The effect of NOM characteristics and membrane type on

microfiltration performance

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Abstract

Efforts to understand and predict the role of different organic fractions in the fouling of low-pressure membranes are presented. Preliminary experiments with an experimental apparatus that incorporates automatic backwashing and filtration over several days has shown that microfiltration of the hydrophilic fractions leads to rapid flux decline and the formation of a cake or gel layer, while the hydrophobic fractions show a steady flux decline and no obvious formation of a gel or cake layer. The addition of calcium to the weakly hydrophobic acid (WHA) fraction led to the formation of a gel layer from associations between components of the WHA. The dominant foulants were found to be the neutral and charged hydrophilic compounds, with hydrophobic and small pore size membranes being the most readily fouled. The findings suggest that surface analyses such as FTIR will preferentially identify hydrophilic compounds as the main foulants, as these components form a gel layer on the surface while the hydrophobic compounds adsorb within the membrane pores. Furthermore, coagulation pre-treatment is also likely to reduce fouling by reducing pore constriction rather than the formation of a gel layer, as coagulants remove the hydrophobic compounds to a large extent and very little of the hydrophilic neutral components.

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1. Introduction

Many factors affect membrane fouling by natural organic matter (NOM), including the nature of the NOM (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) (Taniguchi *et al.* 2003). In a study of hollow fibre microfiltration (MF) membranes treating two surface water sources (Gray *et al.* 2007), we have explored varying solution conditions such as NOM concentration, the ionic strength and the pH level, as well as the improvement gained by prior alum treatment, a topic that has been reviewed recently (Farahbakhsh *et al.*. 2004). The current paper is devoted to the influence of various NOM fractions on membrane performance, so that a better understanding of the mechanism of NOM fouling might be obtained.

The use of NOM fractions from Moorabool River, near Anakie in south eastern Australia to test which types of compounds are responsible for MF membrane fouling revealed that for a polypropylene (PP) hollow fibre system, the neutral hydrophilic fraction was the most strongly implicated (Carroll *et al.* 2000). There was a 40% decrease in flux after a throughput that caused only a 20% decrease for the other fractions – the strongly and weakly hydrophobic acids and charged hydrophilic material. The three less-fouling fractions had their DOC reduced by 48, 49 and 64% respectively following alum treatment, while there was no DOC removal for the neutral hydrophilic fraction. Prior treatment with alum significantly reduced the rate of fouling by the raw water (by a 50% decrease versus 82% for the untreated raw water). Alum treatment had only a small influence on the fouling rate despite substantial removal of the charged fractions, the fouling by the neutral hydrophilic fraction being just slightly less than for alum-treated raw water (Carroll *et*

2

51   *al*, 2000). It is likely that the alum treated water still contained the neutral fraction, as Tran *et al*

52   (2006) has shown coagulation to remove the neutral hydrophilic fraction only slightly, while the

53   other fractions were removed to a far greater extent.

54

55   Other experiments on hydrophobic and hydrophilic MF membranes gave fouling potentials by NOM

56   from surface waters as neutral hydrophilic fraction > strongly hydrophobic acids > weakly

57   hydrophobic acids > charged hydrophilic fraction (Fan *et al.* 2001). The fouling rate for the

58   hydrophobic membrane was considerably greater than for the hydrophilic membrane. In the

59   fractionation process it was found that calcium became concentrated in the neutral fraction,

60   suggesting that organic/Ca^{++} complexes were formed that could become bound to the negatively

61   charged membranes. Pre-filtration of the neutral hydrophilic fraction with a 30 kDa UF membrane

62   significantly reduced fouling rate. Most of the neutral compounds in the neutral hydrophilic fraction

63   were of low MW, showing that it was only the small amount of high MW matter that were the

64   strongest fouling components.

65

66   A small component of the total NOM was also found to be responsible for the major fouling of MF

67   membranes in another study (Howe and Clarke 2002). NOM in natural water samples was

68   fractionated with UF membranes to obtain various MW fractions. The major fouling effect occurred

69   with compounds larger than 3 nm, which corresponded to only 10-15% of the total NOM.

70   Furthermore, marked differences in the extent of fouling between membranes of similar pore size

71   but different composition were observed, leading to the conclusion that adsorption of NOM was the

72   mechanism that led to MF fouling.

73

74   Aquatic NOM fractions have been passed through a hydrophobic polypropylene MF membrane and

75   the flux decline monitored (Gray *et al.* 2004). The fraction containing all the hydrophobic acids

76   fouled the membrane more than the individual strongly hydrophobic acid and weakly hydrophobic

77 acid fractions, suggesting that association between the latter two entities may be occurring to cause

78 the more severe fouling effect. Such interactions have been proposed for similarly charged

79 polyelectrolyte/fatty acid monolayer systems (Gole *et al.* 2003) and for hydrophobically-modified

80 anionic polyelectrolytes and anionic surfactants (Deo *et al.* 2003). Much more work has been

81 carried out on ultrafiltration (UF) and nanofiltration (NF) systems, some of which is summarised in

82 Table 1.

83

84 In a study encompassing several membrane types, the present paper is aimed at understanding the

85 fouling mechanism of each NOM fraction on membranes of varying composition, and when

86 additional salt is added.

