed NOM for the neutral fraction (41%) was significantly higher than for the other fractions (15% for HA; 6% for TA; 2% for Char). The ratio of carbohydrates to DOC for the hydrophilic neutrals was over 50%, whereas for the each of the other three NOM fractions the ratio was less than 5%. Carbohydrates were the major component of the hydrophilic neutral fraction. The neutral fraction contained nearly all (97%) of the calcium

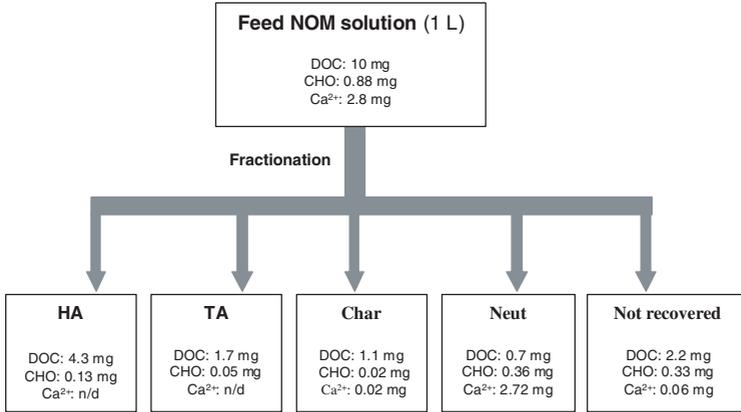


Figure 4 Mass flow of the DOC, carbohydrates and calcium in the fractionation of Mt. Zero NOM. [n/d, not detected]

in the feed NOM solution. There was only a small amount of calcium present in the hydrophilic charged fraction, and non-detectable amounts of Ca²⁺ in the hydrophobic acids and transphilic acids fractions. Significant amounts of DOC (22%) and carbohydrates (38%) were not recovered from the resin columns in the fractionation procedure.

Polysaccharides are the largest fraction (75%) of carbohydrates in most fresh waters (Thurman, 1985). On this basis, and from our experimental finding that carbohydrates concentrate in the neutral fraction, we propose that the polysaccharide substances present in the neutral fraction are involved in the high fouling potential of this fraction. Polysaccharides are generally negative in charge the same as the membrane surface, which leads us to further propose that the adsorption of these compounds on the membrane structure is dominated by the hydrophobic bonding of non-polar segments rather than electrostatic interactions. Similar findings regarding the high fouling capacity of polysaccharides were found to apply for ultrafiltration by Cho *et al.* (1998) and nanofiltration by Mänttari *et al.* (2000). It was not expected that the same components would be involved in the mechanism for the much looser microfiltration membranes.

It was also found that over 7% of the Ca²⁺ in the hydrophilic neutral fraction was retained by a 30 kDa membrane as shown in Table 4, suggesting that Ca²⁺ could interact with polar groups on the hydrophilic neutral compounds to form large complexes/colloids of the form organics-Ca²⁺ causing the greater flux decline. Electrostatic attraction interactions between the organics-Ca²⁺ complexes and the negatively charged membrane also appear to have a role in fouling by the hydrophilic neutral compounds.

FTIR spectroscopy analysis

An investigation using Fourier transform infrared (FTIR) spectroscopy was carried out on the clean and fouled hydrophobic membranes to identify the organic foulants adsorbing on the membranes. Specimens were pre-washed new membranes and membranes fouled by

Table 4 Ca²⁺ content in the hydrophilic neutral fraction of Mt. Zero NOM

Solution	Ca ²⁺ (mg L ⁻¹)
Neut (DOC 5 mg L ⁻¹)	2.72
Neut passing through a 30 kDa membrane (DOC 4.2 mg L ⁻¹)	2.53

filtering NOM solutions at a DOC concentration of 30 mg L^{-1} for 1 hour. There was no detectable difference in the spectral pattern for the clean and fouled hydrophilic GVWP membrane indicating the absence of surface fouling components. The FTIR spectra for the clean and fouled hydrophobic GVHP membranes are shown in Figure 5. The only significant difference between new and NOM-fouled GVHP membranes was Ar-O-Ar stretching vibrations at $1,240 \text{ cm}^{-1}$. This indicated the presence of aromatic alcohols, carboxylic acids and/or esters on the surface layer of the membrane (Colthup and Gore, 1950; Pihlajamäki *et al.*, 1998). Most of the peak heights for the NOM-fouled membrane were lower compared to the clean membrane. The reduced signals were due to the aromatic and carboxylic groups of the membrane being coated with organic foulants (Cho *et al.*, 1998).

