

Extending membrane longevity by using MIEX as a pre-treatment

M. B. Dixon, J. Y. Morran and M. Drikas

ABSTRACT

The use of membrane technology and in particular microfiltration (MF) is becoming more popular as a water treatment technology. The operational lifetime of MF membranes can be reduced by natural organic matter (NOM) which is a known foulant. The MIEX DOC (Magnetic Ion EXchange for Dissolved Organic Carbon removal) process was developed to remove NOM from raw water sources. It was anticipated that a reduction in NOM resulting from the MIEX DOC process would also improve the performance of MF systems. A pilot plant study was undertaken to directly measure the impact of MIEX pre-treatment on MF performance. A long term study with a regular cleaning strategy revealed little benefit in MIEX pre-treatment to improve the lifetime of the MF membrane. However, by applying less frequent cleaning it was immediately apparent that fouling was occurring at a faster rate without MIEX pre-treatment. Further studies showed that irreversible fouling also occurred at a faster rate on the membrane without pre-treatment.

Key words | dissolved organic carbon, microfiltration, MIEX, natural organic matter

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INTRODUCTION

The use of membrane filtration is increasing rapidly within the water industry. MF membranes are very effective for the removal of turbidity and bacteria from raw water supplies but the fouling of such membranes is a limiting factor to their effectiveness and longevity. NOM has been identified as a major fouling agent and can reduce the lifetime of membranes (Schäfer *et al.* 2000; Drikas *et al.* 2003; Lee *et al.* 2004). However, the complex nature of NOM has made the interpretation of fouling mechanisms difficult.

Research to date on the fouling mechanisms of MF by NOM has shown that raw waters with a high hydrophilic fraction of NOM resulted in significant flux decline. Large molecules of a relatively hydrophilic character such as polysaccharides were effectively removed by MF membranes, suggesting that these compounds and/or colloidal organic matter in the hydrophilic NOM fraction may be a foulant of MF membranes (Lee *et al.* 2004).

Further research has shown that reversible fouling, caused by highly aromatic hydrophobic acids that make up the majority of typical natural water NOM, cause significant flux decline (Fan *et al.* 2002). However, irreversible fouling is caused by only a small portion of the total NOM including high molecular weight (MW) polysaccharides, colloidal material, low MW proteins and amino sugars (Fan *et al.* 2001; Her *et al.* 2004; Kimura *et al.* 2005; Kwon *et al.* 2005; Fabris *et al.* 2007). The mitigation of such NOM for the reduction of both reversible and irreversible fouling of MF membranes is a priority for scientific research.

One method of NOM removal is the patented MIEX DOC (Magnetic Ion EXchange for Dissolved Organic Carbon removal) process developed by Orica Watercare and SA Water as a means of removing NOM through continuous ion exchange processes (Morran *et al.* 1996). It has successfully operated at the Mt Pleasant Water Treatment Plant (WTP) in South Australia since 2001 and is

now being adopted by many water authorities around the world. At the Mt Pleasant WTP MIEX is used as a pre-treatment for MF to treat river water and has produced the desired water quality outcomes. However, the long term impact of MIEX on the MF has not been quantified. This study aimed to investigate whether the lifetime of MF membranes could be extended by the removal of NOM using the MIEX process.

As NOM is one of the major foulants of MF membranes, characterisation of the NOM in the two feed waters was carried out to determine the differences in NOM exposed to the membrane. An assessment of the NOM character before and after MIEX treatment was made using several techniques including multi-wavelength high performance size exclusion chromatography (HPSEC). While conventional HPSEC analyses the molecular weight range of NOM at a single wavelength (260 nm) the multi-wavelength HPSEC gives the absorbance for all wavelengths between 200 and 300 nm. While the best single wavelength for NOM characterisation is 260 nm, at times other wavelengths also show specific absorption and this absorption may characterise specific functionalities within the NOM. Multi-wavelength HPSEC assisted in establishing which fraction of NOM was the potential foulant of the membranes.