87

88 **2. Experimental**

89

90 *2.1 Water Source*

91 Reverse osmosis with a 5 μm pre-filter was used to concentrate NOM in water

92 from Lake Eppalock, Bendigo, that had TOC 7.9 mg/L, UV_{254} 0.182 cm^{-1} and $SUVA_{254}$ 2.30

93 L/mg.m. Likewise a concentrate NOM was obtained from the Moorabool River at Anakie. The raw

94 water had TOC 9.1 mg/L, UV_{254} 0.154 cm^{-1} and $SUVA_{254}$ 1.69 L/mg.m. The use of RO to

95 concentrate NOM from fresh waters has been recommended because of the very high percentage of

96 NOM recovered and the rapidity of the process (Serkiz and Perdue, 1990). NOM recovery has been

97 estimated in terms of colour removal as 80-100%, and in terms of permanganate oxidation, 50-99%

98 (Ødegaard and Koottatep, 1982). Other workers quote NOM recovery by RO up to 99.7% (Schäfer,

99 2001). One study has shown that RO isolates have a higher MW than the original raw filtered

100 water, leading to the postulation that some condensation reactions may occur during the isolation

101 process (Maurice *et al.,* 2002). However, a detailed study found that properties such as size,

102   polarity, charge density and isoelectric point were preserved with RO isolation, which gave an

103   organics rejection of >99% (Kilduff *et al.*, 2004).

104

105   Two methods, variations of the published procedure (Carroll *et al.* 2000), were used to isolate

106   different components from the NOM. Procedure A is identical to the fraction procedure used before

107   except that it further divides the hydrophilic neutral fraction into two sub-fractions: hydrophobic

108   bases (HB) and residual hydrophilics (Res).

109

110   A portion of the neutral hydrophilic fraction was retained from procedure A so that it could be

111   compared to its sub-fractions. The other four fractions were: a strongly hydrophobic acids (SHA)

112   fraction separated on Supelite DAX-8 at pH 2; a weakly hydrophobic acids (WHA) fraction

113   separated on Amberlite XAD-4 at pH 2; a hydrophilic charged fraction (Char) of anionic material

114   separated on Amberlite IRA-958 at pH 8; and a hydrophilic neutral fraction (Neut) which does not

115   adsorb on any of the above. The hydrophobic bases were removed from the neutral hydrophilic

116   fraction by adsorption on Supelite DAX-8 at pH 8, while the residual hydrophilics were not

117   adsorbed on the Supelite DAX resin. Fractionation procedure B did not use the DAX 8 resin to

118   isolate NOM, and all hydrophobic compounds were removed on the XAD 4 resin as hydrophobic

119   acids (HA) (Gray *et al.* 2004).

120

121   The NOM fractions were removed from the DAX-8 and XAD-4 resins by elution with NaOH for the

122   hydrophobic acids (SHA, WHA and HA) and by elution with HCl for the hydrophobic bases. The

123   Char components were eluted from the Amberlite IRA-958 by acidic NaCl solution. Once eluted,

124   NOM was de-salted by use of ultra-filtration.

125

126   The make up of the NOM is shown in Table 2. Meredith water was much higher in the SHA

127   fraction at the expense of the WHA material; otherwise the compositions were rather similar.

128

129   Evidence from solid state ^{13}C nuclear magnetic resonance spectra (Wong *et al.,* 2002) has previously

130   shown the hydrophobic fractions to be high in aliphatic and aromatic carbon, while the weakly

131   hydrophobic organics have more carbonyl and alkoxy carbon. Hydrophilic fractions show strong

132   alkoxy signals attributable to carbohydrates, while for one water phenolic carbon was present.

133   Generally, the SHA is considered to contain predominantly humic acids, WHA predominantly fulvic

134   acids, Char predominantly fatty acids and carbohydrates and the neutral hydrophilics predominantly

135   carbohydrates and polysaccharides. However, all fractions undoubtedly contain a mixture of the many

136   compound types present in the original water (Owen *et al.,* 1993).

137

138   The relative concentrations of colloidal NOM were characterized by liquid chromatography using an

139   organic carbon detector (LC-DOC) at Curtin University. The Meredith water was shown to have

140   approximately twice as much colloidal NOM as the Bendigo water, although the absolute concentrations

141   could not be determined. It was assumed that this component of NOM reports predominantly to the

142   hydrophilic fraction of NOM as it is composed of polysaccharide based material (Croué, 2004). This is

143   consistent with the previous NMR analysis of NOM (Wong *et al.,* 2002).

