THE EFFECT OF MEMBRANE CHARACTER AND SOLUTION CHEMISTRY ON
MICROFILTRATION PERFORMANCE


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Abstract

To help understand and predict the role of natural organic matter (NOM) in the fouling of low-pressure membranes, experiments were carried out with an apparatus that incorporates automatic backwashing and long filtration runs. Three hollow fibre membranes of varying character were included in the study, and the filtration of two different surface waters was compared. The hydrophilic membrane had greater flux recovery after backwashing than the hydrophobic membranes, but the efficiency of backwashing decreased at extended filtration times. NOM concentration of these waters (7.9 and 9.1 mg/L) had little effect on the flux of the membranes at extended filtration times, as backwashing of the membrane restored the flux to similar values regardless of the NOM concentration. The solution pH also had little effect at extended filtration times. The backwashing efficiency of the hydrophilic membrane was dramatically different for the two waters, and the presence of colloid NOM alone could not explain these differences. It is proposed that colloidal NOM forms a filter cake on the surface of the membranes and that small molecular weight organics that have an adsorption peak at 220 nm but not 254 nm were responsible for “gluing” the colloids to the membrane surface. Alum coagulation improved membrane performance in all instances, and this was suggested to be because coagulation reduced the concentration of “glue” that holds the organic colloids to the membrane surface.

Keywords: Microfiltration; Membranes; Natural organic matter; Fouling
1. Introduction

The factors influencing membrane fouling by NOM have been comprehensively reviewed (Taniguchi et al., 2003; Zularisam et al., 2006). They include properties of the NOM (composition, size, hydrophobicity, charge), the membrane (hydrophobicity, charge, surface roughness), the solution (pH, ionic strength, hardness ion concentration) and the hydrodynamics of the membrane system (solution flux, surface shear). To this list must be added membrane porosity and pore size.

Membrane polarity has generally been considered the most important attribute when considering the fouling potential of membranes and many studies have shown hydrophilic membranes have significant operational advantages over hydrophobic membranes (Laïné et al., 1989, 2003).

NOM composition has been the subject of much investigation, and the fouling of membranes that arises from NOM has been extremely difficult to predict. The fouling rates do not correlate with basic NOM properties such as DOC or colour, and the apparent fouling rates can vary significantly for two seemingly similar waters. Early experiments with NOM low in hydrophilic components suggested that hydrophobic compounds were the main membrane fouling components (Jucker et al., 1994; Chang et al., 1996; Schäfer et al., 1998; Lin et al., 2001), but later work with surface waters identified the neutral hydrophilic components as contributing most significantly to membrane fouling (Carroll et al., 2000; Amy et al., 2001; Howe et al., 2002; Gray et al., 2003; Kimura et al., 2004; Lee et al., 2004). With better NOM characterisation techniques such as HPSEC-DOC available, the colloidal fraction of NOM was implicated as the main NOM foulant (Lee et al., 2004). This component of NOM is mainly composed of polysaccharide compounds (Croué, 2004). Later work has also suggested that interactions of NOM components is the main determinant of NOM fouling potential (Gray et al., 2004), and analyses of fouling components isolated from membranes suggests that the colloidal polysaccharide component and proteins are the predominant compounds in the gel layer that resides on fouled membrane surfaces (Croué et al., 2003).

