Characterisation of organic matter in IX and PACl treated wastewater in relation to the fouling of a hydrophobic polypropylene membrane

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Abstract:

Extensive organic characterisation of a wastewater using liquid chromatography with a photodiode array and fluorescence spectroscopy (Method A), and UV_{254}, organic carbon and organic nitrogen detectors (Method B) was undertaken, as well as with fluorescence excitation emission spectroscopy (EEM). Characterisation was performed on the wastewater before and after ion exchange (IX) treatment and polyaluminium chlorohydrate (PAC) coagulation, and following microfiltration of the wastewater and pre-treated wastewaters. Characterisation by EEM was unable to detect biopolymers within the humic rich wastewaters and was not subsequently used to characterise the MF permeates. IX treatment preferentially removed low molecular weight (MW) organic acids and neutrals, and moderate amounts of biopolymers in contrast to a previous report of no biopolymer removal with IX. PAC preferentially removed moderate MW humic and fulvic acids, and large amounts of biopolymers. PAC preferentially removed proteins from the biopolymer component, with tryptophan-like proteins removed to a lesser extent than tyrosine-like proteins and UV_{210} adsorbing biopolymers. IX showed no preference for the removal of proteins compared to

general biopolymers. An increase in the fluorescence response of tryptophan-like compounds in the biopolymer fraction following IX treatment suggests that low MW neutrals may influence the structure and/or inhibit aggregation of organic compounds. Fouling rates for IX and PAC treated wastewaters had high initial fouling rates that reduced to lower fouling rates with time, while the ETP wastewater displayed a consistent, high rate of fouling. The results for the IX and PAC treated wastewaters were consistent with the long term fouling rate being determined by cake filtration while both pore constriction and cake filtration contributed to the higher initial fouling rates. Higher rejection of biopolymers was observed for PAC and IX waters compared to the untreated ETP water, suggesting increased adhesion of biopolymers to the membrane or cake layer may lead to the higher rejection.

Key words: organic fouling, microfiltration, liquid chromatography, effluent organic matter, ion exchange, polyaluminium chlorohydrate.

1. Introduction

A major drawback of membrane filtration for drinking water treatment and wastewater reuse is fouling caused by natural organic matter (NOM) (*Lee et al., 2004*). Fouling studies carried out using natural waters have reported that neutral hydrophilic components of NOM are more significant foulants (*Carroll et al., 2000*) than hydrophobic components, these being considered to contain biopolymers. Biopolymers contained in the hydrophilic NOM component of surface waters consist of proteins and/or carbohydrate-like substances such as polysaccharides (*Fan et al., 2008, Howe and Clark, 2002*). Similarly, effluent organic matter (EfOM) is accountable for the observed fouling of microfiltration (MF) and ultrafiltration (UF) membranes when treating wastewaters, and the major foulants of wastewaters also

consist of hydrophilic organic matter (*Gray et. al., 2007*) such as organic colloids, polysaccharides and larger proteins (*Shon et al. 2004*). These findings contradicted earlier fouling experiments where NOM low in hydrophilic components resulted in humic substances being the major foulants (*Jucker and Clark, 1994*). This discrepancy in identifying the major organic fouling components of waters arose from the use of non-representative model solutions incapable of mimicking the complexity of natural surface water or wastewater effluent (*Peldszus et. al., 2011*), and in detecting biopolymers using traditional water characterisation techniques.

Further research to understand the effect of NOM composition on MF/UF membrane fouling led to the development of analytical techniques to provide greater understanding of the chemical and physical properties of dissolved organic carbon (DOC) (*Leenheer and Croue, 2003*, *Her et. al; 2003, Lee et.al; 2006).* Characterisation of dissolved NOM from raw waters based on XAD-8/XAD-4 resin adsorption separated DOC components into hydrophobic, transphilic and hydrophilic (HPO/TPI/HPI) fractions, these groupings providing an indication of the polarity of each organic matter fraction (*Amy et. al., 2008*). The hydrophobic fraction of NOM mainly consists of acids and neutrals (*Thurman and Malcom, 1981; Malcom and McCarthy, 1992; Labanowski and Feuillade, 2009)* corresponding to humic and fulvic substances (*Lee et. al; 2006)*. These humic/fulvic-like substances can easily be detected by UV absorption at 254nm (UV_{254}), a commonly used water characterisation technique. Her et. al., (2002) showed that over estimation of humic-substances in NOM and under estimation of non-humic constituents such as proteins and polysaccharides, which are less UV_{254} sensitive, could occur if only UV_{254} detection was practiced.

76 It was suggested that high molecular weight (MW) hydrophilic DOC, consisting of organic
77 colloids, polysaccharide-like and protein-like substances, could be regarded as an indicative
78 factor for fouling potential (*Amy et. al*; *2008*). This led to the development of analytical
79 techniques for better measurement of all components of organic matter, so that techniques to
80 mitigate membrane fouling or optimise performance for water treatment processes could be
81 identified. Her et al. (2003) developed a simplified LC-UV_{254}-fluorescence-OCD (organic
82 carbon detector) technique to detect high molecular weight organic compounds. Three
83 different types of water were used for their study. They consisted of mainly humic-material,
84 algal organic matter and soluble microbial products from a biological treatment process, as
85 examples of three significantly different water types on which to demonstrate its
86 effectiveness.
87
88 Their characterisation of a secondary effluent showed that the high MW structure, believed to
89 be a pure biopolymer peak and mainly classified as 'non-humic', could be effectively
90 identified by the combination of UV_{254}-fluorescence-DOC detection. The two pairs of
91 excitation and emission wavelengths specific to protein-like substances at EX: 278nm-EM:
92 353nm and fulvic-like substances at EX: 337nm-EM: 423nm were used for the fluorescence
93 detector in their study. This technique suggested that identification of problematic, high MW
94 NOM foulants for membrane processes was possible. Similarly, Humbert et. al., (2007)
95 compared the results obtained from two LC systems (LC-UV_{254}-OCD analyses versus LC-
96 UV_{254}-fluorescence) for their resin treated waters. They showed that LC-UV_{254}
97 chromatograms from both techniques gave similar results and that fluorescence detection at
98 EX: 278nm-EM: 310nm gave additional information on high MW DOC originating from
99 microbial origin (mixture of polysaccharides, proteins, and amino sugars). The high MW

DOC was ascribed the major foulant for the regenerated cellulose acetate UF membrane studied.

Liquid chromatography with organic carbon detection (LC-UV_{254}-OCD) is now considered a reliable method for characterising organic matter in water samples since the technique quantifies biopolymers, humic substances and low molecular weight organic fractions (*Huber et. al., 2011*). The organic carbon detector is capable of revealing the presence of all organic compounds, making it reliable for all waters. The fluorescence detector in the system used by Her et.al (2003) is not commonly used, but has been replaced by an organic nitrogen detector (OND).

Fluorescence excitation-emission matrix (EEM) is another technique used for characterising organic compounds in water samples (*Henderson et. al; 2008, Peldszus et. al; 2011, Sharma et. al; 2011*) and which is increasingly used to characterise the membrane fouling potential of waters (*Peiris et. al; 2010a, Peiris et. al; 2010b, Pledszus et. al; 2011, Henderson et. al; 2011*). This technique is able to distinguish humic/fulvic like substances from protein compounds and colloidal/particulate matter (*Peldszus et. al; 2011*). However, Goslan et. al; (2004) suggested that the accuracy of predicting biopolymer concentrations will be low compared to the hydrophobic fractions (humic and fulvic) following testing of synthetic waters that were rich in humic and fulvic fractions and natural waters mainly composed of hydrophobic fractions. The inaccuracies associated with detection of the biopolymers were due to their lower intensity of fluorescence emission compared to humic and fulvic acids. Therefore, the accuracy of the EEM technique may be limited in effectiveness when detection of biopolymers in wastewaters dominated by humic substances is required.

While many researchers have identified high molecular weight biopolymers as key foulants for MF and UF (*Fan et al; 2008, Howe and Clark, 2002*, *Amy et. al*; *2008)* recent work by Kim and Dempsey (2010) proposed that organic acids were the major foulant for polyethersulphone (PES) UF and polyvinylidene fluoride (PVDF) UF membranes. A secondary wastewater that was post treated with alum for phosphorus removal was further treated by various ion exchange resins. The critical fluxes of the PES and PVDF membranes were shown to increase when greater amounts of organic acids were removed. However, their results also showed that the concentration of high MW organic fraction (>100 kDa) was small and that the amount of organic material >100 kDa decreased as the organic acids were removed. Presumably this water was low in biopolymers because alum coagulation was practiced on the feed water and therefore, the role of biopolymers in the fouling of their membranes remains unclear. Such results, which apparently contradict the results of others, highlight the impact that pre-treatment processes may have on membrane fouling.