144

145   *2.2 Membranes*

146   A single hollow fibre membrane filtration rig was used to examine the fouling characteristics of

147   each NOM fraction, using the previously described procedure (Gray *et al.* 2004). The filtration

148   apparatus allowed the filtration to be performed at a constant pressure of 0.5 bar and the membranes

149   to be backwashed every 30 minutes using a liquid backwash (0.8 bar). The filtration results are

150   presented as a relative flux (membrane flux at 20°C/flux with Milli Q water at 20°C) versus

151   filtration throughput when presented in graphical form, or in tabular form as a relative flux after a

152   given mass of filtrate had passed. The extent of flux recovery upon backwashing could be estimated

153   from the change in relative flux following backwashing (or the width of the line in the relative flux

154   versus filtrate graph).

155

156   The membranes used were three Memcor products, a hydrophobic polypropylene (PP) membrane

157   with a nominal pore size of 0.2 μm and contact angle of 160°, and hydrophobic (PVDF-1; contact

158   angle 115°) and hydrophilic (PVDF-2; contact angle of 61°) polyvinylidene fluoride membranes,

159   which had nominal pore sizes of 0.1 μm respectively. A poly(ether sulphone) membrane from

160   Thames (PES-2) having a nominal pore size of 0.01 μm and a contact angle of 59° was tested also.

161   All filtration experiments were conducted at pH 6, and the DOC concentrations were held constant

162   for each water (ie. Bendigo or Meredith).

163

164   Following the filtration experiments, the microstructures of the PP membrane surfaces were

165   characterised using a Philips XL30 field emission scanning electron microscope (SEM) in both the

166   secondary and back-scattered electrons (BSE) modes operating at 5-15kV. Associated energy-

167   dispersive X-ray spectroscopy (EDS) was also used to obtain chemical information.

168

169   **3.   Results and Discussion**

170

171   *3.1 NOM Fractions*

172   Experiments on MF of the NOM fractions were carried out using the four membranes described

173   above. The effects on flux and throughput were explored. Results for the PP membrane are given

174   in Fig. 1 and 2. It can be seen that the greatest flux decline occurs with the Neut fraction for both

175   Bendigo and Meredith NOM, the next most potent foulants being the Char fraction, followed by the

176   least fouling SHA and WHA fractions. Figures 3 and 4 show SEM photographs of the fresh PP

177   membrane surface and the PP surface following filtration with raw water. Comparison of these two

178   figures shows that filtration of the raw water leads to the formation of a gel layer on the surface.

179

180   The fouling caused by the hydrophobic fractions (SHA and WHA) may be attributed to the

181   adsorption of the hydrophobic acids on the hydrophobic PP membrane. The flux recovery on

182   backwashing is small compared to the Char and Neut fractions (width of lines in Figures 1 and 2)

183   and the SEM photographs following filtration with the WHA fraction has little surface fouling

184   evident (Figure 5). These results are consistent with fouling via pore constriction.

185

186   In comparison, the flux decline curves for the Char and Neut fractions may be attributed to the

187   formation of a cake or gel layer on the membrane surface. There is greater flux recovery upon

188   backwashing for these fractions and the SEM photograph following filtration by the Char fraction

189   (Figure 6) shows the presence of a gel layer.

190

191   Table 3 shows the Bendigo flux results for all membranes after 3 L throughput of the raw water and

192   its various NOM fractions. It is apparent generally that the Neut and HB fractions have the greatest

193   effect on flux, and WHA the least. There was only enough HB material to test on the one membrane

194   and the results were identical to those for the Neut fraction. The formation of the gel layer on the

195   surface of the membrane by the Neut and Char fractions appears to lead to faster flux decline for

196   these waters than pore constriction from the SHA and WHA fractions. The formation of the gel

197   layer on the membrane surface might be regarded as being the result of filtering large particles or

198   organic complexes that are too large to be filtered. While this may be possible, and the presence of

199   large entities in the cake layer will lead to a faster formation of this layer, previous work has also

200   shown that the flux decline of MF and UF membranes does not alter when the permeate is re-filtered

201   through another clean membrane (Makdissy *et al.* 2004). If the cake layer were the result of entities

202   that were too large to pass through the membrane, then these entities should be removed and

203   refiltering the permeate should lead to a lower flux decline. However, the fact that similar flux

204   declines have been observed when the permeate has been re-filtered suggests that the cake layer may

8

205 be formed on the surface by associations between organic compounds. Given the gel layer appeared

206 for the Char and Neut fractions of NOM it is evident that the gel layer is the result of filtering

207 polysaccharide material rather than humic substances.

208

209 Combining the SHA and WHA fractions (1:1; no salt addition) before passing them through the PES-

210 2 membrane resulted in a greater flux decline than either of the two separate fractions, with nearly a

211 halving of the flux at low throughputs. Pore blocking by what seem to be larger species may be

212 occurring. There was little difference in behaviour with the two PVDF membranes. If there is

213 association or clustering of the two hydrophobic fractions, it might be expected to have more

214 influence on the less polar membranes, which is observed to a small extent for the PP membrane, but

215 not for PVDF-1. These results re-enforce the proposition that the hydrophobic compounds do not by

216 themselves lead to the formation of a cake or gel layer except perhaps for the smaller pore size UF

217 membranes.