The pH level can alter flux because of molecular size changes in the NOM and a variation in the ease of adsorption. At low pH levels acidic groups are less dissociated, so there is less electrostatic repulsion within the molecule and less chain extension in macromolecular species. A smaller, coiled molecule results, both according to the traditional view of humic substances as polyelectrolytes and the alternative explanation of an aggregation of small molecules (Piccolo, 2001). On raising the pH level acidic functionalities like carboxylic and phenolic groups are more
ionised. This causes a de-coiling of the macromolecules, brought about by the disruption of intra-
molecular hydrogen bonds. De-coiling and chain extension of the polyelectrolyte molecule is
enhanced with an increase in the number of charged groups due to greater electrostatic repulsion. In
the aggregation model of NOM behaviour, clusters held together by intermolecular hydrophobic
bonding will be enhanced at higher pH levels, so more aggregation will occur (Piccolo, 2001). The
aggregation/disaggregation of peat humic acid has been studied recently (Avena and Wilkinson,
2002). Size exclusion chromatography revealed that there is a marked decrease in molecular size
for an aquatic humic acid at pH 2 relative to that at pH 4-10, which is not observed with fulvic acid
(Xi et al., 2004). There is a lower rejection at pH 4 relative to neutral pH in UF of a surface water
with a cellulose membrane, the rejection of dissolved organic carbon (DOC) falling to 53 versus
62% (Cho et al., 2000). The flux decline for a polyamide reverse osmosis membrane exposed to
Suwannee River NOM is less at pH 6 to 9 than at pH 3, in line with the substantial adhesive force at
the lowest pH, and the zero adhesion force of the other two, as determined by atomic force
microscopy (Lee and Elimelech, 2006). This is consistent with the less charged form of both the
NOM and the membrane surface, and the stronger binding of the NOM to the membranes. As well
as influencing NOM size and shape, pH changes can affect membrane structure by changing the
charge at the membrane surface and altering the thickness of the electrical double layer (Braghetta et
al., 1997). Low pH conditions reduce the charge of a negatively charged membrane surface,
especially if these sites arise from carboxylic acid groups. The membrane matrix will be more
compressed at lower pH due to less intra-membrane electrostatic repulsion. Water permeability then
decreases (Costa and Pinho, 2005).

The present paper aims to investigate the influence of membrane character, the nature and
concentration of NOM, pH and alum treatment on membrane performance, and comprises a study of
hollow fibre microfiltration (MF) membranes treating two different water sources under varying
solution conditions. The membranes were regularly backwashed throughout the experiments and
the significance of backwashing on the influence of these parameters is discussed.

2. Experimental

Water sources

Water samples were collected from Lake Eppalock, Bendigo, and from the Moorabool River as
stored at Meredith, both locations being in Victoria, in South Eastern Australia. A portion of each
water sample was filtered through a reverse osmosis system with a 5 µm pre-filter to produce concentrated NOM samples. The concentrated NOM samples were used as starting waters for characterising the NOM by fractionation of the organic material with adsorption resins, while the non-concentrated water samples were used for the membrane fouling studies. Analytical data for the two waters are shown in Table 1. Although the Meredith NOM is present in higher concentration, the Bendigo NOM contains more UV absorbing compounds, indicating a higher content of unsaturated functional groups.

**Water characterisation**

The organic material in the water was characterised by fractionating the NOM via a series of organic adsorbent resins and the results are set out in Table 2. The fractionation procedure is as described earlier (Gray *et al.*, 2004), and is based on the work of Leenheer, 1981. Fig. 1 shows the procedure diagrammatically. The strongly hydrophobic acids (SHA) were removed on the DAX 8 resin, the weakly hydrophobic acids (WHA) on the XAD 4 resin, the charged compounds (CHAR), mainly proteins and amino polysaccharides, on the IRA 958 resin and the hydrophilic neutrals (NEUT) were not adsorbed on any of the resins. The Meredith Water had a higher percentage of SHA material and less of the WHA than Bendigo water, while the two waters had similar amounts of the CHAR and NEUT fractions.

High performance size exclusion chromatography (HPSEC) was also used to characterise the waters using two difference HPSEC instruments. One HPSEC instrument detected peaks using a photodiode array (PDA) while the other purpose built HPSEC instrument had a dissolved organic carbon detector and a UV detector in series. Samples (100 µl) for the HPSEC fitted with the PDA were pumped through a 600 mm TSK G3000SW column at 1.0 ml/min using a phosphate buffer (0.1 M KH$_2$PO$_4$ + 0.1 M NaH$_2$PO$_4$). These conditions were chosen as previous work (Allpike *et al.*, 2003) had shown these conditions to give good peak resolution. NOM peak detection was obtained by a GBC LC5000 photodiode array that was capable of detecting absorbance between 200-600 nm. The molecular weights are not shown in Figures 6 and 7 because of difficulties with the instrument software. However, calibration of the column with PSS standards indicated that a MW of 4000 Da corresponded to a retention time of 20 minutes, a MW of 1000 Da to a retention time of 21.5 minutes and MW of 500 Da to a retention time of 22.5 minutes.
High performance size exclusion chromatography with dissolved organic carbon detection (HPSEC-DOC) was performed on a purpose built instrument offering in series detection of both UV and DOC response. Size exclusion chromatography was performed using a TSK G3000SWxl (TOSOH Biosep, 5 um resin) column at 1.0 ml/min using a phosphate buffer (0.1 M KH$_2$PO$_4$ + 0.1 M NaH$_2$PO$_4$). Samples were first filtered through a 0.45 µm nylon filter, and then the ionic strength was adjusted to that of the eluent using a concentrated phosphate buffer. Samples (1000 µL) were injected manually with a Rheodyne 7125 6-port injection valve equipped with a 1000 µL sample loop. These SEC conditions have been shown to give good peak resolution (Allpike et al., 2005, 2006). The UV signal was recorded with a filter photometric detection (FPD) set at 210 nm. DOC was recorded by a novel technique which uses UV-persulfate oxidation to convert organic carbon to CO$_2$ which is subsequently detected by a modified lightpipe detector conventionally used for FTIR spectroscopy (Allpike et al., 2006). Data analysis was performed using HP Chemstation software.