METHOD

Mt Pleasant WTP

In July 2001 SA Water Corporation commissioned the first plant incorporating MIEX at the 2.5 ML/day Mt Pleasant WTP to serve the towns of Mt Pleasant, Springton and Eden Valley in the northern Adelaide Hills. The raw water source is the River Murray via the Mannum-Adelaide pipeline, a variable water source with a 5 year average turbidity of 55 NTU, and peaks commonly above 200 NTU.

The Mt Pleasant WTP consists of two separate treatment trains; both utilise the MIEX DOC Process as the first treatment process but are followed by two different particulate removal streams—either conventional treatment (comprising coagulation, flocculation, sedimentation, rapid filtration) or MF. Stream 1 at the Mt Pleasant WTP incorporates MIEX followed by conventional treatment. Stream 2 incorporates MIEX followed by MF. The product water from each stream is combined and chlorinated prior to the distribution system. A plant diagram can be seen in Figure 1.

The MF rig was constructed by Veolia Water and is a submerged continuous MF (CMF-S) unit. The unit is comprised of a single submersion tank with 72 PVDF

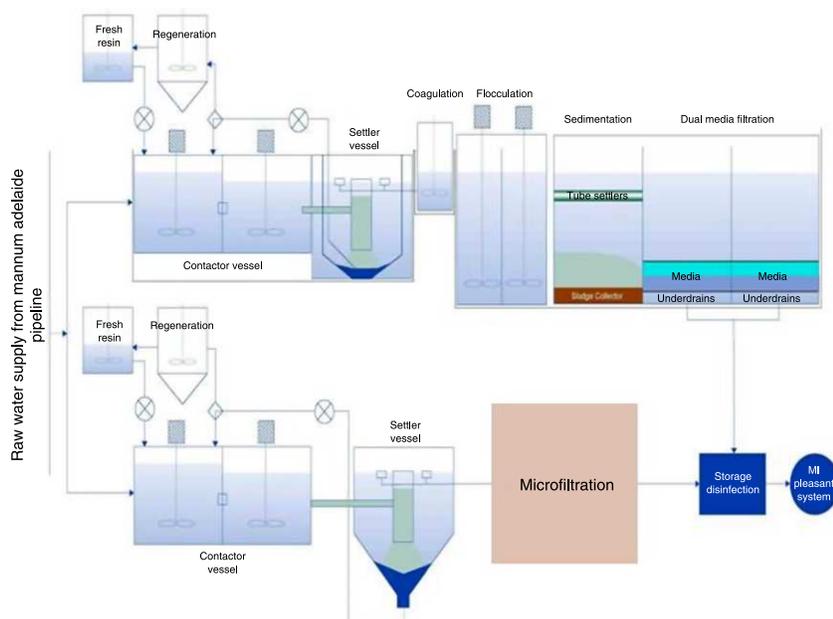


Figure 1 | Mt Pleasant WTP schematic.

modules in two banks of 36. The membrane modules are supplied by Memcor and are the 'S10V' variety. Each module has 14,000 hollow fibre filaments which have a nominal pore size of 0.04 μm . The modules have performed to a consistent turbidity removal to 0.06 NTU. The modules' fresh weight was 6.5 kg and they were capable of withstanding 200 ppm of free chlorine. The membranes were operated on a 45 min backwash cycle until early 2007 when it was concluded that a 45 min backwash was only necessary if the plant was operating at full flow. As the plant seldom operates at full flow, currently membranes are backwashed every 120 min or when transmembrane pressure (TMP) becomes unworkable, whichever ever comes first. Since 2007, a chlorine residual of ~ 2.5 mg/L has been maintained in the membrane and when required an alum dose of 3–5 mg/L is employed in order to remove diatoms. Alum is dosed as $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. The clean in place (CIP) strategy, a strategy for *in situ* membrane cleaning without the need for time consuming removal of membrane modules, was changed in early 2006 at the recommendation of the membrane manufacturer from EDTA/Sulfuric acid and is currently citric acid, which is dosed until the pH reaches 2. The CIP is performed at 40°C.