218

219 The effect of the various Meredith NOM fractions on membrane behaviour is shown in Table 4.

220 With the PP membrane the Char fraction has the greatest effect on flux, and the hydrophobic

221 fractions the least, whereas for the PVDF-2 membrane the Char fraction fouls insignificantly. This

222 is due to the greater flux recovery upon backwashing for the PVDF membrane compared to the PP

223 membrane (see Figure 7 for a typical comparison of flux recoveries between PP and PVDF

224 membranes) when the Char fraction is filtered, and re-enforces the notion that the adhesion between

225 the membrane and the gel layer is critical in determining the rate of flux decline.

226

227 The most severe flux decline for the PP membrane was with the Char and Neut fractions. For the

228 PVDF-2 membrane the Neut fraction was again the worst offender, similar to the raw water. The

229 Char, SHA and WHA fractions are much less fouling, and HA the least.

230

231   The addition of salt to raw Meredith water and its NOM fractions had pronounced effects in some

232   cases, as also shown in Table 4. For the hydrophobic PP membrane there was a dramatic reduction

233   in flux for the WHA compounds, a similar effect but in the reverse direction for the Char fraction, a

234   slight reduction in flux for the HA fraction and a negligible change for the raw water, SHA and Neut

235   fractions. However for the Type B Neut fraction salt enhanced the flux markedly. Interactions that

236   could account for the PP membrane results may involve calcium ion binding the WHA to the

237   membrane. The presence of calcium, here at only 0.05 mM concentration, has been observed at 1

238   mM concentration to decrease the size of soil-derived NOM from 300 nm to ~100 nm, but at higher

239   calcium levels a size increase was observed that was ascribed to chelation between the species,

240   although a concentration of >2 mM was required (Xi *et al.* 2004). In the present work a flux

241   reduction at low calcium levels may result from calcium linking the WHA molecules to the

242   membrane, which is not happening to the same extent with the SHA fraction, a fact that could be

243   ascribed to the much greater content of carboxylic acid groups in the WHA molecules, estimated to

244   be some 2.5 times for a French river NOM (Garnier *et al.*2004). This proposed mechanism is also

245   consistent with the formation of a gel layer with the WHA when the additional salt (NaCl and

246    $CaCl_2$) are added, as is shown in Figure 8. An analogous explanation has been proposed for an

247   NOM surrogate in the form of a carboxylated latex particle, where it been shown that calcium ions

248   greatly enhanced fouling of a thin film composite membrane made from a semi-aromatic piperazine

249   based polyamide (Li and Elimelech 2004). The calcium ions complex to carboxylic acid groups on

250   the solution NOM and the NOM deposited on the membrane, to form bridges between the two

251   surfaces.

252

253   The Char fraction is probably made up of polysaccharide and protein fragments that will contain

254   negative and in the latter case positive sites that can interact electrostatically, providing bonds

255   between molecules. Adding salt will shield the charges and result in disaggregation, giving smaller

256   molecules and a greater flux. Increased ionic strength results in a strong improvement in flux with

257   the Type B Neut fraction. This fraction also contains hydrophobic basic compounds, and adsorption

258   of these compounds on the membrane, possibly initially by hydrophobic bonding of the basic moiety

259   to hydrophobic patches on the membrane surface, will be more pronounced at the higher ionic

260   strengths. The resulting increased hydrophilicity of the membrane as a result of adsorbing these

261   compounds may be responsible for the higher flux. The effect should be more pronounced for the

262   more hydrophobic PP membrane than for PVDF-2, and indeed the former membrane shows the

263   greater flux increase, nearly threefold that for the PP membrane. This sort of surface modification

264   has been achieved by coating membranes with surfactants (Maartens *et al.* 2000). Non-ionic

265   surfactants of the polyethylene oxide type increased the relative fluxes in UF of a natural brown

266   water. Recovery from a flux decline in UF is also documented for distilled water-detergent systems

267   (Bhattacharyya *et al.* 1979), and flux improvements have been obtained for UF of bovine serum

268   albumin through detergent-pretreated regenerated cellulose, polyacrylic and polyamide membranes

269   (Fane *et al.* 1985).

270

271   For the hydrophilic and probably more negatively charged PVDF-2 membrane there appears to be

272   minor changes in the opposite direction to that found for the PP membrane and the WHA fraction,

273   suggesting that a disaggregation mechanism may dominate. But for the Char fraction there is a

274   pronounced effect in the opposite direction, with salt encouraging flux decline.   It could be that the

275   greater negative charge on the membrane is enhancing calcium ion binding of the anionic species to

276   the membrane. As with the PP membrane, the Type B Neut fraction enhances flow because of the

277   increased hydrophilicity of the membrane, as organics adsorption is again strong.

278

279   The different fouling mechanisms between the hydrophobic and hydrophilic compounds may

280   explain why polysaccharides, proteins and carbohydrates are usually found to be the cause of

281   fouling when FTIR is used to identify the composition of surface coatings. The results from this

282   work indicate that hydrophobic compounds foul by blocking the internal pores of the membrane

283   while the hydrophilic compounds form surface layers. As FTIR only analyses the surface coatings,

284   only the hydrophilic compounds will be detected, as the hydrophobic compounds are likely to be

285   adsorbed within the membrane pores. Given the poor rejection of NOM by MF, the gel layers that

286   form on the membrane surface are unlikely to reject hydrophobic compounds, so they would be

287   available for adsorption and fouling within the membrane pores even when once the gel layer has

288   formed.