A different spectral pattern was observed for the hydrophobic polypropylene membrane WPP as shown in Figure 6. The fouled membrane produced some changes in the regions of C-C and C-N stretching vibrations at $1,000\text{--}1,080 \text{ cm}^{-1}$ and C-H rocking vibrations between $670\text{--}740 \text{ cm}^{-1}$. These observations were indicative of polysaccharides with an IR peak at $1,000 \text{ cm}^{-1}$ and protein (Cho *et al.*, 1998). The changes in the spectral patterns for the hydrophobic membranes, GVHP and WPP, appeared in different frequency ranges, indicating that the interactions between the NOM components and the membranes were

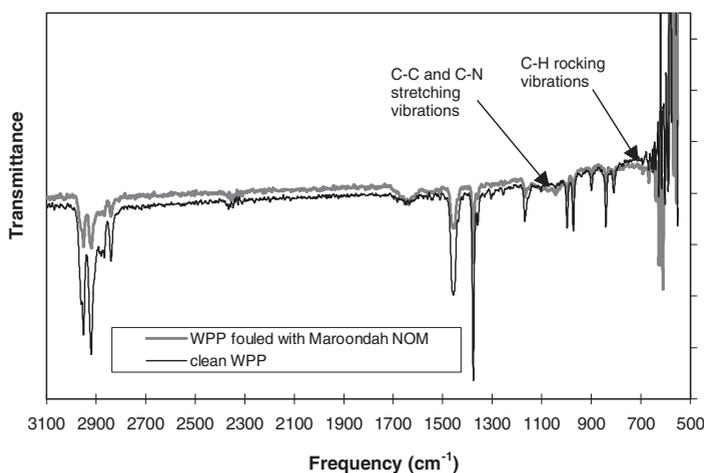


Figure 5 FTIR spectra of the clean and NOM-fouled GVHP membranes

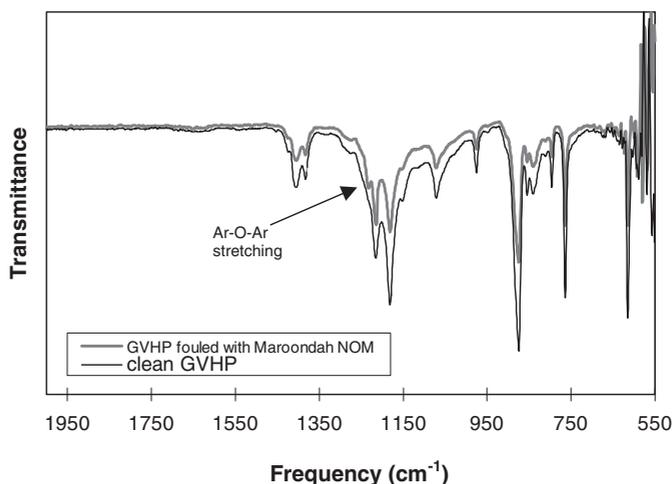


Figure 6 FTIR spectra of the clean and NOM-fouled WPP membranes

dependent on the presence of the functional groups on membrane material. In overall terms, the FTIR spectral patterns of the new and fouled membranes were not greatly different because FTIR analysed only the surface layer of membranes, while NOM fouling occurred mostly in the inner structure of the membranes.

Conclusions

The fouling potential of the four NOM fractions isolated on the basis of hydrophobicity and charge was compared in the stirred cell filtration experiments using 0.22 μm hydrophilic and surface-modified hydrophobic PVDF membranes. The rate and extent of fouling for each of the NOM fractions on the hydrophilic GVWP membrane were significantly less compared to the hydrophobic GVHP membrane, which was due to the reduced organic interactions (i.e., hydrophobic adsorption, electrostatic repulsion) between the NOM and hydrophilic membranes. On the basis of comparable DOC concentration, the order of the fouling potential of the fractionated NOM for both the hydrophilic and hydrophobic PVDF membranes was hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged. Calcium and carbohydrates (mainly polysaccharides) were found to concentrate in the neutral fraction. The FTIR spectra for the fouled hydrophobic membranes revealed some changes in the regions of Ar-O-Ar, C-C, C-N stretching and C-H rocking vibrations, indicating that aromatics and polysaccharides were the major foulants on the hydrophobic membranes. It was proposed that the mechanism for the strong fouling by the hydrophilic neutral fraction was a combination of adsorption of polysaccharides on membrane structure due to hydrophobic bonding of non-polar segments of the polysaccharides, and electrostatic attraction interactions between the organics-Ca²⁺ complexes and the negatively charged membrane.

Membranes with hydrophilic surface properties have low fouling tendency and are the preferred choice for the drinking water filtration. However, polypropylene membranes are employed in most microfiltration water treatment plants in Australia and they are hydrophobic in surface character. An approach for minimizing NOM fouling in current industrial applications would be a pretreatment process targeting the removal of the hydrophilic neutral fraction which contains the strong fouling components of NOM. However, the high molecular weight (size) hydrophobic acids can be effectively removed by conventional coagulation processes, but the neutral compounds remain recalcitrant (Bolto *et al.*, 1999). An effective removal of the hydrophilic neutral compounds from water requires the development of a novel treatment process.

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