**Alum treatment**

Aluminium sulphate [Al$_2$(SO$_4$)$_3$.18H$_2$O] was supplied by BDH Laboratory. To evaluate the coagulation efficiency, standard jar tests were carried out with the pH maintained at 6 by the sodium hydroxide addition. The appropriate coagulant dose, as determined by the best removal of dissolved organic carbon, was then added and the solution flash mixed for 1 min at 130 rpm. The speed was then reduced to 50 rpm for 15 min, after which the treated water was left to settle for 1 h. All water was filtered through GF-C filter paper (nominal 1.3 µm) before use to remove suspended material that would otherwise settle out in the membrane apparatus.

**Membranes**

A single hollow fibre membrane filtration rig was used to examine the fouling characteristics of each water. The filtration experiments were performed at constant pressure and the water was pumped from the outside to the inside of the hollow fibres. The filtrate was weighed on a balance and liquid backwashing of the membrane was achieved via pressurised water and a series of valves. The backwashing regime consisted of flow reversal for 20 seconds, so that filtered water entered the inside of the hollow fibres and forced out any accumulated foulant to the outside. The outside of the fibre was then flushed by flowing feedwater past the membrane in a cross-flow manner for a further 20 seconds. A data acquisition system was used to control the filtration pressure and backwash sequence as well as record the filtrate mass and ambient air temperature. The membranes used were
three Memcor products, a hydrophobic polypropylene (PP) membrane with a pore size of 0.2 µm, and hydrophobic (PVDF-1) and hydrophilic (PVDF-2) polyvinylidene fluoride membranes with pore sizes of 0.1 µm. These pore sizes were obtained from the membrane supplier. The membrane contact angles were determined with a Cahn Dynamic Contact Angle Analyser. The membrane fibres were 600 mm in length and the clean water fluxes were determined before each test to be in the ranges shown in Table 3, which lists the membrane characteristics.

Method

The membrane fibres were wet with ethanol and flushed with Milli Q water before use. The transmembrane pressure (TMP) of all experiments was held at 0.5 bar and the backwashing regime was a 20 second liquid backwash every 30 minutes at 0.8 bar. All results are expressed as relative flux (membrane flux at 20°C/flux with Milli Q water at 20°C) versus filtrate mass. Experiments were carried out at pH 6 unless otherwise stated.

3. Results and Discussion

Membrane type

For Bendigo water, the initial rate of flux decline was greatest for the PVDF-1 membrane, followed by the PP and the PVDF-2 membrane (see Fig. 2). While the hydrophobic PVDF-1 membrane showed rapid initial fouling, it reached a plateau flux after which the rate of flux decline was dramatically slower although flux decline was still apparent. This fouling behaviour was observed quite often, and we shall refer to the end of the initial fouling phase and the start of the flux plateau as the end of phase 1 fouling. The observed plateaus probably do not represent a flux at which no further fouling occurs, but rather the fouling rate slows to a rate much lower than observed in the initial phase. The hydrophobic nature of the PVDF-1 membrane meant there was little flux recovery upon backwashing and this led to the faster rate of flux decline at short filtration times when compared to its sister membrane of similar pore size (0.1 µm), PVDF-2. The hydrophilic PVDF-2 displayed significant flux recovery upon backwashing and also a slower rate of initial fouling compared with the PVDF-1 membrane. With extended filtration the extent of flux recovery upon backwashing diminished and a steady flux decline was established.
Of the hydrophobic membranes, the PP membrane (0.2 \( \mu \text{m} \)) had a flux decline that was slower than that for the PVDF-1 membrane, both having a small flux recovery upon backwashing. Furthermore, the PP flux appeared to plateau at a value higher than the PVDF-2 membrane, so that while it had significantly faster rate of initial fouling, its performance after extended filtration was similar or superior to the other membranes. This behaviour may be linked to the larger pores of the PP membrane, as this is the most distinctive characteristic of the PP membrane when compared to the other membranes. Alternatively, differences in unmeasured membrane properties such as surface charge and surface roughness may also play a role in the resultant fouling properties.