Indeed, many researchers (*Shon et al; 2004, Guo et al; 2004, Galjaard et al; 2005, Tran et al; 2006*) have sought to understand the effect of NOM composition on MF/UF fouling and the impact of pre-treatments on reducing membrane fouling. Mergen et al; (2008) showed that magnetic ion exchange resin (MIEX™) removed low molecular weight, negatively charged organic matter from water dominated by hydrophilic acids and the extent of removal was water specific, while Humbert et. al; (2007) observed no removal of biopolymers by IX. Allpike et al; (2005) compared the character of DOC removed by two treatment processes- MIEX™ and enhanced coagulation with alum. MIEX™ ion exchange resin was shown to remove the smaller molecular weight, charged organics while enhanced coagulation removed higher molecular weight humic and fulvic acids. MIEX™ pre-treatment combined with

149 conventional alum coagulation not only improved the removal of DOC, but also the range of
150 DOC fractions removed compared to each process in isolation.
151 The complex nature of organic fouling and the potential to achieve extremely low rates of
152 fouling by tailoring water quality for specific membrane materials has been demonstrated in
153 at least two studies. Galjaard et al; (2005) compared the fouling rates of different
154 polyacrylonitrile (PAN) UF membranes following either enhanced alum coagulation or
155 MIEX™ treatment of lake water. They demonstrated no fouling for a positively charged
156 PAN membrane following MIEX™ treatment, and proposed that MIEX™ resin removed all
157 negatively charged organic species while the positively charged PAN membranes repelled
158 any cation bridging of organics to the membrane. Similarly, Tran et al; (2006) showed that
159 polysilicato iron removed only slightly more hydrophobic organic material from surface
160 water than polyaluminium chlorohydrate, but resulted in significantly lower fouling for a
161 hydrophilic PVDF membrane but not for a hydrophobic polypropylene membrane. Both
162 studies demonstrate that the mixture of organic components had a dramatic effect on
163 membrane fouling, and that outcomes were also governed by the membrane properties.
164
165 The significance of interactions between specific organic components and membrane
166 properties has also been highlighted by Gray et al; (2008), who investigated the fouling of
167 different surface waters on membranes of varying composition. A water with minimal low
168 MW UV_{210} adsorbing compounds had substantially greater flux recovery upon backwashing
169 for a hydrophilic PVDF membrane than a hydrophobic membrane. By comparison, a surface
170 water higher in concentration of low MW UV_{210} adsorbing compounds resulted in greater
171 irreversible fouling of the hydrophilic PVDF membrane. It was suggested that the low
172 molecular weight UV_{210} adsorbing compounds assisted in adhering the higher molecular
173 weight biopolymers to the surface of the hydrophilic membrane, and that the biopolymers

could adhere to the hydrophobic membrane in the absence or presence of these compounds. Similar effects have also been reproduced in laboratory tests using protein and alginate solutions (Gray et al; 2011).

Therefore, better understanding of the removal of specific organic species by pre-treatments and their subsequent effect on membrane fouling may enable the selection of membrane types to compliment pre-treatment processes for specific waters, so as to reduce the extent of membrane fouling. The proof of concept for this has been shown by the work of Galjaard et al; (2005) and Tran et al; (2006).

The aim of this investigation was to gain further insights into organic fouling of MF/UF membranes by undertaking greater characterisation of organic compounds in feed waters. Liquid chromatography (LC) with a photodiode array (PDA) and fluorescence detectors in series (Method A), LC with UV_{254} detection, OCD and OND (Method B), and EEM were used to characterise a secondary wastewater effluent. LC Method B provides data on organic carbon and nitrogen concentration as a function of molecular weight, while LC Method A provides complimentary information on the functional groups associated with each molecular weight. EEM provides broad compositional analysis but no information on molecular weights.

The EfOM removal performances of ion exchange resin (IX) and coagulation with Poly Aluminium Chlorohydrate (PAC) from a secondary wastewater effluent were also characterised with these analytical techniques. Membrane fouling studies on single fibres with extended operation and backwashing were conducted to identify the impact of the pre-treatments, and thereby the organic composition of waters on membrane fouling performance

for a hydrophobic membrane. Greater insight into possible organic fouling mechanisms of membranes was sought by undertaking this extensive characterisation of the organic compounds in the feed waters.

2. Materials and methods

2.1. Source water

Water from Melbourne Water's Eastern Treatment Plant (ETP) was used for this investigation. The ETP treats circa 400 MLD of wastewater via extended aeration, and receives wastewater from both domestic and industrial sources. The secondary wastewater effluent was taken from the settler overflow, and had high colour and a relatively high DOC.

2.2. Pre-treatments

Particulate matter was removed from untreated ETP wastewater by vacuum filtration through a 1 μm pore size filter (Whatman GF/C). This water is referred to as ETP water throughout the following discussion.

Two different pre-treatment methods were chosen to assess the removal of organic compounds. MIEX^{TM} is a macroporous anion exchange resin specifically developed for the removal of NOM in drinking water treatment (*Mergen et. al; 2008)*. The secondary wastewater was treated with 5 mL/L of settled MIEX™ by stirring at 180 rpm for 15 minutes with a 60 mm x 20 mm paddle in a 1 L square glass jar. Settled water was decanted and vacuum filtered through a 1 μm pore size filter (Whatman GF/C) to move resin fines. This

224 was repeated 5 times using the same MIEX™ resin, such that the dose of MIEX™ was
225 equivalent to treating 1000 bed volumes (BV) of water (5 L water treated with 5 mL of resin).
226 This is a comparatively low dose of MIEX™ resin, with greater doses commonly used
227 commercially (i.e. 600 BV). This water is referred to as IX water in the following discussion.
228
229 For coagulation treatment with Poly Aluminium Chlorohydrate (PAC), a 10,000 mg/L Al_2O_3
230 (23% w/w) solution was dosed at 70 mg/L, which was equivalent to 27 mg/L Al^{3+}. The
231 wastewater samples were mixed at 185 rpm for 5 minutes with a 60 mm x 20 mm paddle in a
232 1 L square glass jar, followed by 10 minutes of slow mixing at 50 rpm. The mixing was
233 stopped and the solids left to settle for 30 minutes before samples were vacuum filtered
234 through a 1 μm pore size filter (Whatman GF/C). This water is referred to as PAC water
235 throughout the following discussion.
236
237 2.3. Water quality analyses and characterisation
238
239 The quality of wastewater samples before and after pre-treatments were analysed for pH,
240 conductivity, ultraviolet absorbance at 254 nm (UV_{254}), DOC and true colour. DOC was
241 measured using a total organic carbon analyser (TOC-V $_{CPH/CPN}$) (Shimadzu, Japan). Both
242 colour and UV_{254} were measured using a HACH DR 5000 spectrophotometer. True colour
243 was measured using a 5 cm quartz cell at 456 nm and converted to Pt-Co units following
244 calibration against a Platinum/Cobalt standard. UV_{254} was measured through a 1 cm quartz
245 cell. Quantitative measurement of selected ions, namely calcium, sodium, magnesium and
246 potassium, were performed using inductively coupled plasma atomic emission
247 spectrophotometer (ICPE 9000-AES) (Shimadzu, Japan).
248

249

250

251 2.3.1 Fluorescence EEM (EEM)

252

253 EEM spectrophotometry measurements were conducted using a Perkin-Elmer LS-55
254 Fluorescence Spectrometer. The Spectrometer used a xenon excitation source. The scans
255 were performed from 200 to 550 nm at increments of 5 nm, and the total number of
256 scans/sample was 70. For direct comparison of the EEM results for ETP, IX and PAC waters,
257 the samples were diluted by a factor of 2. This ensured all samples were within the organic
258 carbon range required for reliable measurement (<10 mg/L).

259

260 2.3.2 Size exclusion chromatography

261

262 Molecular weight distributions by LC analyses were performed with a PDA and fluorescence
263 detector in series (Method A), and with LC coupled with UV_{254}, OCD and OND (Method B).
264 LC Method A was performed using a TSK gel column (G3000 SW, C-No. SW 3600482) at
265 room temperature with a phosphate buffer (10 mM KH_2PO_4 + 10 mM Na_2HPO_4, 0.04M, pH
266 6.8) as the mobile phase. The column was operated with a flow-rate of 0.5 mL/min and a 50
267 µL injection volume. This was coupled with sequential on-line detectors consisting of a UV-
268 visible photodiode array (λ = 200-800 nm) and a fluorescence detector (RF-10AXL). The
269 response of the on-line fluorescence detector depends on the chosen excitation and emission
270 wavelengths. In this study, fluorescence excitation and emission wavelengths of 278 nm/304
271 nm and 278 nm/343 nm (ex/em) were applied, since such wavelengths were known to be
272 specific for protein-like compounds. When EEM of bovine serum albumin (BSA) solution
273 was performed at a similar ionic strength and pH as ETP water, the peak maxima location

was found at 278-280 nm/340-360 nm (ex/em) (data not shown). Additionally, Salinas et. al; (2011) has shown that tryptophan-like amino acids fluoresce at 270-280 nm/320-350 nm and tryosine-like amino acids fluoresce at 270-280 nm/300-320 nm. Both tryptophan and tyrosine amino acids are commonly contained in proteins. Polystyrene sulphonate (PSS) molecular weight standards of 3420, 4600, 6200, 15,650 and 39,000 Da were used to calibrate the LC column used for Method A. Analysis by Method B (DOC-Labor) was carried out by the University of New South Wales.

