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PERGAMON

THE FOULING OF MICROFILTRATION MEMBRANES BY NOM AFTER COAGULATION TREATMENT

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Abstract—Microfiltration membranes used in drinking-water treatment are fouled by both colloidal material and natural organic matter (NOM) present in the raw water. The relative importance of these contributions to fouling may depend on whether or not the water is pretreated before microfiltration, and on the type and extent of any pretreatment. In this study, the causes of fouling were determined for microfiltration of a surface water through a polypropylene hollow-fibre membrane. Fouling was caused by colloidal material when the raw water was filtered untreated, and by NOM when the raw water was coagulated before filtration. The components of NOM which cause fouling of microfiltration membranes are not yet well-established, and were also investigated in this study. NOM from the raw water was fractionated into four specific classes of compounds on the basis of hydrophobicity and charge. The rates of fouling by each NOM fraction were measured separately. The major contribution to fouling was attributed to the NOM fraction comprising small, neutral, hydrophilic compounds. The NOM fractions comprising humic and fulvic acids made only a minor contribution to fouling. © 2000 Elsevier Science Ltd. All rights reserved

Key words—fouling, microfiltration, natural organic matter

INTRODUCTION

Membrane microfiltration is a drinking-water treatment process which is particularly suitable for the removal of suspended solids, especially bacteria, algae, and protozoa, such as *Giardia* and *Cryptosporidium* (MacCormick, 1995). However microfiltration is less successful for the removal of dissolved contaminants such as natural organic matter (NOM) (MacCormick, 1995). NOM is a well-established cause of colour in water, and is also linked to the formation of disinfection by-products with potential health implications (Rook, 1974). The conventional approach to removing NOM from drinking water is coagulation with aluminium-based or iron-based coagulants (Crozes *et al.*, 1995; Pontius, 1993). Coagulation upstream of a microfiltration process can also be used as a pretreatment to meet water quality requirements for NOM removal where microfiltration alone is inadequate (Vickers *et al.*, 1995).

Membrane filtration processes are prone to fouling, with a progressive decline in membrane flux with time on stream because of the accumulation of retained material. In the case of drinking-water microfiltration, colloidal material may cause fouling by forming a cake on the membrane surface, while dissolved material may cause fouling by precipitating at the membrane surface or adsorbing within the membrane pore space. In the former two cases the resistance to filtration is related to the permeability of the surface cake, while in the latter case the filtration resistance is related to the effective size of the membrane pores (i.e. the effective membrane permeability). These filtration resistances are generally incorporated into a Darcy's Law model, in which the membrane flux per unit transmembrane pressure is inversely related to a time-dependent resistance, which is calculated as the sum of separate filtration resistances assumed to be in series (Weisner and Aptel, 1996). The effect of colloidal fouling on microfiltration performance is well described, and common models range from the simple particle-size-based Kozeny–Carman model (McCabe *et al.*, 1993), to more sophisticated interparticle and membrane-particle interaction models (Faibish *et al.*, 1998; Meagher *et al.*, 1996). The effect of adsorptive fouling on microfiltration performance is also well-described (Weisner and Aptel, 1996), although the causes of fouling by dissolved NOM are not well understood. This is because the extent of interactions of NOM with a membrane can depend on features such as membrane hydrophobicity (Laine *et al.*, 1989), the pH, salinity and

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hardness of the water (Nystrom et al., 1996), and the characteristics of the NOM (Jucker and Clark, 1994). The latter is a particularly challenging area, since NOM represents a broad range of structurally complex compounds with a wide size distribution, and heterogeneous functional chemistry (Stevenson, 1994). Historically NOM is divided into hydrophobic and hydrophilic (humic and non-humic) components. The hydrophilic components were thought to impact water quality less than the hydrophobic components, although they are also less amenable to physicochemical treatment (Owen et al., 1995).