For Meredith water, the two hydrophobic membranes showed rapid flux decline and little or no flux recovery upon backwashing (see Fig. 3). The hydrophilic membrane, PVDF-2, also displayed rapid initial rates of fouling, but significant flux recovery upon backwashing of this filter was evident. For the PVDF-2 membrane, the extent of flux recovery was significant, as with Bendigo water, but for Meredith it was quite dramatic, and greatly improved the performance of the membrane after extended operation. This is a probably a reflection of the different water qualities, with Meredith containing more of the strongly hydrophobic organic matter which is less polar than that from Bendigo (Table 1), and is hence more readily released from the hydrophilic membrane. The long term backwashing behaviour was not determined in these experiments, although long term operation of UF is known to result in further fouling irrespective of backwash frequency and backwash time (Kim and DiGiano, 2006).

The initial fouling results fit well with previous investigations into membrane fouling, with high molecular weight compounds significant contributors to the overall rate of fouling and hydrophobic adsorption also significant. However, fouling results obtained after extended filtration suggest that the fouling potential of membranes is dynamic in nature, with the initial fouling layer affecting the ability of subsequent layers to form on the membrane surface. The adsorption of NOM on to the membrane surface changes the surface properties of the membrane, and may either increase or decrease the potential for fouling. Interactions between NOM entities will also be important, as these will determine the potential for subsequent fouling layers to form. Interactions between the membrane and NOM layers will affect the effectiveness of membrane backwashing, and hydrophilic membranes generally appear more efficient with respect to enhancing flux recovery upon backwashing.
The HPSEC-DOC data are shown in Fig. 4 and indicate that both waters have very similar DOC responses. The main difference is that the Meredith water had approximately twice the amount of high molecular weight compounds as the Bendigo water. It has previously been suggested that these high molecular weight compounds or colloids are able to foul membranes via pore blocking (Farahbakhsh et al., 2004). Such a mechanism would be consistent with the greater rate of fouling observed with the Meredith water compared to the Bendigo water. The hydrophobic membranes were unable to be effectively backwashed for either water, presumably because the colloids and other NOM in the water could not be removed via backwashing. If only a portion of the small molecular weight NOM is retained by the membrane but all of the colloid material is retained on the membrane surface, then the rate of flux decline will be proportional to the amount of colloid material present. Therefore, we observe faster flux decline for the Meredith water compared to the Bendigo water. However, the effectiveness of backwashing with the PVDF-2 membrane was vastly superior for the Meredith water compared to the Bendigo water, even though it contained more of the colloidal material or the highest molecular weight fraction as seen in HPSEC results (MW approx. 30,000 Da, Fig. 4 and 5). Therefore, the presence of this material alone cannot be sufficient for increasing the fouling rate in a practical sense, as in some circumstances the colloids can be effectively managed via backwashing.

A possible mechanism to describe this phenomenon would involve the colloids effectively blocking pores or forming a filter cake quickly, but instead of direct adherence are glued to the membrane by other NOM compounds. The colloidal materials are predominantly polysaccharides (Croué, 2004) which are anticipated to be hydrophilic and not strongly adhered to the membrane surface. Indeed, these components are generally concentrated in the hydrophilic neutral fraction, a fraction that does not adsorb onto any of the three organic adsorbent resins used in the NOM fractionation process.

While the HPSEC-DOC and UV$_{254}$ spectra look similar for both waters (Fig. 5a and 5b), the HPSEC data collected with the photo diode array shows that the Bendigo water had a peak at 220-230 nm at lower molecular weights than a separate peak at 254 nm, while the Meredith water did not (Fig. 6 and 7). When observed in the contour plot, this additional peak appears as a shoulder on the peak at 22.5 minutes, with no absorbance occurring at 254 nm and hence it was not detected in the HPSEC UV$_{254}$ nm spectra. This shoulder has also been observed previously for algal laden water (Whitfield), which demonstrated extremely rapid membrane fouling and a propensity to form NOM multi-layers (Gray et al., 2004). Peaks in this spectral region may be due to proteins or organic acids (Amy, 2004) and these compounds may be capable of coupling polysaccharide material. This
hypothesis for the fouling of membranes via the interaction of different NOM components does require further validation.