289

290   Furthermore, coagulation is known to preferentially remove the hydrophobic and charged

291   compounds and to remove very little of the hydrophilic neutral compounds (Tran *et al*, 2006).

292   Therefore, coagulation prior to MF acts to reduce pore blocking from the hydrophobic compounds,

293   but will have little effect on the formation of a gel layer resulting from the filtration of the

294   hydrophilic neutral components.

295

296   **4.   Conclusions**
297

298   Hydrophobic membranes fouled more readily then hydrophilic membranes, as did those of small

299   pore size. The most potent foulants were the neutral and charged hydrophilic compounds, as they

300   formed a gel layer on the membrane surface. The SHA compounds were next, then the WHA

301   compounds, neither of which formed cake or gel layers on the surface. Interactions between

302   hydrophobic components may be occurring in some instances, where the level of strongly

303   hydrophobic compounds is high, while the addition of calcium to the WHA fraction led to the

304   formation of a gel layer through associations between the WHA components.

305

306   The different fouling mechanisms between hydrophobic and hydrophilic compounds suggests that

307   FTIR analysis will always identify the hydrophilic compounds as the main fouling compounds.

308   FTIR analyses the composition of the surface layers, and therefore will determine the composition

309 of the gel layer.   This was shown to be formed by the hydrophilic compounds, while the

310 hydrophobic compounds fouled the membrane by adsorption within the pores.

311

312 The results also suggest that pre-treatment with coagulation will not prevent the formation of a gel

313 layer but will reduce the level of pore constriction by hydrophobic compounds, as coagulation is

314 known to preferentially remove the hydrophobic and charged compounds.

315

316 **Acknowledgements**

319

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Table 1   Summary of UF and NF membrane performance (hollow fibre systems)

Membrane Type	Membrane Polymer	Organics Source	Main Foulant	Membrane Most Affected	Reference
UF, both hydrophobic and hydrophilic	Various	Suwannee River reference samples	Humic acid > fulvic acid	Hydrophobic and less negatively charged	Jucker and Clark 1994
UF, both hydrophobic, hydrophilic	Polyamide, polyethersulphone (PES), cellulosic	Horsetooth Reservoir, Colorado	Neutral hydrophilic compounds	Hydrophobic	Amy and Cho 1999
UF, both hydrophobic, hydrophilic	PVDF	Three Australian waters	High MW neutral hydrophilics	Hydrophobic	Fan *et al.*2001
UF, both hydrophobic, hydrophilic	Polysulphone, regenerated cellulose acetate	Fractionated soil-derived humic acid	$ArCO_2H$ > ArOH	Hydrophobic; PAC of no assistance	Lin *et al..* 2001
UF, hydrophilic	Cellulose acetate	Lake water; soil-derived humic acid	High MW hydrophobic acids	Only hydrophilic tested	Chang and Benjamin 1996; Gu *et al.* 1995
UF disc membranes, hydrophilic	Regenerated cellulose, cellulose diacetate	Suwannee River humic acid; BSA	Humic acid > protein since easier pore entry	Similar performance for all	Jones and O'Melia 2001
UF, both hydrophobic & hydrophilic	Polysulphone, acrylic copolymer, cellulosic	Lake Decatur, Illinois	Not determined	Hydrophobic	Laîné *et al.* 1989
UF and NF membranes, both hydrophobic & hydrophilic	Polyamide, PES, sulphonated PES, polysulphone, cellulose acetate, regenerated cellulose	Various surface supplies in California and Japan	Neutral hydrophilics a major foulant, except for very hydrophobic NOM	Hydrophobic membranes adsorbed more humic acids	Amy *et al.*2001; Kimura *et al.* 2004
NF, of varying hydrophilicity	Thin film composite, cellulose acetate	Suwannee River, and Australian Dam	Humic acid > fulvic acid especially at high $[Ca^{++}]$	Hydrophobic	Schäfer *et al.*1998
NF, hydrophobic	Polysulphone	Fractionated Tar River, N. Carolina	Hydrophobic compounds	Only one tested	Nilson and DiGiano 1996

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407 Table 2

408 Amount of each NOM fraction in Meredith and Bendigo waters

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NOM	% TOC in each Fraction					
Source	SHA	WHA	Char	Neut	Res	HB
Meredith	43.8	21.9	19.2	15.3	15.1	0.2
Bendigo	38.6	26.0	19.3	16.1	15.7	0.4

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411 **Table 3**

412 **The effect of Bendigo NOM fractions on flux, DOC 3.8 mg/L, 3 L throughput**