The contributions of colloidal material and NOM to the fouling of microfiltration membranes may depend on the characteristics of the raw water, the membrane material, and on the type and extent of any water pretreatment. Coagulation pretreatment is known to reduce the rate of fouling of microfiltration membranes, possibly by aggregating fine particles to increase cake permeability or prevent pore blockage, conditioning of the cake by incorporation of fine particles into highly-porous flocs, or precipitation or adsorption of dissolved material

into flocs (Wiesner and Laine, 1996). One or more of these processes could alter the respective contributions of colloidal material and NOM to membrane fouling by untreated and pretreated waters. In this study the contributions of colloidal material and NOM to the fouling of a polypropylene hollow-fibre microfiltration membrane, and the rate-controlling fouling mechanisms, were investigated for both untreated and alum-treated surface water. The components of NOM which foul a polypropylene membrane were studied by fractionating the surface water NOM on non-functionalised resins into four specific classes of compounds based on hydrophobicity and charge, and measuring the rates of fouling by these compounds. The NOM fouling mechanism was inferred from the types of compounds responsible for fouling.

MATERIALS AND METHODS

Raw water fractionation

The surface water source was the Moorabool River near Anakie, Victoria, Australia. This water had a turbidity of 3.9 NTU, a salinity of 62 ppm (as Na^+), a hardness of 4.3
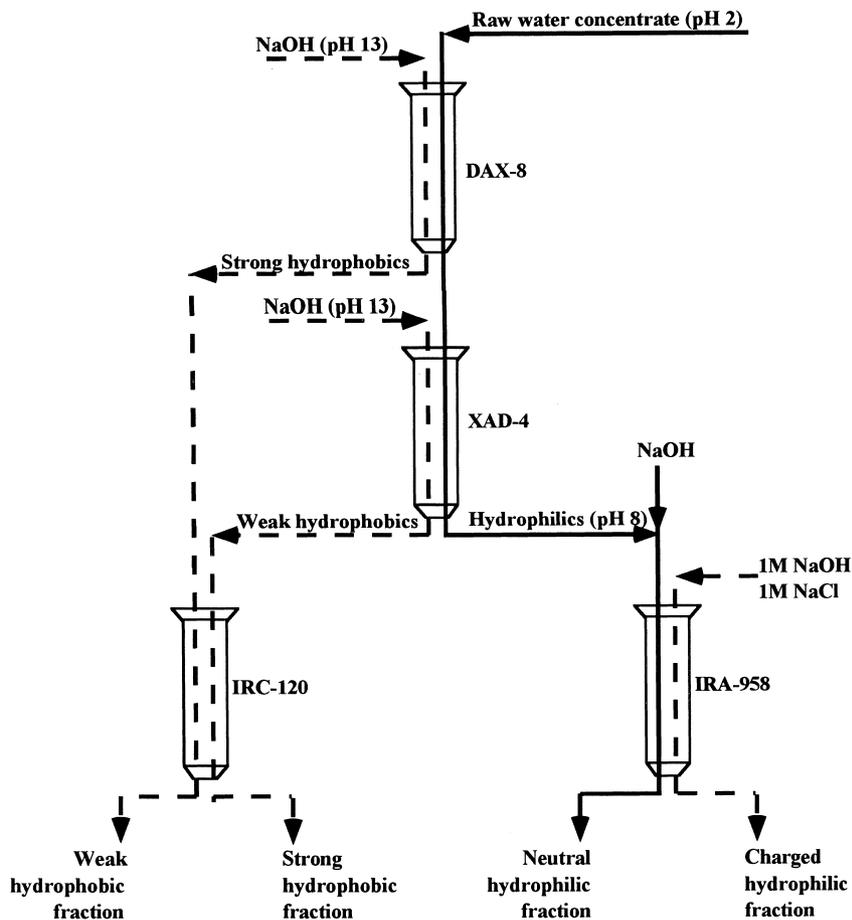