Pilot scale membranes

In order to directly compare the effects of MIEX-treated water vs. raw water, a pilot plant scale membrane rig was installed onsite at Mt Pleasant WTP. MIEX-treated water for the study was taken from Stream 1 (conventional stream), prior to any coagulant dosing. This stream was used because the dosing of MIEX and the flow was kept constant. While the feed water to the WTP membrane is from Stream 2, it was not suitable to utilise treated water from this stream as the flow in Stream 2 was varied to meet the demands of the local towns and thus the MIEX dose and NOM removal was not reliably constant.

The pilot plant installed was a single module CMF-S membrane pilot plant provided on lease from Veolia Water (Figure 2). The unit incorporated a suspended S10V membrane module supplied by Memcor which was the same as that used by the Mt Pleasant WTP.



Figure 2 | Membrane Rig provided by Veolia Water.

It was necessary to produce MF treated water from MIEX and raw source waters and so two modules were utilised in a staggered parallel mode. Each membrane was stored in a refrigerator in chlorinated WTP treated water when not in use. During the change over the membranes were rinsed with WTP treated water. Each membrane was operated for one week before changing to the other membrane. Some programmable logic controller modification was required to allow the membrane to run in staggered parallel fashion.

The rig was operated at 1,000 L/h flow rate (39.5 L/h/m² flux rate) and was backwashed by air scour every 45 min. A weekly pressure decay test was performed to detect any broken membrane fibres. A clean in place (CIP) was conducted after 25 days operation of each module which involved a 3 h recycling and soaking cycle at pH 2 with 4 g of EDTA at 40°C.

Fouling of the membranes was determined using the resistance, a value calculated from the trans-membrane pressure (TMP). The TMP is normalised for flow and

temperature (via viscosity) by Equation (1).

$$R = (\text{TMP} \times N \times A \times 10^{-3}) / (\eta \times Q) \quad (1)$$

where

R	Resistance (R units or $\text{m}^{-1} \times 10^{12}$)
TMP	Average Transmembrane Pressure (kiloPascals)
N	Number of S10V Modules filtering
A	Surface area of each submodule (m^2)
η	Viscosity of water at the feed temperature (centipoise)
Q	Average filtration flow rate (L/s)

Instrumental Analysis included DOC, molecular weight distribution by chromatography (HPSEC), rapid fractionation, scanning electron microscopy (SEM) and electron disperse X-ray analysis (EDAX). Samples for DOC were filtered through $0.45 \mu\text{m}$ membranes. DOC was measured using a Sievers 820 Portable TOC analyser (Ionics, USA). HPSEC was analysed using a Waters Alliance 2690 separations module and 996 photodiode array detector (PDA) at 260 nm and at 200–300 nm for multi-wavelength HPSEC (Waters Corporation, USA). Phosphate buffer (0.02 M) with 0.1 M NaCl was flowed through a Shodex KW802.5 packed silica column (Showa Denko, Japan) at 1.0 mL/min. This column provides an effective separation

range from approximately 50 Da to an exclusion limit of 50,000 Da. Apparent molecular weight was derived by calibration with polystyrene sulphonate (PSS) molecular weight standards of 35, 18, 8 and 4.6 kDa. The rapid fractionation technique developed by Chow *et al.* (2004) was also used to determine the character of the organics prior to and at the end of the treatment process.

RESULTS AND DISCUSSION

The long term effect of MIEX pre-treatment on MF

The CMF-S pilot plant was set up in April 2005 and fully operational by August 2005. The pilot plant was set up to trigger backwash after 45 min of operation. A CIP was carried out after every 25 days of operation on each membrane. To simulate WTP operation, the pilot plant was operated for almost two years before any changes to this strategy were proposed.