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Membrane	Relative Flux							
	Raw	**SHA**	**WHA**	**SHA + WHA**	**HA**	**Char**	**Neut**	**HB**
PP	0.3	0.5	0.7	0.5	0.7	0.5	0.3	0.3
	0.3*	0.7*	0.8*	0.6*	-	0.6*	0.5*	0.5*
PVDF-1	-	0.2	0.3	0.3	-	-	-	-
	0.09*	0.2*	0.4*	0.2*	-	0.3*	0.1*	-
PVDF-2	0.3	0.7	0.8	0.8	-	0.8	-	-
	0.6*	0.6*	0.9*	0.9*	-	0.9*	0.2*	-
PES-2	0.1	0.3	0.3	0.2	-	-	-	-
	0.2*	0.4*	0.5*	0.3*	-	0.2*	0.08*	-

414   * At 1 L throughput
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416

417 **Table 4**

418 **The effect of NOM fractions on flux, with and without added salts, DOC 3 mg/l, 1.5 L**

419 **throughput**

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Membrane	Added Salts*	Relative Flux					
		Raw	SHA	WHA	HA	Char	Neut**
PP	N	0.12	0.22	0.32	0.45	0.07	0.07
	Y	0.12	0.21	0.10	0.42	0.31	0.19
PVDF-2	N	0.48	0.75	0.77	0.97	0.74	0.45
	Y	0.72	0.65	0.85	0.94	0.57	0.60

421 * Final concentration 50 mg/L NaCl and 5 mg/L $CaCl_2$
422 ** Type B, containing hydrophobic bases as well
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Fig. 1   Bendigo NOM fractions and PP membrane (p. 19)

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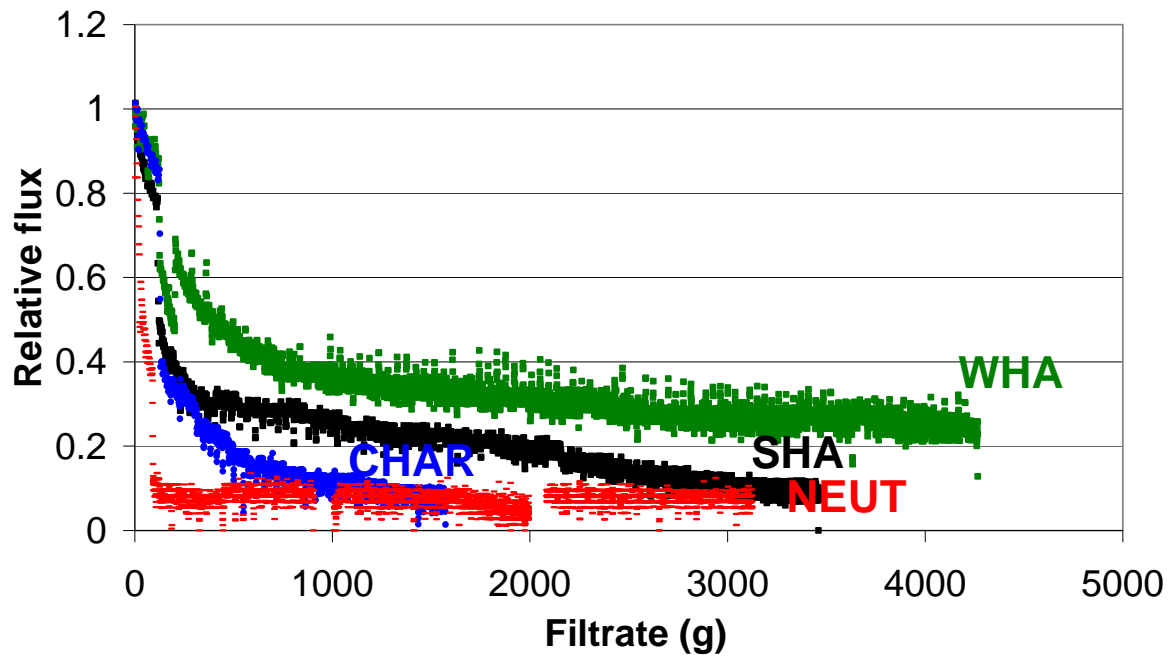
Fig. 2   Meredith NOM fractions and PP membrane.