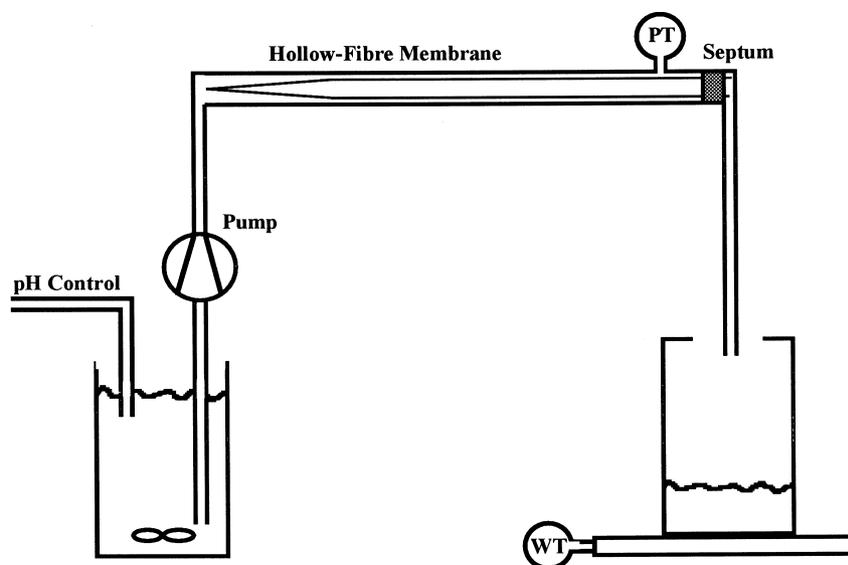Fig. 1. Outline of raw water fractionation procedure.

Fig. 2. Single-fibre microfiltration apparatus.

ppm (as Ca^{2+}), and a dissolved organic carbon (DOC) concentration of 9.0 mg/l. The NOM in the raw water was concentrated to approximately 500 mg/l DOC by reverse osmosis, and fractionated according to an ion-exchange procedure as described by Aiken et al. (1992), Croue et al. (1993) and Bolto et al. (1998) (Fig. 1). The raw water concentrate was filtered through a 0.45-μm membrane, adjusted to pH 2, and fed onto a Supelite DAX-8 non-functionalised resin which retains strongly hydrophobic organic matter attributed to humic and fulvic acids (Croue, 1999). This fraction was eluted with NaOH and acidified on an IRC-120 cation exchange resin. The unadsorbed concentrate from the DAX-8 resin was fed onto an Amberlite XAD-4 resin, which retains weakly hydrophobic (or transphilic) organic matter (Croue, 1999). This fraction was also eluted with NaOH, and separately acidified on an IRC-120 resin. The unadsorbed concentrate from the XAD-4 resin, which consists of hydrophilic (non-humic) organic matter attributed to proteins, amino acids, and carbohydrates (Owen et al., 1995) was fed onto an Amberlite IRA-958 anion exchange resin, which retains charged material (Bolto et al., 1998). This fraction was eluted with a NaOH/NaCl mixture. The remaining neutral material is not retained by any of the resins.

Membrane fouling

Microfiltration experiments were carried out on single polypropylene hollow-fibre membranes using the filtration apparatus shown in Fig. 2. The fibres had a nominal pore size of 0.2 μm, an internal diameter of 250 μm, an outer diameter of 550 μm, and a length of 0.9 m. The fibres had a nominal surface area of 700 mm^2 and a nominal pure water flux of 0.3 l s^{-1} m^{-2} bar^{-1}. Filtration occurred from the outside to the inside of the fibre. Fibres were opened at both ends and sealed at the outer wall by threading the ends through a silicone septum. The fibres were wetted and degreased with ethanol, and flushed thoroughly with ultrapure water (MilliQ). The feed water was prepared in a stirred vessel, and pumped onto the membrane at 80–100 kPa with a peristaltic pump. The feed was forced through the hollow-fibre membrane under pressure and the permeate emerged from the opened ends. The permeate was collected in a vessel mounted on an analytical bal-