However, Galjaard et al (2005) have also proposed a similar mechanism of UF fouling, where low molecular weight charged organic compounds are the main foulants. They proposed that complexation of low molecular weight organics with cations such as calcium and iron, increases the binding between the organic layer and oppositely charged membranes, and that the low molecular organics could combined with the high molecular weight organics to form a film or gel layer on the membrane. Such a mechanism may explain the behaviour observed for these waters.

**NOM concentration**

The effect of increasing the NOM concentration on the membrane fouling rates is shown in Table 4. The data in Table 4 report the relative flux after 1 L throughput (1 L of water had been filtered) and the end of “phase 1” in the flux decline curve. The end of phase 1 is not a precise measurement, but it does provide information regarding the shape of the flux decline curve. Not all water/membrane combinations reached a plateau within the time frame of the experiments, and there will be no entry in the “throughput for phase 1” for these systems.

The hydrophobic PVDF-1 and PP membranes had similar flux decline curves. There was a rapid decline as the membrane fouled quickly, and then the flux plateaud at a relatively constant flux. The DOC concentration made a difference to the initial rate of fouling, but because the fouling was so rapid, it has little practical consequence. The DOC concentration had little effect on the final flux value. The results for the PP membrane with Bendigo water were a little different, but this is because the initial fouling rates were less rapid and the run times were shorter because of low water availability. Hence, the final plateau flux values were not reached in the course of these experiments.

The results for the hydrophilic PVDF-2 membrane were again similar to those of the hydrophobic membranes, with the initial flux decline being more rapid for higher DOC concentrations. Flux recoveries were also greater for the higher DOC concentrations, but similar after backwashing for all DOC concentrations tested with the Meredith water (see Fig. 8). The average flux values where therefore a function of the extent of flux recovery and the rate of fouling between backwashes. There was a gradual decline in the average flux for each concentration, and the flux for both DOC
concentrations appeared to converge. For the Bendigo water, the rate of flux decline was significantly slower than the other membrane water combinations, but the same general trends appeared although the extent of flux recovery was significantly lower and the end of phase 1 was not observed for all concentrations because the experiments were not run for sufficient time.

The concentration of DOC had little effect on membrane performance in these trials, as backwashing was effective in controlling the extent of fouling. Where rapid fouling of the clean membranes was observed, the significance of DOC concentration appeared to be minor as a plateau flux stabilised the filtration process. Where the initial rate of fouling was slower, the effect of initial DOC concentration appeared to be more significant over the time frame of these experiments, but the same general trend was observed. It is suggested that once the membrane is coated with fouling material, the highest filtration resistance arises from the filter cake. Backwashing of the membrane controls the build up of the filter cake and the plateau flux value is controlled by the porosity of the filter cake.

**Effect of pH**

The membrane results are shown in Table 5, and indicate that variation between pH 5 and 8 had little effect on membrane filtration for either water or any of the membranes. For the Meredith water, all membranes showed a rapid initial fouling stage (phase 1) followed by a plateau in relative flux. While there may have been some minor differences between the initial fouling rates, contrary to expectations, pH had little influence over the ultimate relative flux once it reached the plateau region.

A similar trend was also observed for the Bendigo water, although the slower rates of fouling compared to Meredith Water did extend the initial fouling phase. However, the relative flux values in the plateau region were all within experimental error. For the PVDF-2 membrane, the initial fouling region extended almost the entire length of the tests so there were differences in throughput after 33 hours of filtration, but the relative fluxes at this time were all similar.

The variations in fouling during the initial fouling stage were generally small, and the only possible difference in performance was a faster rate of initial fouling at pH 5 for the hydrophobic membranes (PP, PVDF-1). This effect may be due to lower dissociation of organic acids at this pH, and hence
increased rates of NOM adsorption and fouling occurred. However, the initial fouling rate did not significantly affect the longer term membrane performance.