2.4. Membrane filtration

A single hollow fibre membrane filtration apparatus was used to examine the fouling rate of the ETP, IX and PAC waters. Single hollow fibre membranes of 600 mm length were folded about the mid-point and inserted into transparent polyurethane tubing. The open ends of the membrane were sealed at one end of the tubing with an epoxy resin such that water entered the outside of the membrane and left from the inner, hollow side of the membrane known as the lumen. The hydrophobic membrane material was polypropylene with a nominal pore size of 0.2 μm, an outer diameter of 0.50 mm and an inner diameter of 0.25 mm. Tran et al; 2006 has previously determined the contact angle of this membrane material with a Cahn Dynamic Contact Angle Analyser, and it was reported to be 160˚. Before the feed solution was introduced into the membrane unit, deionised water was filtered at different set flow rates until a stable pressure was reached for each flow rate. The permeability of the PP membrane with deionised water was calculated before each fouling experiment commenced, with values ranging from 800 to 1000 $Lm^{-2}hr^{-1}.bar^{-1}$.

298 Scanning electron microscopy (SEM) was performed using a Joel Neoscope to observe
299 surface fouling on the membranes. Following membrane filtration tests, the membranes were
300 removed from the filtration apparatus and dried at 30-40 °C. Samples of membranes were
301 taken from the ends (near seal with housing) and middle of the potted fibre, gold coated and
302 mounted on a stub for examination.
303
304 2.4.1 Filtration Method
305
306 The water was pumped from the outside to the inside of the hollow fibre at constant flux (50
307 $L.m^{-2}.h^{-1}$). A low flow positive displacement pump from Fluid Meter Instruments (model no.
308 348745) was used to provide constant flux throughout the experiments. Liquid backwashing
309 was performed periodically via pressurized water and a series of valves. The backwash was
310 set to occur after every 30 min of filtration. The backwashing regime consisted of flow
311 reversal for 40 s at a backwash pressure of 1.4 bar, allowing permeate to flush accumulated
312 foulants from the membrane. The outside of the fibre was then flushed by flowing feedwater
313 past the membrane for a further 40 s. The membrane was then re-wetted using compressed air
314 at 5 bar to pressurize water in the single fibre tubing before filtration recommenced. The
315 pressure was logged continuously by a pressure transducer (± 0.1%, -1 to 9 bar), and the
316 increase of pressure with time was a measure of fouling rate. A data acquisition and control
317 system was used to control the solenoid valves (labelled as 1 to 5 in Fig. 1) for the filtration
318 and backwash sequences, as well as for continuous recording of pressure. The ambient air
319 temperature was also recorded (± (0.2% reading + 1 °C) during all experiments. A schematic
320 diagram of the experimental apparatus is shown in Figure 1.
321
322

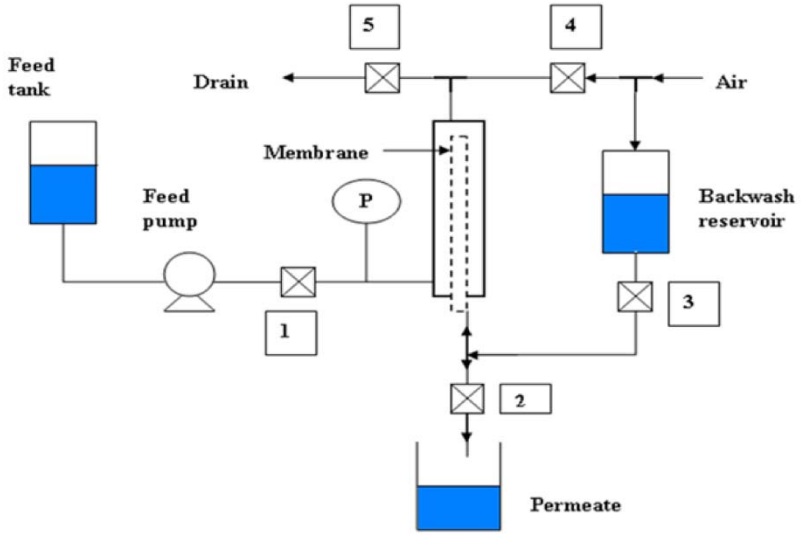


Fig. 1.Schematic diagram of dead-end hollow fibre microfiltration unit (numbers refer to solenoid valves)

2.4.2. Trans-membrane pressure (TMP) measurements and data analysis

Trans-membrane pressure (TMP) was continuously monitored and recorded every 1 s. The raw data from each second was averaged, and the 1min average data recorded throughout the filtration period of 4-5 days. The TMP data was temperature corrected to a reference temperature of 20 °C using the equations (1 and 2) (United States EPA, 2005). Additionally, TMP was also corrected for the effect of the backpressure in the fibre arising from the potting of the membrane by measuring the pressure drop across the potted fibre at the conclusion of the experiment. A typical temperature corrected TMP vs. time profile is shown in Fig. 2a. TMP data from the backwashing period were omitted for the clarity (Fig. 2b) and the last TMP point of each filtration cycle before backwashing was used to represent the TMP vs. time profile (Fig. 2c). Flux was calculated based on the volume of permeate collected during 24 h of filtration time to identify any slight changes of flux with time.

$$TMP_{20} = TMP_T \times \frac{\mu_{20}}{\mu_T} \quad (1)$$

$$\mu_T = 1.784 - (0.0575 \times T) + (0.0011 \times T^2) - (10^{-5} \times T^3) \quad (2)$$

where; TMP_{20} = Transmembrane pressure at 20°C

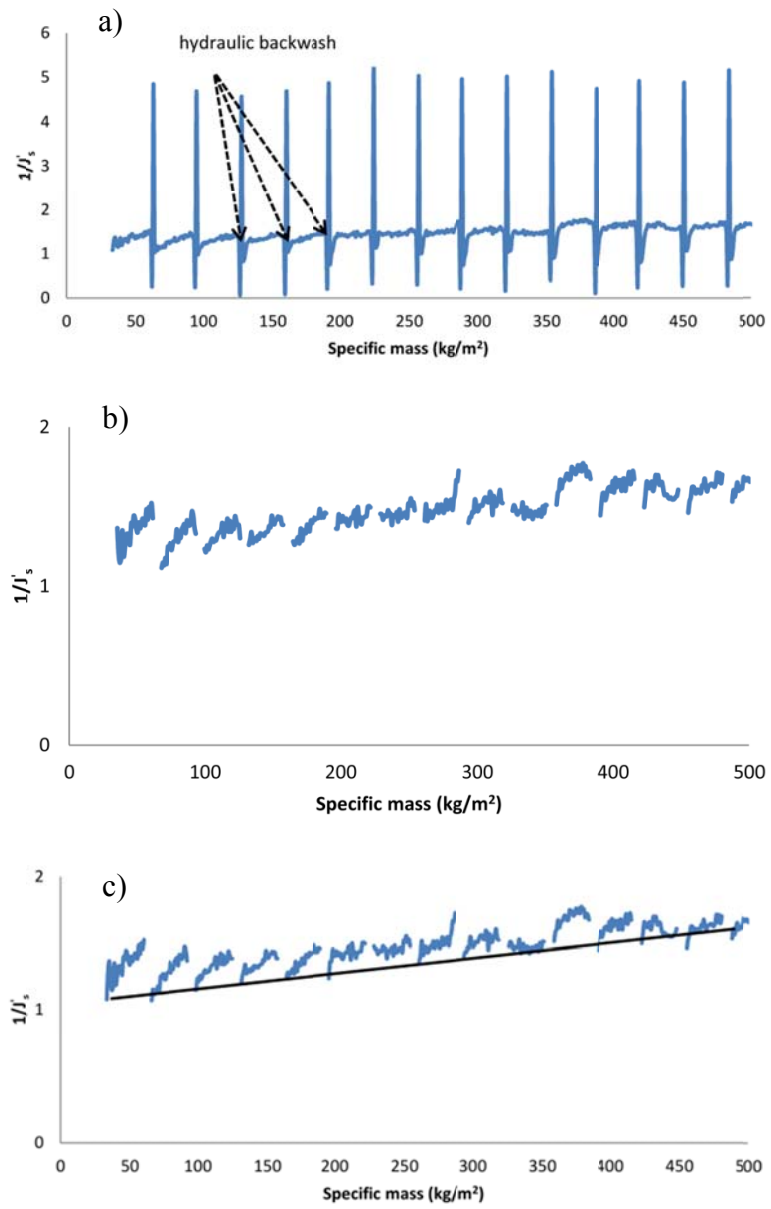
TMP_T = Transmembrane pressure at temperature, T

μ_{20} = Viscosity of water at 20°C

μ_T = Viscosity of water at temperature, T

In analysing fouling of MF/UF systems, flux decline curves are often fitted to models so as to identify whether fouling occurred by pore constriction, pore blockage or cake filtration (*Yuan et al; 2002*). However, for such models to be valid they require a uniform, constant pressure drop across the membrane. For the hollow fibre membranes used in these experiments, the pressure drop inside the lumen of the fibre was similar to that across the membrane resulting in a non-uniform flux along the membrane (*Carroll and Booker, 2000; Carroll 2001*). Additionally, the membranes were operated in constant flux rather than constant pressure mode. Therefore, the mode of fouling cannot be determined from the data without assuming a fouling mode and foulant properties. Therefore, no attempt was made to identify the fouling mode.