ance (WT). Feed pressure was monitored with a pressure transducer (PT), and allowed to follow the peristaltic pump curve uncontrolled. The signals from the analytical balance and pressure transducer were processed with data acquisition software to calculate the permeate flowrate as a function of permeate throughput. The duration of experiments ranged from 100 to 600 min depending upon the rate of fouling. Microfiltration experiments were carried out on the four NOM fractions and on the unfractionated raw water, subjected to following pretreatments; coagulation with alum ($Al_2(SO_4)_3 \cdot 18H_2O$, Akzo–Nobel), adsorption with a commercially available powdered activated carbon (PAC, Sigma), and filtration through a 0.2-μm membrane (Gelman GH Polypro). All microfiltration experiments were done at pH 6 (optimal for NOM removal by alum).

Analytical methods

The DOC was measured by wet chemical oxidation (O/I Analytical 1010 Wet Oxidation TOC Analyser), and ultraviolet absorbance was measured at 254 nm (Shimadzu UV-160 UV-visible spectrophotometer). All samples were filtered through a 0.45-μm filter (Selby-Biolab HPLC-certified) prior to analysis. Calcium and sodium concentrations were measured by inductively-coupled plasma spectroscopy (Jobin-Yvon JY24 ICP spectrometer) and concentrations in the four fractions were made up to the raw water concentrations by adding calcium chloride and sodium chloride, respectively. Turbidity was measured using a Hach Ratio/XR Turbidimeter.

Table 1. DOC concentrations of Moorabool NOM fractions

Fraction	DOC (%)	DOC (mg/l)
Strongly hydrophobic	34	3.1
Weakly hydrophobic	18	1.6
Charged hydrophilic	33	3.0
Neutral hydrophilic	15	1.4
Unfractionated	100	9.0

Table 2. The fate of calcium and sodium in the fractionation procedure

Fraction	Ca^{2+} (mg/l)	Na$^+$ (mg/l)
Strongly hydrophobic	0.00 ($\pm$0.001)	0.1
Weakly hydrophobic	0.00 ($\pm$0.01)	0.2
Charged hydrophilic	0.01	143
Neutral hydrophilic	3.72	70
Unfractionated	4.30	62

RESULTS

Characterisation of the Moorabool NOM fractions

The DOC concentrations and their relative percentages in the four Moorabool NOM fractions are shown in Table 1. The DOC distribution was approximately 1/3 strongly hydrophobic, 1/6 weakly hydrophobic, 1/3 charged hydrophilic, and 1/6 neutral hydrophilic.

It was necessary to follow the fate of both calcium and sodium from the raw water in the fractionation procedure, as ionic strength and calcium concentration can each influence both adsorption of NOM onto membranes and aggregation of NOM through moderation of electrostatic effects (Yoon *et al.*, 1998; Yuan and Zydney, 1999). The concentrations of calcium and sodium in the four fractions are compared to those of the raw water in Table 2. The concentrations of calcium and sodium were negligible in the hydrophobic fractions. The sodium concentration in the neutral hydrophilic fraction was slightly higher than in the raw water because of the addition of NaOH for pH adjustment before feeding to the IRA-958 resin. The sodium concentration in the charged hydrophilic fraction was elevated by the elution procedure used on the IRA-958 resin.