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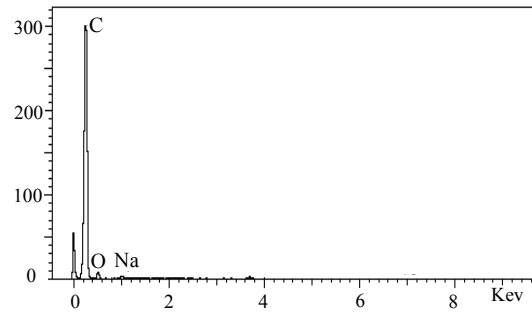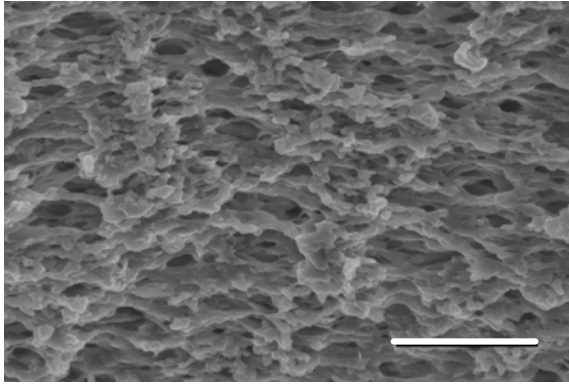
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451 **Figure 3:** SEM micrograph (bar = 5 µm) and EDS spectrum of a fresh PP membrane, showing
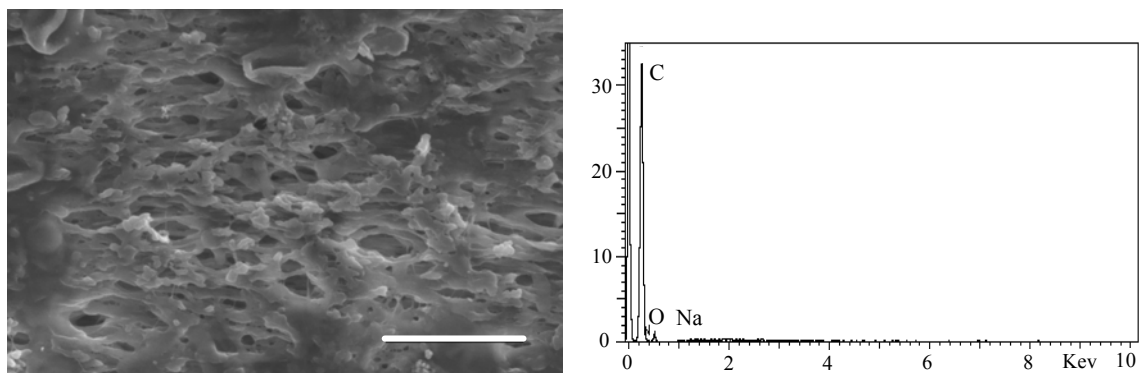452 mostly carbon and some oxygen.

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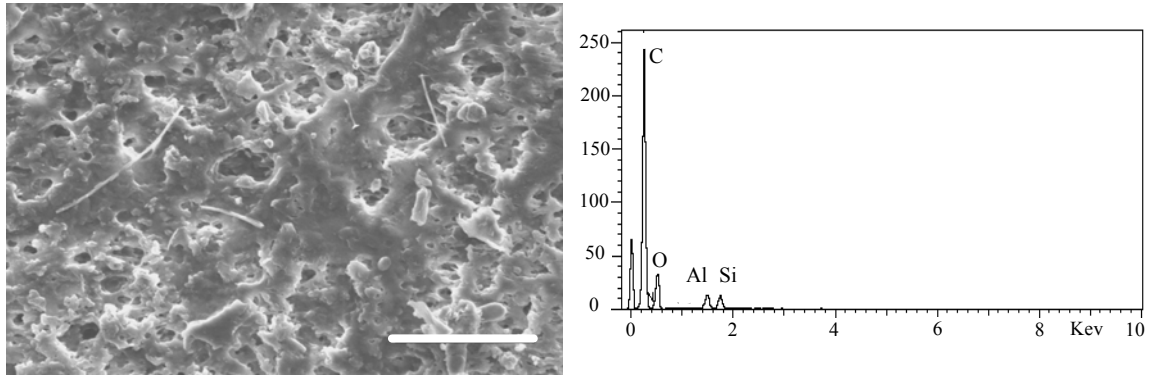
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456 **Figure 4:** SEM micrograph (bar = 10 μm) and EDS spectrum of a PP membrane following filtration
457 of raw Meredith water, showing higher levels of oxygen, aluminium and silicon than those on fresh
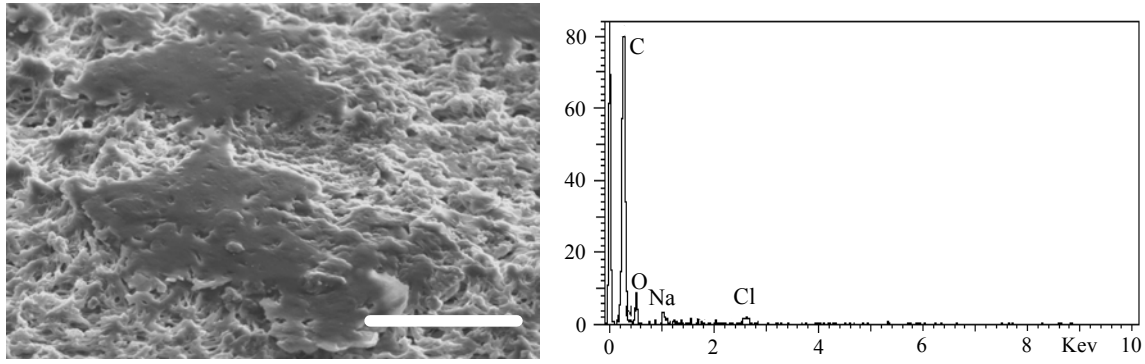458 PP membrane.
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465 **Figure 5:** SEM micrograph (bar = 5 μm) and EDS spectrum of a PP membrane following filtration
466 of the Meredith WHA fraction.
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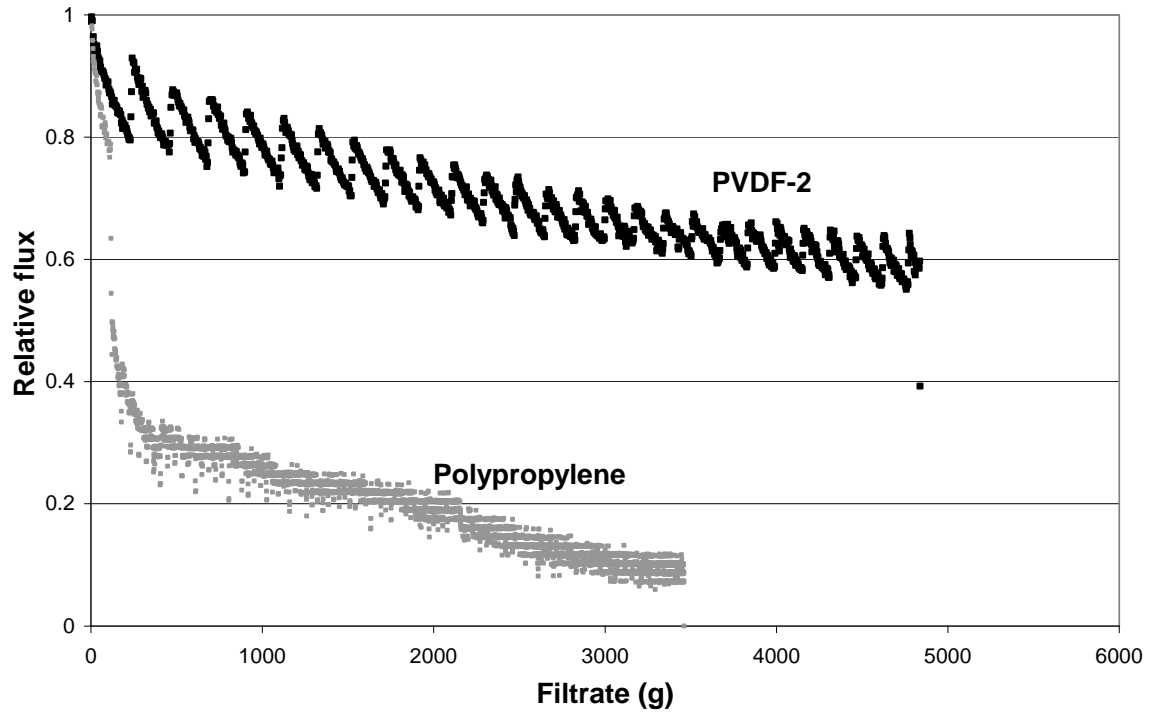