The water quality of the raw water during the trial averaged 0.121/cm for UV absorbance at 254 nm, 17 Hazen Units (HU) for true colour at 456 nm, $381 \mu\text{S}/\text{cm}$ for conductivity and 30 NTU for turbidity. Turbidity of the raw water and MIEX treated water was practically identical. Raw water dissolved organic carbon (DOC) prior to any treatment varied between 2.8 and 5.8 mg/L

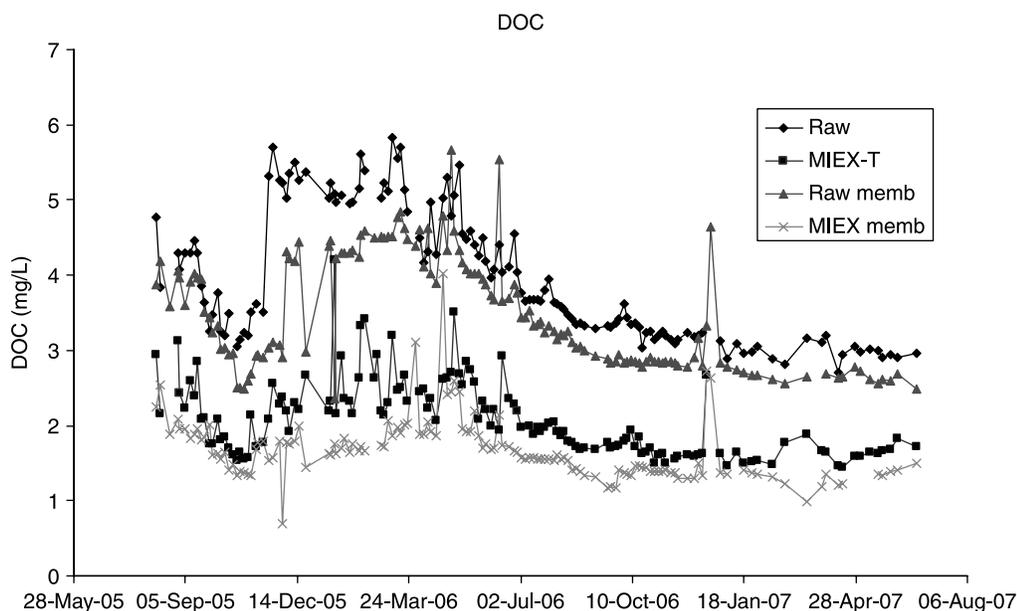


Figure 3 | DOC trend from Aug 2005 to June 2007 at Mt Pleasant WTP.

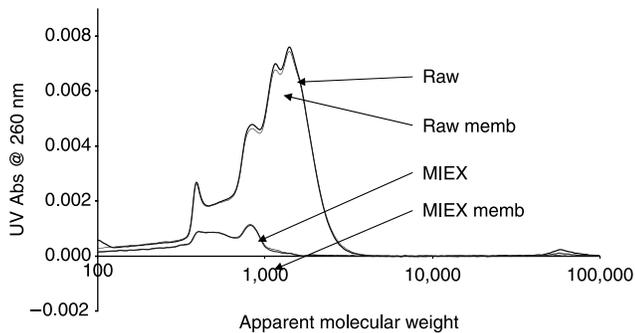


Figure 4 | An example of an HPSEC profile of Membrane treated waters at Mt Pleasant WTP.

(average 4.1 mg/L) between August 2005 and June 2007 as can be seen in Figure 3. The average removal of DOC by MIEX treatment was 46%. A small amount of DOC was removed by each of the membranes. The raw membrane removed 13% of the DOC while the MIEX membrane removed 21% of the DOC. The difference in the character of the organics contained in the raw and MIEX feedwaters is shown in the HPSEC (Figure 4).

During the first two years the resistance varied only slightly between 1 and 2 units (Figure 5). There was no noteworthy difference between the MIEX membrane and raw membrane, when run at 45 min backwash interval and operated in a staggered parallel mode. It was noted however that the weight of the membranes were 6.8 kg for the raw membrane and 6.5 kg for the MIEX membrane, indicating a minor variation in fouling.