The four NOM fractions were reconstituted as stock solutions with DOC concentrations similar to those of each fraction in the raw water. The calcium and sodium concentrations of the stock solutions were adjusted to the approximate values of the raw water (and also in the neutral hydrophilic fraction), although the sodium concentration of the charged hydrophilic fraction was not reduced. The DOC, turbidities, calcium and sodium concentrations in the reconstituted NOM fractions are given in Table 3. As turbidities were low and uniform, each reconstituted NOM fraction reflected that component of the raw water NOM without colloidal material.
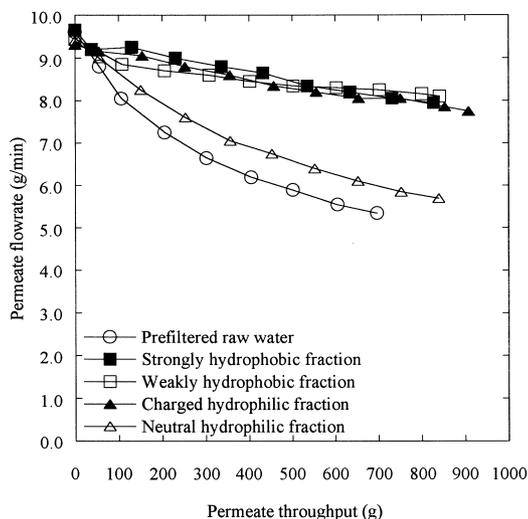
In previous work, the Moorabool NOM fractions were characterized by size exclusion chromatography with DOC and ultra-violet absorbance detection (Bolto *et al.*, 1999). The size distributions of both hydrophobic fractions were similar to that of the raw water. The charged hydrophilic fraction was predominantly larger-sized material whereas the neutral hydrophilic fraction was predominantly smaller-sized material.

Membrane fouling of the reconstituted Moorabool NOM fractions

The declines in permeate flowrates with permeate throughput during microfiltration of the four reconstituted Moorabool NOM fractions are shown in Fig. 3. The rates of fouling were relatively low for the strong and weak hydrophobic fractions, and for the charged hydrophilic fraction. In these three cases, the permeate flowrate declined by approximately 16% after 800 g of the solution was filtered. However in the case of the neutral hydrophilic fraction, the rate of fouling was considerably faster, the permeate flowrate declining by approximately 40% after 800 g of the solution was filtered. In all cases, the change in DOC after filtration was below the

Fig. 3. The declines in permeate flowrate with permeate throughput for the four Moorabool NOM fractions and for prefiltered unfractionated water.

Table 3. DOC, turbidity, calcium and sodium concentrations in the reconstituted NOM fractions

Fraction	DOC (mg/l)	Turbidity (NTU)	Ca^{2+} (mg/l)	Na$^+$ (mg/l)
Strongly hydrophobic	3.0	0.2	4.3	70
Weakly hydrophobic	1.5	0.2	4.4	69
Charged hydrophilic	3.0	0.3	4.4	143
Neutral hydrophilic	1.4	0.2	4.4	70
Unfractionated[a]	9.0 (8.0)	3.9 (0.2)	4.3	62

[a]Values after filtration pretreatment are shown in parentheses.

limit of detection of the TOC Analyser (± 0.2 mg/l). The rate of fouling by the unfractionated raw water after filtration pretreatment was only slightly faster than for the neutral fraction, the permeate flowrate declining by approximately 45% after 800 g of the solution was filtered. The raw water after filtration pretreatment had already passed through a 0.2-μm membrane, so the fouling in this case can be attributed to dissolved NOM. The rate of fouling by the neutral hydrophilic fraction did not improve when the permeate was refiltered through a fresh membrane.

Membrane fouling of raw Moorabool water with coagulation pretreatment

The declines in permeate flowrates with permeate throughput during microfiltration of the untreated water and the water after alum coagulation pretreatment are shown in Fig. 4. In the latter case, the water was treated with alum at the optimum dose (3.2 mg/l as Al^{3+}) for both DOC and UV_{254} removal (46% and 69%, respectively). The rate of fouling for the untreated Moorabool water was relatively high, with the permeate flowrate declining by 82% after 800 g was filtered. In contrast, the rate of fouling for the alum-treated water was considerably lower, with the permeate flowrate declining by approximately 50% after 800 g was filtered. If the alum flocs were settled rather than stirred before microfiltration (so that only the supernatant solution was filtered) the rate of fouling was not reduced.