359



360

361

362 Fig. 2.TMP vs. time profiles, representing the data processing procedure as described in

363 section 2.4.2 a) ETP water, b) IX water, c) PACl water

364

365 **3. Results and Discussion**

366

367 3.1. Pre-treated water quality

368

369 Table 1 shows the water quality data for the ETP raw and two pre-treated waters. It is

370 evident that both IX and PAC waters were very effective for colour, UV absorbance and

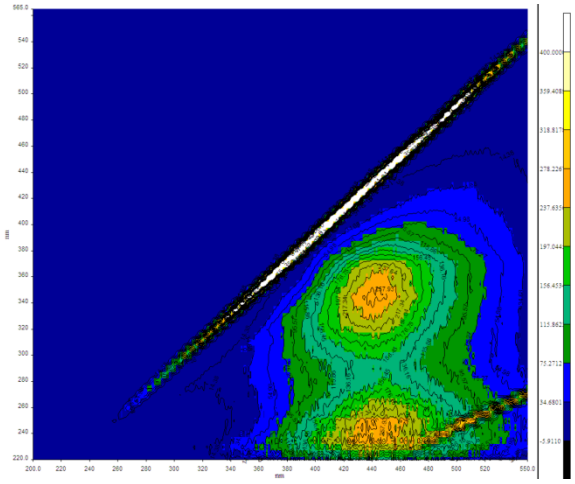
DOC removal. PAC removed slightly more UV_{254} and colour than IX, and slightly less DOC. The increase in sodium concentration for the PAC water was due to the adjustment of pH by 1M sodium hydroxide (NaOH) during coagulation.

Table 1: ETP wastewater solutions before and after the treatments

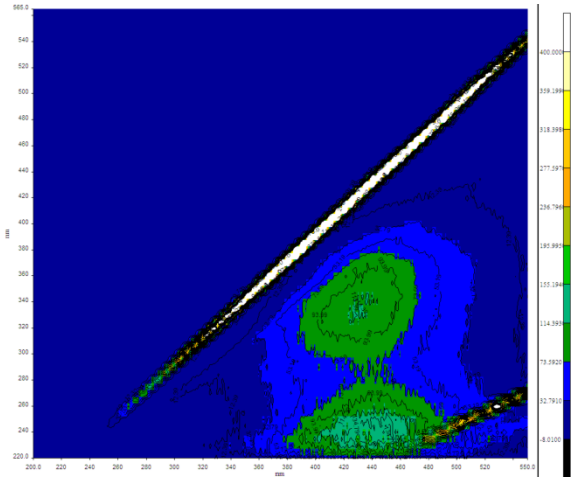
	Raw	IX	PACl
UV_{254} (cm^{-1})	0.363	0.139	0.132
pH	7.68	7.58	7.59
DOC (mg/L)	11.8±0.2	6.8±0.2	7.4±0.2
SUVA (L/m-mg)	3.08	2.05	1.78
Colour (Pt-Co)	82	25	18
Ca (mg/L)	28.9±0.2	27.7±0.2	30.0±0.2
Na (mg/L)	66.3±0.3	66.5±0.3	80.9±0.3
Mg (mg/L)	10.7±0.1	10.5±0.1	11.8±0.1
K (mg/L)	15.6±0.1	15.0±0.1	17.6±0.1

3.2. EEM spectra

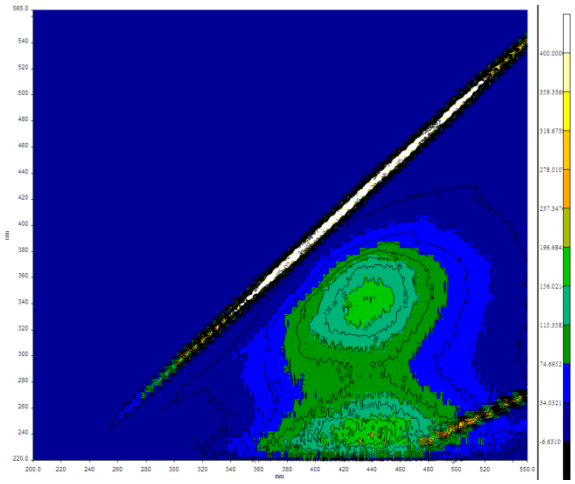
EEM spectra for ETP raw water before and after the treatments are shown in Figs 3a to 3c. The EEM spectra of all the water samples show at least two peak locations (350 nm/447 nm, 240 nm/447 nm ex/em). EEM spectrum for ETP raw water (Fig. 3a) shows responses for only humic and fulvic like substances. Both IX and PAC waters (Fig. 3 b and c) show less intensity at 350 nm/447 nm indicating that humic-like compounds were removed by these treatments. Notably, there were no significant spectra for biopolymers at the shorter excitation and emission wavelengths.



(a) ETP water



(b) IX water



(c) PAC water

Fig. 3. EEM of (a) ETP (b) IX (c) PAC waters

396

397 3.3. Liquid chromatography

398

399 Method B analysis of ETP water estimated the DOC concentration to be 15.1 mg/L (SUVA:
400 3.47L/m-mg), and that of the IX and PAC waters to be 10.8 mg/L (SUVA: 1.54 L/m-mg) and
401 8.1 mg/L (SUVA: 1.93 L/m-mg) respectively, as shown in Table 2. The results show that
402 ETP NOM consisted of 51.8% humic-like substances, 5.8% bio-polymers with the balance
403 composed of "building blocks" (breakdown products of humics), low MW neutrals and low
404 MW acids.

405

406 Both Method B and EEM analyses identified humic-like substances as the major constituents.
407 However, EEM analysis failed to detect the presence of biopolymers at the shorter excitation
408 and emission wavelengths in the region where protein like substances fluoresce (*Salinas et.*
409 *al; 2011*). This result is consistent with the suggestion by Goslan et. al; (2004) that EEM is
410 not sensitive for the detection of biopolymers in humic dominated waters and it is therefore
411 of limited use when characterising humic dominated waters for membrane fouling propensity.

412

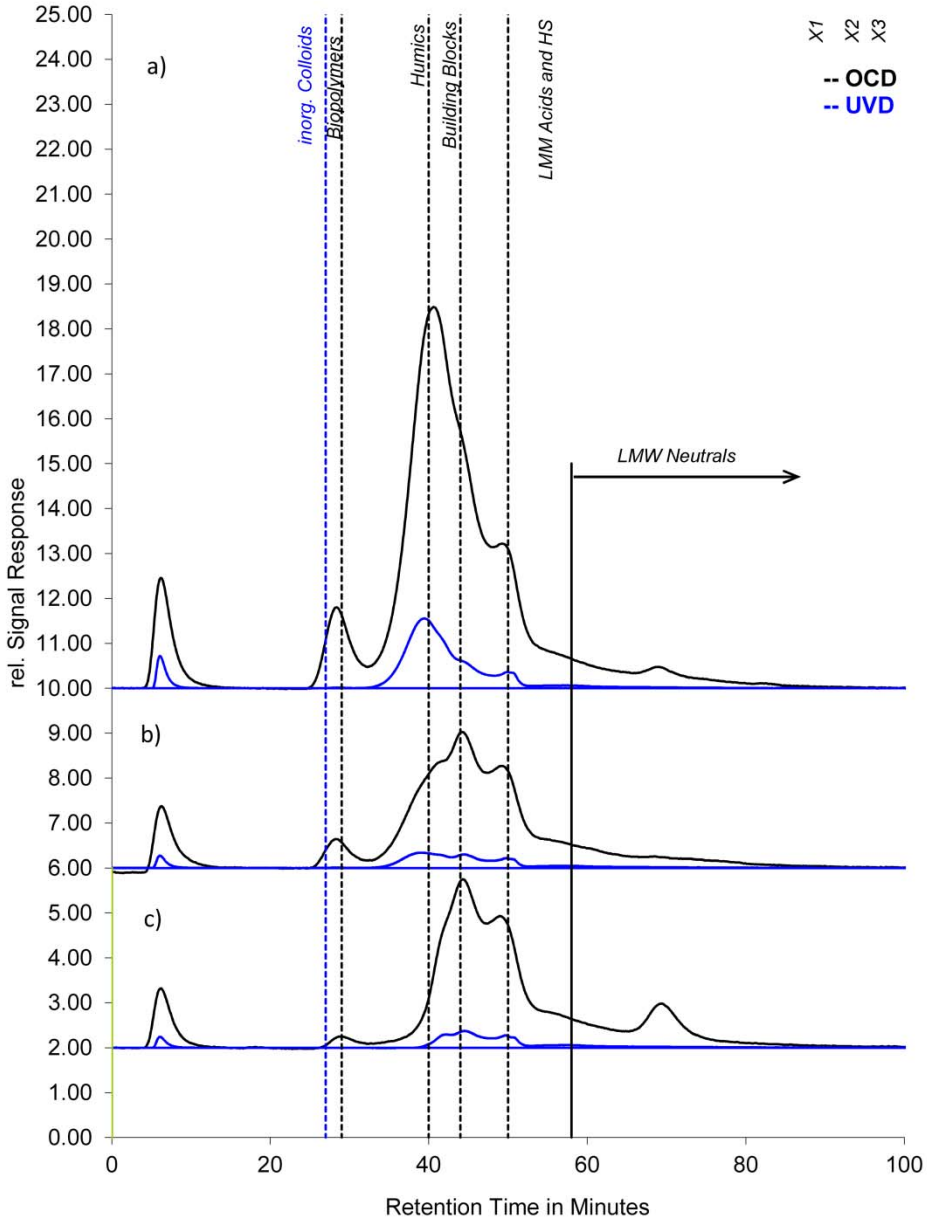
413 Table 2 : LC Method B results for ETP, IX and PAC waters