The effect of extending backwash interval to 120 min

After observing no clear difference between the membrane fouling after 18 months operation, changes were made to

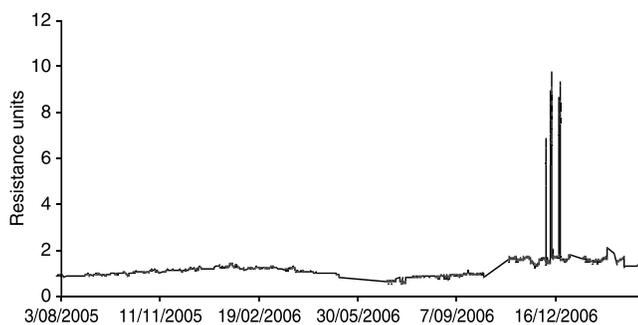


Figure 5 | Combined resistance values of both membranes for the first two years of operation.

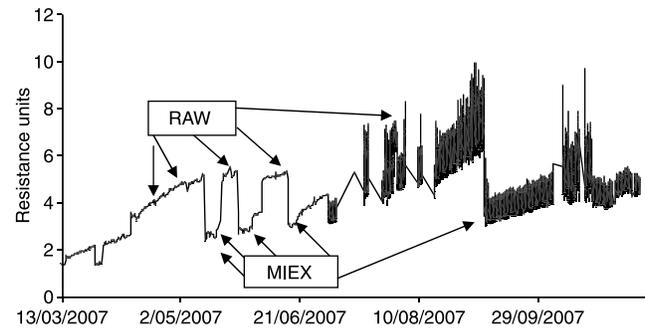


Figure 6 | Resistance values after extending backwash interval to 120 min.

the operation of the membranes to accentuate any differences between the two membranes. The interval between backwashes was originally set at 45 min based on manufacturer's recommendations to minimise fouling and reduce the rate of foulants becoming irreversibly attached to the membrane based on previous experience with similar raw water quality. Decarolis *et al.* (2001) saw a similar effect on operation time by extending backwash intervals. By extending the interval between backwashes, potential fouling on the membranes would be increased, emulating effects that would normally be seen towards end of a membrane's operational life, and differences between membrane performance would be enhanced. When the backwash interval was extended to 120 min, an immediate difference was apparent between the MIEX membrane and the raw membrane. The resistance of the raw membrane increased considerably while the MIEX membrane resistance increased at a slower rate as illustrated in Figure 6. This suggests that the raw membrane fouled more rapidly than the MIEX membrane.

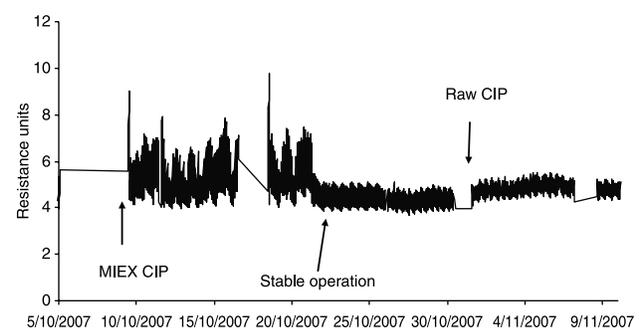


Figure 7 | Resistance values after extended CIP interval.

Calculation of the rate of the resistance increase for the two membranes confirmed that the raw membrane (0.099) was fouling at three times the rate of the MIEX membrane (0.032).

Effect of extending the period between CIP

In order to further challenge the membranes after changing the backwash interval to 120 min, membrane operation was continued beyond the 25 day period when CIP was

required. Operation of each membrane was allowed to extend to 66 days. Persisting without a CIP further enhanced the difference between the membranes. Resistance continued to rise linearly at a steady rate. The rate of fouling for the raw membrane continued to be higher than with the MIEX membrane. That is the raw membrane continued to foul three times faster than the MIEX membrane.