Membrane fouling of raw Moorabool water with adsorption pretreatment

The declines in permeate flowrates with permeate throughput during microfiltrates of the untreated

water and the water after PAC adsorption pretreatment are compared in Fig. 5. In the latter case, the water was treated with an excess of PAC (100 mg/l for 68 h) which resulted in 68% DOC removal. The rate of fouling by the PAC-treated water was similar to the raw water with the permeate flowrate declining by 83% after 800 g was filtered. A 100 mg/l suspension of PAC in ultrapure (MilliQ) water did not cause an appreciable decline in permeate flowrate, indicating that the PAC particles themselves did not contribute a resistance to filtration.

DISCUSSION

Microfiltration of untreated Moorabool water caused a severe decline in permeate flowrate with permeate throughput, indicative of rapid fouling (Fig. 4). The rate of fouling was unaffected by adsorption pretreatment with PAC (DOC 3.0 mg/l, Fig. 5), but was significantly reduced by coagulation pretreatment with alum (DOC 4.6 mg/l, Fig. 4), and filtration pretreatment (DOC 8.0 g/l, Fig. 3). These results indicate that for this low-turbidity, high-NOM surface water, colloidal material rather than dissolved NOM determined the rate of fouling. Although partial NOM removal was achieved using either an adsorbent or a coagulant, only the latter treatment option reduced the rate of fouling. The rate of fouling after filtration pretreatment although lower than the untreated water, was still appreciable indicating a contribution from dissolved NOM under these conditions.

The reduction in the rate of fouling after coagulation could be caused by aggregation of fine particles, incorporation of particles into flocs, or adsorption or precipitation of dissolved material
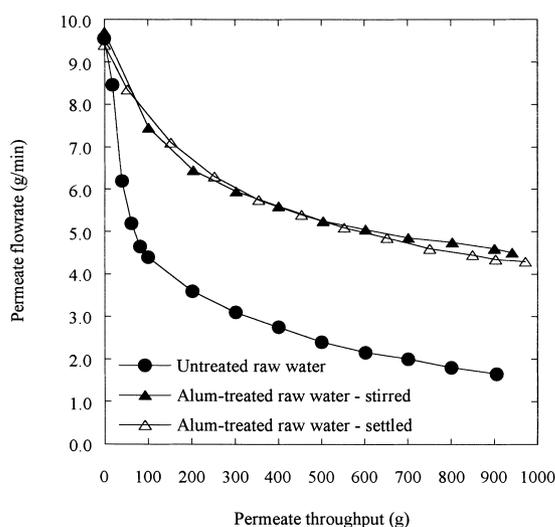

Fig. 4. The declines in permeate flowrate with permeate throughput for untreated and alum-treated Moorabool water.
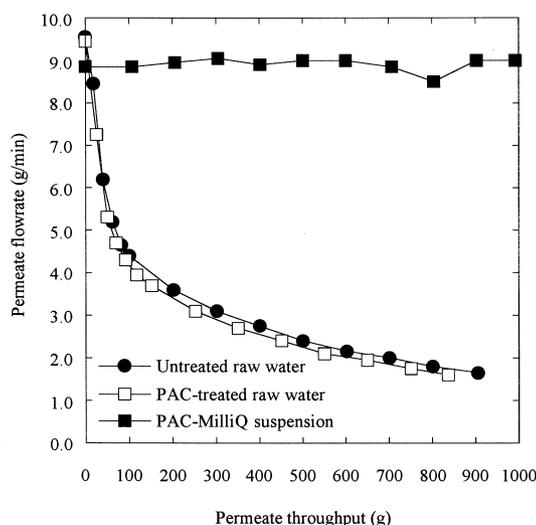

Fig. 5. The declines in permeate flowrate with permeate throughput for untreated and PAC-treated Moorabool water.