	Biopolymers	Humic substances	Aromaticity (SUVA – HS)	Building blocks	LMW neutrals	LMW Acids	Inorganic colloids	SUVA
Molecular Weight (Da)	>>20,000	~1,000	~1,000	300-500	<350	<350		
Water	ppb-C	ppb-C	L/(mg*m)	ppb-C	ppb-C	ppb-C	m^{-1}	L/(mg*m)
ETP	874	7844	3.16	1913	1417	n.q.	0.19	3.47
IX	283	2958	3.13	1142	1097	77	0.14	1.54
PACl	206	2908	2.21	1182	1736	n.q.	0.01	1.93

414

415 LC- UV_{254} chromatograms from both Methods A and B gave similar results, and the Method
416 B chromatograms are presented in Fig. 4 for each water. High MW structures or
417 biopolymers, have significant peaks in the DOC chromatograms and smaller peaks in the

418 UV_{254} chromatograms. Similar information was also obtained from the UV_{254} response from
419 the LC-PDA-Fluorescence analysis (Method A: see Fig. 5b). Biopolymers, such as proteins
420 and polysaccharides, cannot usually be detected by UV_{254} absorbance, and the lack of a
421 biopolymer peak at this wavelength is commonly observed. However, for UV_{210} (Method A),
422 there was a peak at circa 50 kDa indicative of the presence of protein-like biopolymer. The
423 chromatograms in Fig. 5a show that the high MW compounds contribute to the UV_{210} signal
424 for the raw and IX waters, but it is absent following PAC coagulation.



425

426 Fig. 4. LC-UV-OCD chromatograms of the a) ETP b) IX and c) PAC waters

UV_{210} absorbance is characteristic of amino groups (*Her et. al; 2004*), suggesting this peak corresponds to protein-like substances. Her et. al; (2007) used the UV absorbance ratio index (URI), in which the ratio of UV_{210} to UV_{254} was measured, to distinguish protein-like substances from other NOM components. They demonstrated that URI values were highest for proteins (13.50 for bovine serum albumin) and lower for other components such as humic and fulvic acids. The URI of the peaks at circa 50 kDa cannot be calculated because of the very low (~0) reading at UV_{254} nm, but these peaks for raw and IX waters were assumed to be protein-like substances.

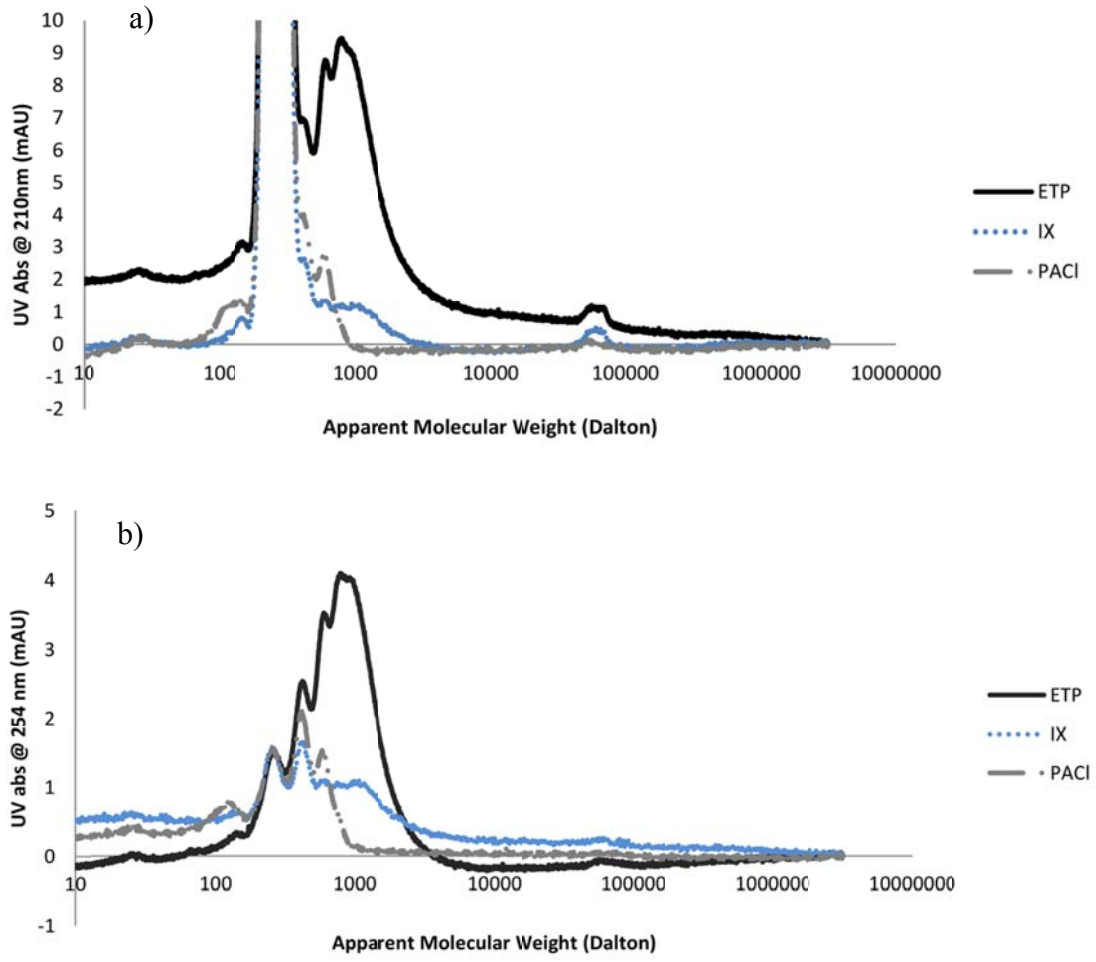
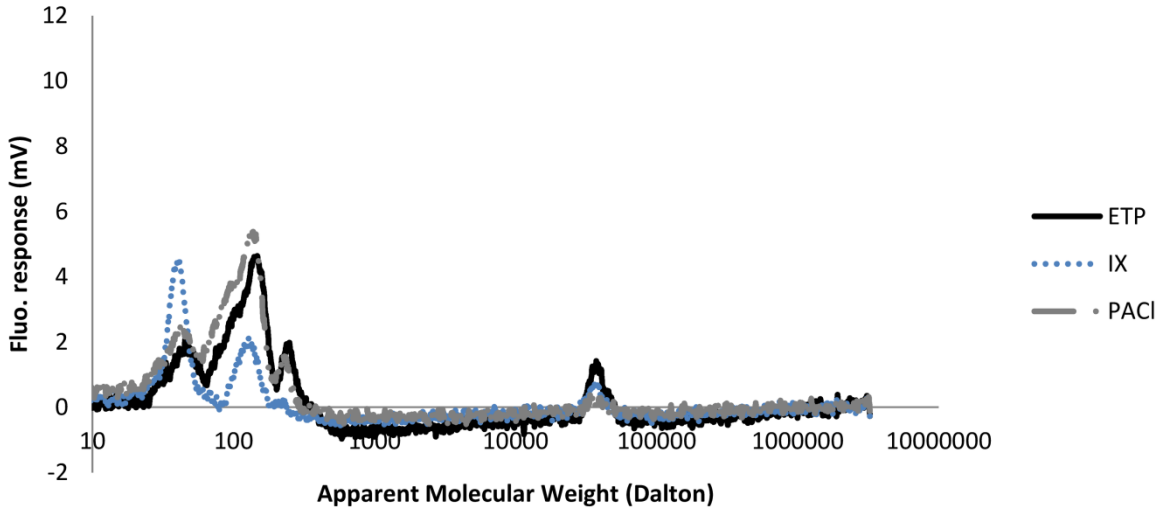