After 66 days without a CIP on both membranes, a normal pH2/EDTA CIP was performed. The resistance of

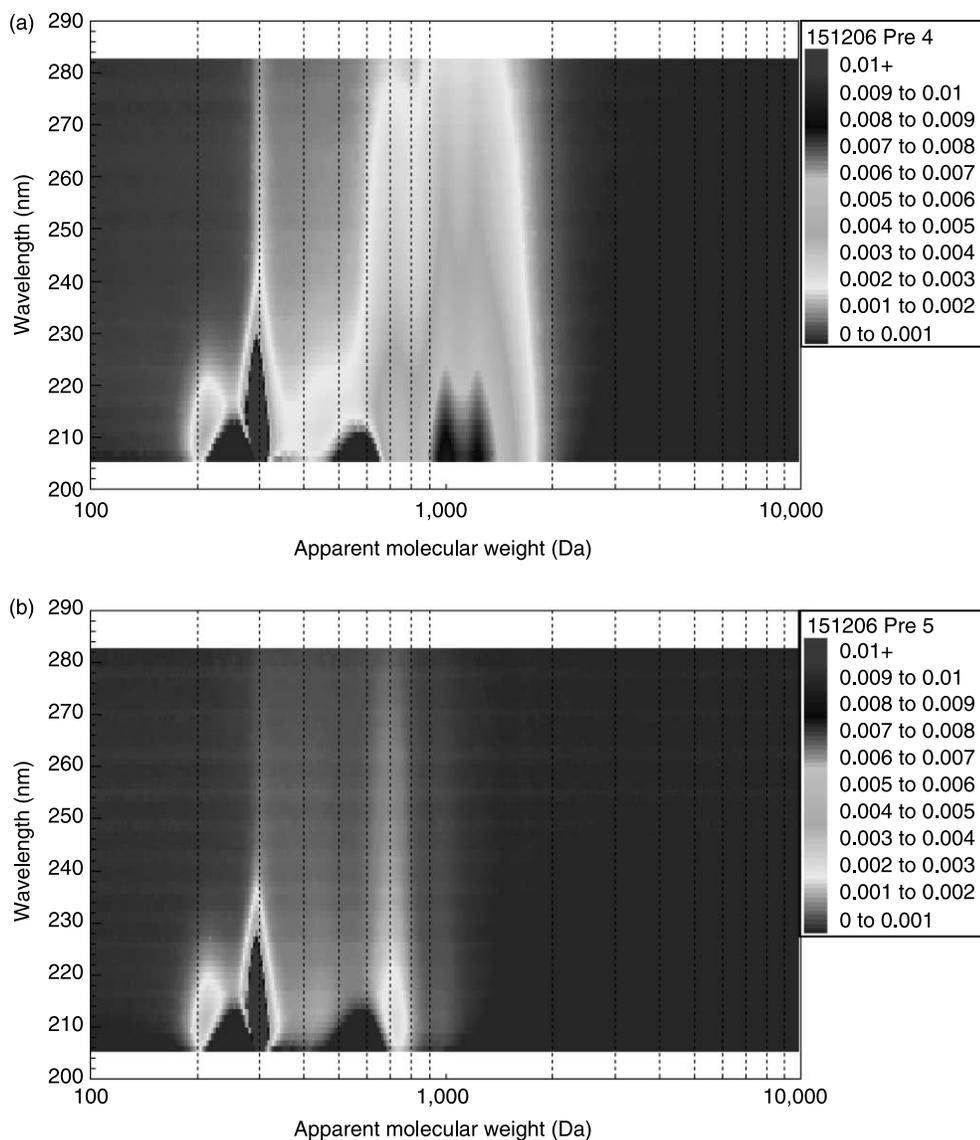


Figure 8 | (a) Multi-wavelength HPSEC data for raw membrane feed water. Colour regions represent absorbance ranges (μcm); (b) Multi-wavelength HPSEC data for MIEX membrane feed water. Colour regions represent absorbance ranges (μcm).