**Addition of alum**

Prior treatment with alum is known (Bolto *et al.*, 1998) to reduce fouling of membranes, and markedly improves the throughput, as illustrated by the result for Bendigo water and the PP membrane (Fig. 9). A similar effect was observed with the other two membranes, as shown in Table 6. The superiority of the hydrophilic membrane PVDF-2 over the PVDF-1 membrane was apparent, as significantly larger fluxes were maintained after extended operation with alum. The PP membrane, however, had a higher relative flux than the PVDF-2 membrane after 1L and 2L of filtrate had passed the membrane, consistent with the fouling curves with no alum pre-treatment (see Fig. 2). This confirms that for Bendigo water, the PP membranes begin to perform better than the PVDF-2 membranes after extended operation whether alum pre-treatment is practiced or not.

For Meredith water, (Table 7) alum treatment was again shown to greatly reduce the rate of fouling of all membranes by efficient removal of fouling material. The improved membrane performance cannot be ascribed to a mere reduction in total DOC, as the previous results showed that DOC concentration had little effect on the ultimate membrane flux. Addition of alum did significantly reduce the rate of membrane fouling but it also appeared to increase the flux in the plateau region for several of the membranes.

As alum coagulation does not effectively remove the hydrophilic neutral fraction (Bolto *et al.*, 1998), hence also colloids, these are assumed to remain in the water that was fed to the membranes. Therefore, the slower fouling rates were assumed to occur because many of the components of NOM that “glue” the colloids to the surface are removed by coagulation. Similar effects have been observed with polysilicato iron pre-treatment (Tran *et al.*, 2005).

The hydrophilic PVDF-2 membranes had significantly smaller rates of initial fouling following alum coagulation, and the flux recovery upon backwashing was maintained for longer periods when coagulation pre-treatment was practiced. For the hydrophobic PP and PVDF-1 membranes, there were only small rates of flux recovery on backwashing and this was not changed when alum coagulation was practiced, although the rate of fouling was dramatically lower following coagulation. This suggests that the NOM components that remain in solution after alum coagulation
strongly adhere to hydrophobic membranes, but the strength of adhesion is reduced sufficiently for hydrophilic membranes to allow improved backwashing.

4. Conclusions

The fouling and backwashing characteristics of three different low pressure membranes were compared using two different waters. The hydrophobic membrane PVDF-1 membrane displayed rapid initial fouling, but then a steady decline in flux after the initial fouling phase. The hydrophilic PVDF-2 membrane and the PP membrane displayed similar fouling rates before backwashing, but the greater flux recovery upon backwashing for the PVDF-2 membrane resulted in slower long term fouling rates compared to the PP membrane.

The PVDF-2 membrane had dramatically larger flux recoveries after backwashing for the Meredith water compared to the Bendigo water. The difference in the fouling and backwashing characteristics of these two waters could not be ascribed to the presence of colloidal material alone, and the presence of smaller molecular weight material that had an adsorption peak at 220 nm but not at 254 nm (proteins and organic acids) also appeared influential. It was suggested that the colloidal material forms the filter cake and the 220 nm adsorbing material “glues” the colloids to the membrane surface.

The backwashing efficiency of the hydrophilic membrane was greater than the hydrophobic membranes, although the backwashing efficiency decreased with time for all membranes. Backwashing efficiency effectively controlled the steady state flux for hydrophilic membrane filtering the Meredith water and limited the rate of flux decline for the Bendigo water. Backwashing was ineffective for the hydrophobic membranes filtering Meredith water and only minor flux recovery was achieved with the Bendigo water. Backwashing of the membranes was also shown to reduce the influence of NOM concentration on the fouling rate, as the flux values after backwashing were largely independent of NOM concentration. The solution pH also had only a minor effect on the initial fouling rate, and had no measurable effect on the flux after extended filtration.

Alum coagulation prior to filtration significantly increased the efficiency of backwashing for the hydrophilic membrane, but had no discernable effect on the backwashing efficiency of the hydrophobic membranes. Coagulation prior to filtration did reduce the fouling rate in all instances,
and this was ascribed to reducing the concentration of those compounds that “glue” the colloids to the membrane surface.