into flocs (Wiesner and Laine, 1996). These mechanisms imply that fouling after coagulation pretreatment can be attributed to the filtration resistance due to formed flocs, or to the fraction of dissolved NOM which is not removed by a coagulant. The contributions of these two filtration resistances to fouling can be separated by comparing the rates of fouling for stirred and settled alum pretreatments (Fig. 4). The rates of fouling for both pretreatments were similar, indicating that the filtration resistance due to settleable aggregates and flocs is small compared to that due to residual dissolved NOM. Furthermore, the rates of fouling after both filtration pretreatment (Fig. 3) and coagulation pretreatment (Fig. 4) were also similar, indicating that the filtration resistance due to dissolved NOM is similar to that due to residual NOM and formed flocs. The rate of fouling was determined by dissolved NOM, regardless of whether colloidal material was coagulated or removed by prefiltration.

Coagulation pretreatment selectively removes certain types of dissolved NOM. Aluminium-based and iron-based coagulants are known to preferentially remove hydrophobic rather than hydrophilic substances (Dryfuse et al., 1995; Singer and Harrington, 1993; White et al., 1997), charged rather than neutral substances (Bose et al., 1993; Korshin et al., 1997), and larger-sized rather than smaller-sized substances (Dryfuse et al., 1995; Sinsabaugh et al., 1986). These trends were also observed when the four Moorabool fractions were treated with alum. The resulting DOC and UV_{254} removals are given in Table 4 (Bolto et al., 1998). Alum removed upwards of 65% of UV absorbers of the hydrophobic and charged hydrophilic fractions, but only 24% of the UV absorbers from the neutral hydrophilic fraction. The relative concentration of neutral hydrophilic substances was therefore substantially higher after coagulation pretreatment than for the untreated water. As a first approximation, the contribution of dissolved NOM to fouling after coagulation pretreatment can be attributed to fouling by neutral hydrophilic substances. Indeed the rate of fouling by the neutral hydrophilic fraction (Fig. 3) was only slightly lower than the rate of fouling by alum-treated water (Fig. 4). This difference may be due to both the substantial removal of the other three NOM fractions (comprising approximately

3.0 mg/l of the alum-treated water), or a contribution from unsettleable flocs. In either case, residual NOM played an important role in determining the rate of fouling in microfiltration with coagulation pretreatment. The substantial removal of the hydrophobic and charged fractions by alum had little impact on the rate of fouling by Moorabool water.

The interpretation of the rates of fouling in hollow-fibre microfiltration membranes is presently qualitative. The rate of fouling of hollow-fibres depends upon the fibre length, diameter and thickness, as well as properties of retained material from the feed stream (Carroll and Booker, 2000). Quantitative determination of filtration resistances attributed to colloidal material or dissolved NOM would require isolation of these contributions from those due to fibre dimensions. This is not a trivial undertaking, requiring the development of a detailed model significantly more complex than existing Darcy's Law models. However, even in the absence of such a model, fouling can be attributed to colloidal substances in microfiltration of untreated water, and to residual NOM in microfiltration of alum-treated water.

The extent to which the rate of fouling is determined by colloidal or dissolved NOM will depend on the characteristics of both the raw water and coagulant used in any pretreatment. The Moorabool water used in this study was low in turbidity and high in DOC. Water of a different quality may require a different alum dose to meet NOM removal requirements. This may alter the relative contributions to fouling by residual NOM and flocs. The relative concentrations of each NOM fraction in the raw water is also important. The rate of fouling by a raw water with a relatively high concentration of neutral hydrophilic substances, and low turbidity may not improve substantially after coagulation pretreatment. Finally, both the coagulant and treatment conditions used will determine the permeability, size and stability of flocs formed in pretreatment. These properties in turn determine the filtration resistance due to the flocs. Alum treatment of Moorabool water produces flocs whose filtration resistance is less significant than that of the residual NOM. This finding may not be applicable to treatment of other water sources and by other coagulants. On the basis of results given here, the rate of fouling will not improve if alum is replaced by a similar coagulant. However it is important to consider other factors in coagulant assessment such as cost, backwash effectiveness and sludge properties, etc.