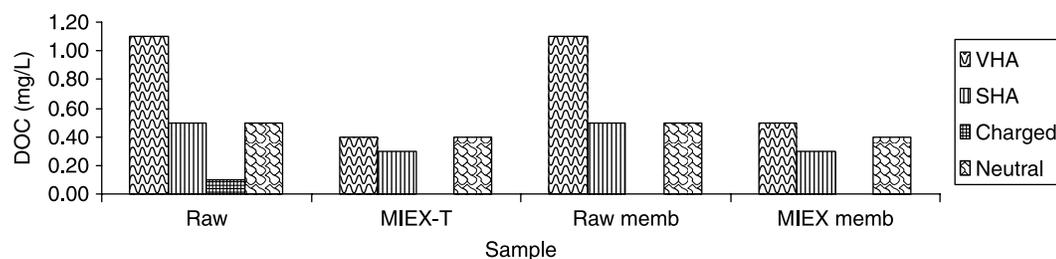


Figure 9 | An example of rapid fractionation of membrane treated waters (very hydrophobic acids (VHA), slightly hydrophobic acids (SHA)).

the MIEX membrane required a week to stabilise after showing poor initial values which were due to operational issues that included the disruption of MIEX fines, which had accumulated over 2 years, in the feed tank to the MIEX MF. Once these issues were rectified, the MIEX membrane was operated for 2 more weeks over which time the resistance improved. The CIP on the raw membrane showed an immediate improvement but the CIP did not bring the resistance down to the same level as for the MIEX membrane. The difference in resistance between the membranes after a period of settling was 0.5 of a resistance unit (Figure 7). The improvement in resistance may be attributed to the organic and inorganic anions that are removed by MIEX (Boyer & Singer 2006). The reduced fouling on the MIEX membrane suggests that whilst NOM may have contributed to fouling the MF irreversibly, this fouling may have been minimised by using MIEX pre-treatment. Previous research has shown that irreversible fouling of MF membranes can be caused by high MW organics (Fan *et al.* 2001; Her *et al.* 2004; Kimura *et al.* 2005; Kwon *et al.* 2005). Figure 4 shows that these high MW organics present in the raw water are removed by MIEX pre-treatment and no longer able to foul the membrane. Time restraints within the project did not allow for continued operation of the membranes to ascertain whether this difference was reproducible after successive CIPs.

Further analysis involving multi-wavelength HPSEC profiling showed that the fraction of NOM that MIEX removes is more evident in the 210 nm to 230 nm range than that usually measured by UV absorbance at 254 nm (Figures 8(a) and (b)). Removal of the portion of NOM at 1,000 Da is most evident using MIEX (at 210 nm). Organic acids and proteins show absorbance at these wavelengths (Gray *et al.* 2007).

Gray *et al.* have suggested that these organic acids and proteins aid DOC in fouling membranes by providing an adhesive surface to the membrane. By removing these, the mechanism for fouling is disrupted and the resistance will therefore not increase as rapidly. This supports the resistance differences seen between the raw membrane and the MIEX membrane as described above.

Rapid fractionation, a technique used to separate NOM into its various charged and hydrophobic constituents, was applied to the raw and MIEX-treated waters. Four fractions are produced in this process, very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), charged hydrophilics (CHA) and neutral hydrophilics (NEU). Rapid fractionation showed that MIEX removed significant amounts of the VHA, SHA and all the CHA within the NOM (Figure 9). Whilst the extent of NOM removed by either of the membranes is not large enough to be detected by this technique, it is likely that the presence of the components removed by MIEX would impact on the fouling of the raw membrane. This further supports the notion that the NOM portion fouling the membranes was organic acids, which make up a portion of the negatively charged NOM.

CONCLUSION

By extending the backwash interval and CIP interval the effect of long term fouling on MF membranes was emulated. An immediate difference was seen between the MIEX membrane and the raw membrane. After several months this showed that fouling occurred more rapidly in the raw membrane than in the MIEX membrane as seen in the resistance data. MIEX pre-treatment can remove NOM, a potential foulant, from feed water and thus extend longevity

of membranes. It appears that a portion of the irreversible fouling is caused by the fraction of NOM that may correspond to organic acids which are removed by MIEX.

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