## Acknowledgements

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## References


Table 1: Properties of the waters utilised, as measured on the original source waters

<table>
<thead>
<tr>
<th>Original Source Water</th>
<th>TOC, mg/L</th>
<th>$\text{UV}_{254}$, cm$^{-1}$</th>
<th>SUVA, L/mg.m</th>
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<tr>
<td>Bendigo</td>
<td>7.9</td>
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<td>Meredith</td>
<td>9.1</td>
<td>0.154</td>
<td>1.69</td>
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Table 2: NOM fractions in Bendigo and Meredith raw waters

<table>
<thead>
<tr>
<th>Water source</th>
<th>% DOC</th>
<th>SHA</th>
<th>WHA</th>
<th>CHAR</th>
<th>NEU</th>
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<td>38.6</td>
<td>26.0</td>
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<td>16.1</td>
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<tr>
<td>Meredith</td>
<td></td>
<td>43.8</td>
<td>21.9</td>
<td>19.2</td>
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</table>
### Table 3: Membrane properties

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Fibre Dimensions</th>
<th>Pore Size, µm</th>
<th>Clean Water Flux, L/h/bar/m²</th>
<th>Contact Angle, degrees</th>
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<td></td>
<td>Outer diam., mm</td>
<td>Inner diam., mm</td>
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Table 4: DOC concentration effect on membrane flux and throughput

<table>
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<tr>
<th>Membrane</th>
<th>DOC, mg/L</th>
<th>Relative Flux after 1 L</th>
<th>Throughput for Phase 1, Throughput mL</th>
<th>DOC, mg/L</th>
<th>Relative Flux after 1 L</th>
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<td>1200</td>
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<td>0.6</td>
<td>5000</td>
<td>4.55</td>
<td>0.4</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>7.70</td>
<td>0.4</td>
<td>3000</td>
<td>9.10</td>
<td>0.3</td>
<td>50</td>
</tr>
</tbody>
</table>

NR = Plateau not reached
NR* = Short run and plateau not reached
Table 5: Performance of different membranes at varying pH

<table>
<thead>
<tr>
<th>Membrane</th>
<th>pH</th>
<th>Bendigo</th>
<th>Meredith</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Relative Flux after 1 L</td>
<td>Relative Flux after 2 L</td>
</tr>
<tr>
<td>PP</td>
<td>5</td>
<td>0.20</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.26</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.26</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.20</td>
<td>0.17</td>
</tr>
<tr>
<td>PVDF-1</td>
<td>5</td>
<td>0.15</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.07</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>PVDF-2</td>
<td>5</td>
<td>0.31</td>
<td>0.38*</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.20</td>
<td>0.23*</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.28</td>
<td>0.38*</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>0.23</td>
<td>0.31*</td>
</tr>
</tbody>
</table>

* phase 1 fouling regime not completed
Table 6: Flux changes caused by adding 30 mg/L of alum to Bendigo water

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Alum</th>
<th>Relative Flux after 1 L throughput</th>
<th>Relative Flux after 2 L throughput</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>N</td>
<td>0.25</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.75</td>
<td>0.64</td>
</tr>
<tr>
<td>PVDF-1</td>
<td>N</td>
<td>0.10</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.46</td>
<td>0.21</td>
</tr>
<tr>
<td>PVDF-2</td>
<td>N</td>
<td>0.20</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.42</td>
<td>0.29</td>
</tr>
</tbody>
</table>
Table 7: Flux changes caused by adding 30 mg/L of alum to Meredith water

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Alum Added</th>
<th>Relative Flux after 1 L throughput</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>N</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.68</td>
</tr>
<tr>
<td>PVDF-1</td>
<td>N</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.13</td>
</tr>
<tr>
<td>PVDF-2</td>
<td>N</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>Y</td>
<td>0.67</td>
</tr>
</tbody>
</table>
Figure 1: NOM fractionation procedure

Raw Water

1 M HCl, pH 2

1 M NaOH, pH 8

Neut
Figure 2: Flux decline and backwashing comparisons for the three membranes – Bendigo water
Figure 3: Flux decline and backwashing comparisons for the three membranes - Meredith
Figure 4: HPSEC-DOC data for Meredith and Bendigo Waters (yellow: Meredith, blue: Bendigo)
Figure 5a: HPSEC-DOC and HPSEC-UV\textsubscript{254} data for Bendigo Water

Figure 5b: HPSEC-DOC and HPSEC-UV\textsubscript{254} data for Meredith Water
Figure 6: HPSEC data for Bendigo concentrate.
Figure 7: HPSEC data for Meredith Water
Figure 8: Flux decline curves for Meredith Water and PVDF-2 membranes for various NOM concentrations.
Figure 9: Effect of alum addition on PP membrane performance with Bendigo water