Fig. 5. Chromatograms of UV response at a) 210nm and b) 254nm for ETP, IX and PAC waters (Method A)

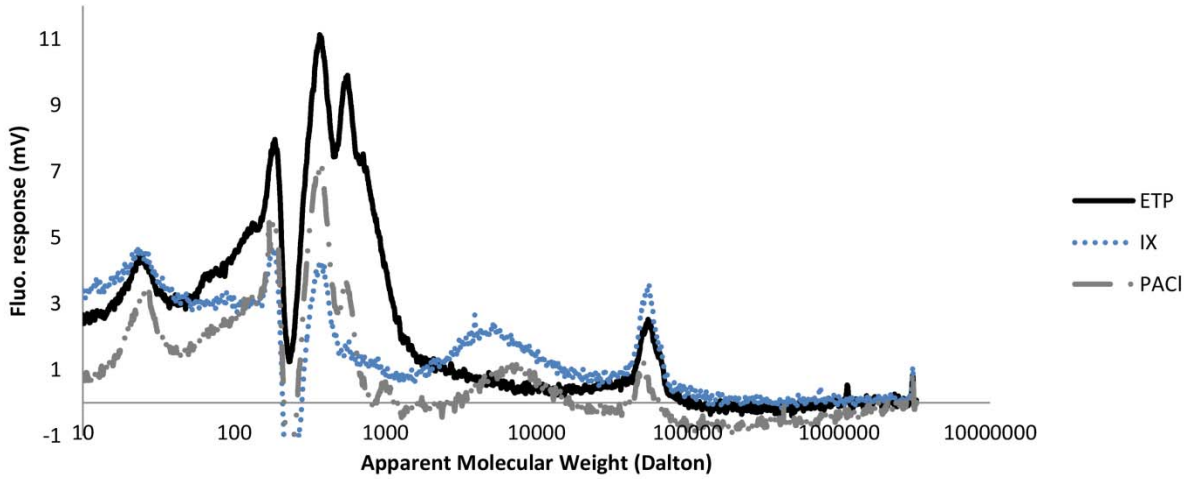
441 The biopolymer peaks were also detected by the fluorescence response at wavelengths of 278
442 nm/304 nm (ex/em) and 278 nm/343 nm (ex/em), and by the organic nitrogen response in
443 Method B. The fluorescence responses of each water are shown in Figs. 6 and 7.
444 Fluorescence peaks were observed at circa 50 kDa for both wavelength pairs indicative of
445 biopolymers.
446
447 Peaks were detected at 278 nm/343 nm ex/em for both IX and PAC waters. After coagulant
448 treatment, there was no peak detected at 278 nm/304 nm (ex/em), while some remained
449 following IX treatment, indicating that a proportion of the protein-like substances could be
450 removed by IX treatment and a greater amount by PAC treatment.
451
452 The removal of tyrosine-like substances at 278 nm/304 nm (ex/em) from ETP water by IX
453 treatment was 39% and by PAC treatment it was 72%. Similarly, the percentage removal of
454 proteins as determined by UV_{210} by the two pre-treatment methods also showed higher
455 removals of proteins by PAC treatment (70%) compared to IX treatment (4%).
456
457 Removal of tryptophan-like substances detected at 278 nm/343 nm (ex/em) was 42% by PAC
458 treatment, while an increase in fluorescence was detected following IX treatment. PAC was
459 more effective at removing tyrosine-like proteins (278 nm/304 nm) than tryptophan-like
460 proteins (278 nm/343 nm). This is not known to have been previously reported and additional
461 analysis of other waters is required to understand if this is a general outcome or a result
462 specific to this particular water.
463
464 LC-OND results (see Table 5) also identified greater removal of protein compounds by PAC
465 compared to IX, with approximately 100% removal achieved by PAC and 73% by IX. The

466 OCD biopolymer results (see Table 5) also identified a similar trend with organic carbon
467 removals of 68% and 76% for IX and PAC treatments. The significantly lower removal of
468 organic carbon compared to organic nitrogen by PAC treatment indicates that this process
469 preferentially removes nitrogen containing compounds such as proteins and amino acids,
470 while for IX treatment such a preference was not observed. Polysaccharides are considered to
471 be the major non-protein constituent of biopolymers, and therefore these results indicate that
472 IX removes these compounds to the same extent as proteins, while for PAC their removal is
473 reduced in comparison to proteins. The results for IX water are significant, as the removal of
474 biopolymers by IX is not generally considered to occur (*Humbert et. al; 2007*) but was
475 observed for this water.
476
477 The tryptophan-like peak (278 nm/343 nm) at circa 50kDa increased in size following IX
478 treatment (see Fig. 7). A similar observation has also been seen on another ETP sample
479 following IX treatment (results not shown), indicating this observation was reproducible. IX
480 treatment does not add organic compounds to the treated water, and therefore an increase in
481 fluorescence response at these higher molecular weights indicates either an increase in
482 sensitivity of the fluorescing compounds due to a change in their chemical environment, or
483 aggregation of low MW fluorescing compounds into larger entities. Tryptophan containing
484 proteins may increase their fluorescence intensity upon binding to carbohydrates such as
485 polysaccharides (Lee, 1997), and the resultant increase in fluorescence response following IX
486 treatment may, therefore, indicate increased association between tryptophan proteins and
487 polysaccharides. Such an increase in the degree of binding between proteins and
488 polysaccharides following removal of small MW acids by IX may occur, as the small MW
489 acids compete with proteins for binding sites on the polysaccharides and proteins. The
490 properties of the resultant aggregate will depend on how the molecules are arranged. For

491 instance, encapsulation of the protein within a polysaccharide coating will leave the
492 aggregate with properties similar to that of polysaccharide, while partial coating may present
493 surfaces with properties similar to both proteins and polysaccharides. Self aggregation of low
494 MW tryptophan-like compounds is also a possibility.
495
496 The proposition of aggregation amongst organic compounds in water is supported by the
497 work of Kim et. al; (2007) who observed re-aggregation of organic matter following
498 filtration. An increase in aggregation tendency of tryptophan-like compounds following the
499 removal of small MW "building blocks" and neutrals (see Table 3) by ion exchange, would
500 suggests that these small MW compounds act to inhibit aggregation. Such a mechanism may
501 arise by low MW neutrals and "building blocks" terminating aggregation by competing for
502 binding sites and thereby reducing the likelihood of further aggregation, or by making weaker
503 interactions between entities (fewer bonding sites). Weaker interactions would increase the
504 aggregates sensitivity to shear rates resulting in smaller aggregates at a given shear rate.



505
506 Fig. 6. Fluorescence spectrum at 278 nm/304 nm (ex/em) specific for tyrosine-like proteins a)
507 Raw, b) IX and c) PAC waters
508
509



510

511 Fig. 7. Fluorescence spectrum at 278 nm/343 nm specific for tryptophan-like substances a)

512 Raw, b) IX and c) PAC waters

513

514 Table 3: Method A (LC-PDA-fluorescence) biopolymer data of ETP, IX and PAC waters

515 (calculated by peak area units at circa 50kDa from Figs. 5a, 6 and 7)

		Protein like substances (Biopolymer fraction)		
		UV_{210}	278/343 (tryptophan-like)	278/304 (tyrosine-like)
ETP		92.0	461.9	337.4
IX		88.3	601.9	204.4
PACl		27.8	266.3	93.6
% removal IX		4%	-30%	39%
% removal PACl		70%	42%	72%

516
517
518 3.4. Pre-treated water quality

519

520 Tables 4 and 5 list the calculated total peak areas at all retention times for wastewater before

521 and after pre-treatments by the different technologies. Results from LC Methods A and B

522 show similar removals of humic substances by IX and PAC treatments. For PAC treated

523 water, the percentage reduction in peak area for Method A UV_{254} was 65-69% and for the

524 Method B it was approximately 60%. For IX treated water, the percentage peak area

reduction with UV_{254} nm (Method A) was ~59-63%, and for Method B it was approximately 60%. Overall, IX removed similar amounts of humic acids, more low MW acids and neutrals and less biopolymers than PAC, and both Methods A and B confirm these trends.