The rates of fouling of the four Moorabool fractions were similar for the hydrophobic and charged hydrophilic fractions, and substantially faster for the neutral hydrophilic fraction (Fig. 3). The fouling of a hydrophobic polypropylene microfiltration membrane by small, neutral hydro-

Table 4. NOM removal from Moorabool fractions by alum treatment

Fraction	DOC removal (%)	UV_{254} removal (%)
Strongly hydrophobic	48	71
Weakly hydrophobic	49	65
Charged hydrophilic	64	83
Neutral hydrophilic	0	24[a]
Unfractionated	46	69

[a]Low ultra-violet absorbance at 254 nm.

philic substances is consistent with previous reports of fouling of ultrafiltration membranes by low molecular weight model organic compounds in the absence of particulate material (Crozes *et al.*, 1993), and by residual dissolved NOM following treatment with ferric chloride (Lahoussine-Turcaud *et al.*, 1990). In both studies, fouling was attributed to adsorption of organic compounds, and could not be reversed by hydraulic cleaning alone. In the former study both hydrophobic and hydrophilic ultrafiltration membranes were fouled by a tannic acid solution which had a molecular weight well below the membrane cut-off. In the latter study a polysulphone ultrafiltration membrane was fouled after a coagulation pretreatment which produced a water consisting predominantly of low molecular weight polysaccharides.

In contrast, a recent study attributed fouling of a microfiltration membrane by commercial humic acid solutions to formation of a retained surface deposit rather than adsorption within the pore space (Yuan and Zydney, 1999). In this study prefiltration through membranes with progressively tighter molecular weight cut-offs reduced fouling as more smaller material was removed. Furthermore, fouling by prefiltered NOM was increased when exposed to elevated temperatures or added calcium. This increase was attributed to aggregation and subsequent retention of prefiltered NOM at the membrane surface.

In the present work the rate of fouling was highest for the smaller molecular-sized fraction. The size exclusion chromatogram for the neutral hydrophilic fraction was taken in the presence of the calcium from the raw water (Bolto *et al.*, 1999), so any aggregation would be reflected in the size measurements. In any case, although aggregation of hydrophilic neutral material may proceed through interaction of calcium with polar groups, aggregation of larger charged and hydrophobic material (such as in a commercial humic acid) should be even more favourable in the presence of calcium. This tendency is reflected in the treatability of these fractions by aluminium-based and iron-based coagulants. Small hydrophilic substances are also less likely to precipitate at a membrane surface than large hydrophobic substances, as they have higher solubility limits, and higher rates of transport back into the bulk solution or through the membrane. As the neutral hydrophilic fraction of NOM was essentially colourless direct visual observation of surface deposits was not possible. However an adsorptive fouling mechanism seems most likely, based on the physical and chemical characteristics of this fraction. A better understanding is required of both the properties of small, non-humic neutral hydrophilic substances which are responsible for fouling a microfiltration membrane, and the mechanism by which this fouling occurs.

CONCLUSIONS

Natural organic matter can play a rate-determining role in the fouling of drinking-water microfiltration membranes. The contribution of NOM to fouling depends on the raw water quality, characteristics of the NOM, and the type and level of any pretreatment. Coagulation pretreatment improves NOM removal and reduces membrane fouling compared to microfiltration of the raw water. Residual dissolved NOM is strongly implicated in controlling the rate of fouling after coagulation pretreatment. This residual NOM is composed primarily of small, neutral hydrophilic substances. Measurement of the levels of this class of compounds in a water source, in combination with traditional water quality parameters should improve benefit analysis of combined coagulation–microfiltration processes. Improvements in the rate of fouling may be possible if neutral hydrophilic substances are specifically targeted for removal. Improvements may also result from selection of a membrane material specifically for low rates of fouling by these substances, or preferential fouling by the NOM which is targeted by a coagulant.

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