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Figure 6: SEM micrograph (bar = 10 μm) of a PP membrane following filtration of the Meredith
Char fraction showing discrete surface patches and aggregation of small particulate matter.
Corresponding EDS spectrum shows mostly carbon, oxygen, some sodium and chlorine.

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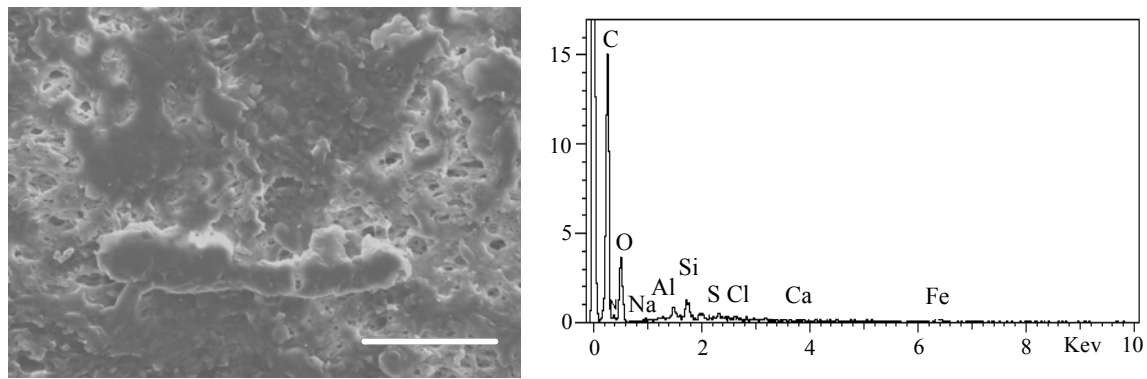
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480 Fig. 7   Meredith NOM SHA fraction filtered through a PP and PVDF-2 membranes. Flux recovery
481   on backwashing is indicated by the width of the lines.
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Figure 8: SEM micrograph (bar = 10 μm) and EDS spectrum of a PP membrane following filtration of the Meredith WHA fraction with salt addition (50mg/L NaCl and 5 mg/L $CaCl_2$). Note that addition of salt to WHA fraction caused 3-fold reduction in flux.

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