Table 4: Method A (LC-PDA-fluorescence) data for ETP, IX and PAC waters (calculated by peak area units from Fig. 5a, 5b, 6 and 7)

	Method A (LC-PDA-Fluorescence)			
	Humics	Amino acid like substances (all MWs)		
	UV_{254}	UV_{210}	278/343	278/304
ETP	3030.5	56791.4	10857.9	3012.5
IX	892.0	51964.0	1324.7	2029.0
PACl	1002.6	55499.0	9142.7	2690.1
IX % removal	71%	9%	88%	33%
PACl % removal	67%	2%	16%	11%

Table 5: Method B (LC-UVD-OCD-OND) data for ETP, IX and PAC waters (values represented as area units)

	Method B (LC-UVD-OCD)				
	Humics		Biopolymers	LMW Acids	Neutrals
	UV_{254}	OCD	OCD	OCD	OCD
ETP	7.936	64.044	7.499	3.294	12.167
IX	2.844	23.172	2.427	2.882	9.416
PACl	1.863	21.45	1.769	3.508	14.907
IX % removal	64%	64%	68%	13%	23%
PACl % removal	77%	67%	76%	-7%	-23%

It is interesting to observe that the UV_{210} results indicate that little material was removed by either IX or PAC treatment when all retention times are considered. However, there was a

dramatic removal of UV_{210} biopolymers (see Table 3). Additionally, IX removed greater amounts of the tyrosine and tryptophan like-compounds across all MWs (Table 4) than did PAC, but less in the biopolymer fraction (Table 3). Therefore, characterisation of the waters via LC-fluorescence rather than EEM provides greater insight to the composition of the water, as the changes in molecular weight for tryptophan and tyrosine-like compounds can be observed following IX and PAC treatments which EEM is unable to detect.

3.5. Membrane fouling results

3.5.1. Fouling experiments using a polypropylene (PP) membrane

Filtration of ETP and treated wastewaters using polypropylene membranes at a constant flux of 50 L/m^{2}h, the TMP has been found to increase as a function of volume as shown in Fig. 8.

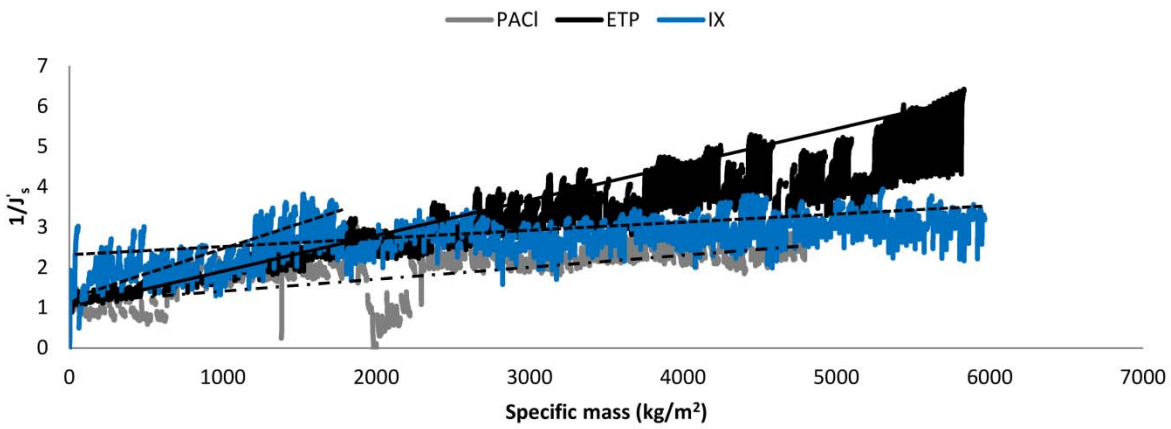


Fig. 8. TMP increase during filtration (approximately 120 h) for Raw, IX and PAC waters

The fouling rates (bar/h) were calculated from the data represented in Fig. 8 and are given in Table 6. It is interesting to note that the highest fouling rate was observed for IX treated water during the first 24 h of filtration (i.e., after 41 backwash cycles). However, at longer filtration times the fouling rate with IX treated water decreased to approximately 15% of its initial

560 value. This change in fouling rate after 400 L/m^2 of water had been filtered (24 hours of
561 filtration) with IX treated water was reproducible, being observed for multiple filtration tests.
562 Similarly, the PAC treated water also had a reduced fouling rate after 24 h of filtration
563 (approx. 20%), although it commenced at a significantly lower initial fouling rate than the IX
564 water. The fouling rate of the ETP water remained constant throughout filtration at a rate
565 higher than either the >24 hour IX or PAC fouling rates. The order of decreasing fouling rates
566 of PP membrane for raw and treated waters was: IX (<400 L/m^2) > ETP > PAC (<400 L/m^2)
567 > IX (>1800 L/m^2) > PAC (>600 L/m^2).
568
569 The change in fouling rate with time for the IX and PAC waters suggests that short term
570 laboratory fouling trials may not be representative of long term fouling trends. This may
571 result from the mode of fouling changing from pore constriction via adsorption of organic
572 compounds to the membrane, to filter cake build up via multilayer foulant layers. Such
573 changes in fouling mode were described by Kim et. al; (2007), and suggest that filter cake
574 build up occurs over long time periods while pore constriction reduces with time. Pore
575 constriction resulting from adsorption of organic compounds on the membrane surface is
576 likely to be a competitive process, as competitive adsorption of organic components in NOM
577 is known to occur for activated carbon (*Newcombe et al; 2002*). IX preferentially removes
578 the lower MW compounds, leaving a greater proportion of higher MW compounds available
579 for adsorption by the membrane. Large MW humics will result in greater pore constriction
580 than smaller MW compounds by virtue of their size, and therefore their increased tendency to
581 protrude from the surface. Additionally, the increase in the high MW tryptophan-like
582 response following IX treatment suggests that there was an increased tendency for either self
583 aggregation or with polysaccharides following IX treatment. Such a tendency would also
584 increase the degree of pore constriction as a result of the larger aggregates.

585

586 Conversely, PAC preferentially removes the high molecular weight humics and therefore
587 contains greater proportional amounts of low MW compounds, leading to reduced pore
588 constriction. The proportion of low MW: high MW organic compounds in ETP water will lie
589 between IX and PAC waters, and the resultant initial fouling rate was between the IX and
590 PAC fouling rates.

591

592 Cake filtration dominates the latter stages of filtration (>24 hours), and high MW
593 biopolymers are the major component of the cake layer. Therefore, greater removal of
594 biopolymers by PAC produces lower fouling rates in this region compared to IX. ETP water
595 has higher concentrations of biopolymers than either IX or PAC waters, and so had the
596 highest fouling rate at long filtration times.

597

598 Table 6: Fouling rate of ETP and treated waters

Fouling index ($m^2/kg \times 10^{-3}$)						
Time (h)	Raw		MIEX™		PACl	
24	1.00	100%	1.25	100%	0.75	100%
48	0.83	83%	0.17	13%	0.17	22%
72	0.83	83%	0.17	13%	0.17	22%
96	0.83	83%	0.17	13%	0.17	22%
120	0.83	83%	0.17	13%		

599 Percent reduction is relative to the initial fouling index of the particular water

Permeate samples were collected and characterised by Method A (278/343 nm) at the completion of each test. Figs. 9 and 10 show the UV_{210} and fluorescence 278/343 nm chromatograms for the filtered permeate. Comparison of these results show that humic-like substances in the molecular weight range of approximately 300-3000 Da were not retained by the 0.2 µm pore size polypropylene membrane. Similar findings were observed by other researchers (*Fabris et al; 2007*), and no physical straining of these compounds from solution would be expected given the small size of these compounds in relation to the pore size.

The high MW fraction (>50 kDa) biopolymers decreased in concentration following filtration of the ETP, IX and PAC waters (see Table 7). The UV_{210} response from Fig. 9 showed large removal efficiencies for the high MW fraction (>50 kDa) of both the IX and PAC waters, with UV_{210} adsorbing biopolymer for PAC permeate below the detection limit of the technique. The fluorescence response in Fig. 10 and Table 7 for the tryptophan-like proteins (278 nm/343 nm) showed a similar trend to the UV_{210} biopolymers, with high rejection for IX and PAC waters. Again the tryptophan-like biopolymer peak for PAC water permeate was close to the detection limit. The rejection of biopolymers from ETP water was moderate (64% for UV210 and 38% for tryptophan-like compounds), and their incomplete rejection during filtration suggests that size alone is not the basis for the removal of the biopolymer compounds from non pre-treated wastewaters.

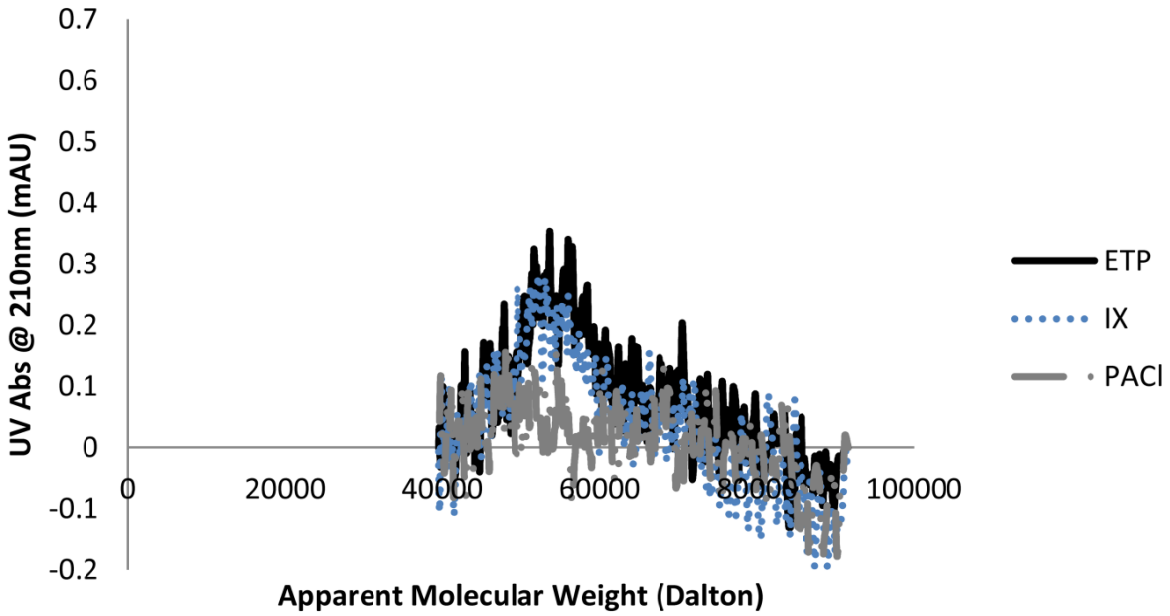
The increased rejection of biopolymers for the IX and PAC waters compared to ETP water may arise from their aggregated state. The LC column used in Method A is only capable of differentiating compounds up to 50 kDa, and therefore the difference in size of the biopolymer aggregates may not be fully evident in the LC results. Additionally, aggregation

arising from removal of acids from solution may expose binding site on the biopolymers and increase their likelihood of removal in the filter cake. Similarly, the addition of multi-valent ions during coagulation may increase both the aggregation tendency and subsequently their removal in the cake layer.

While rejection efficiencies provide information on the likely removal of biopolymers during filtration, the extent of fouling is related to the amount of material removed. The PAC water had lower initial concentrations of both high MW UV_{210} and tryptophan-like proteins, and in parallel with fouling by large MW compounds, it showed a reduced membrane fouling rate. The SEM images shown in Fig. 11 show that the amounts of gel layer present on the surface of the PP membranes were lowest for the PAC filtered membrane and that the IX water resulted in a reduced gel layer compared to ETP water. This corresponds to the same order as the long term fouling rate and the amount of biopolymer present as determined by the OCD, and is consistent with fouling by cake filtration arising from biopolymers.

Table 7: Method A data for permeate solutions of ETP, IX and PAC (calculated by peak area units at circa 50 kDa from Figs. 9a, 9b and 10)

	Biopolymer (feed)		Biopolymer (permeate)	
	UV_{210}	278/343	UV_{210}	278/343
ETP	92.0	461.9	32.8	284.7
IX	88.3	601.9	18.0	112.7
PACl	27.8	266.3	6.4	158.1
% removal ETP			64%	38%
% removal IX			80%	81%
% removal PACl			77%	41%



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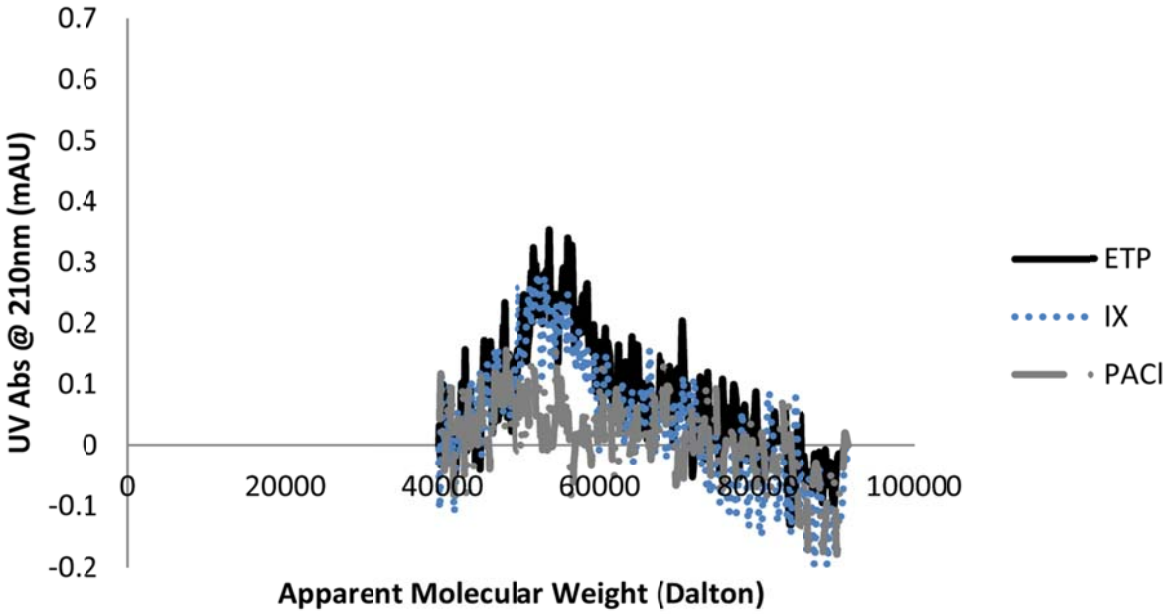
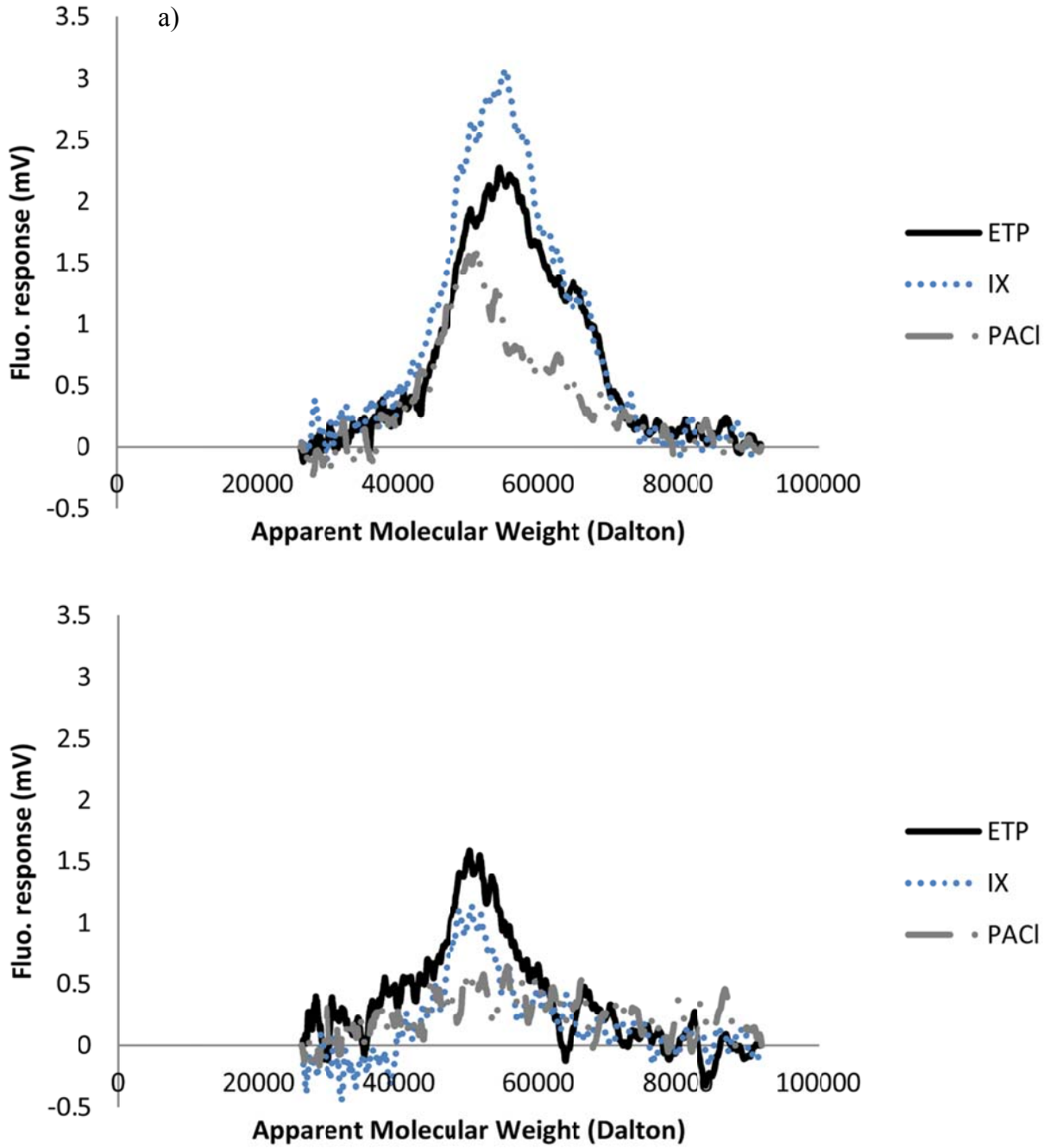


647

648 Fig. 9. Chromatograms of UV response at 210 nm of for a) feed and b) permeate solutions of

649 ETP, IX and PAC waters.

650



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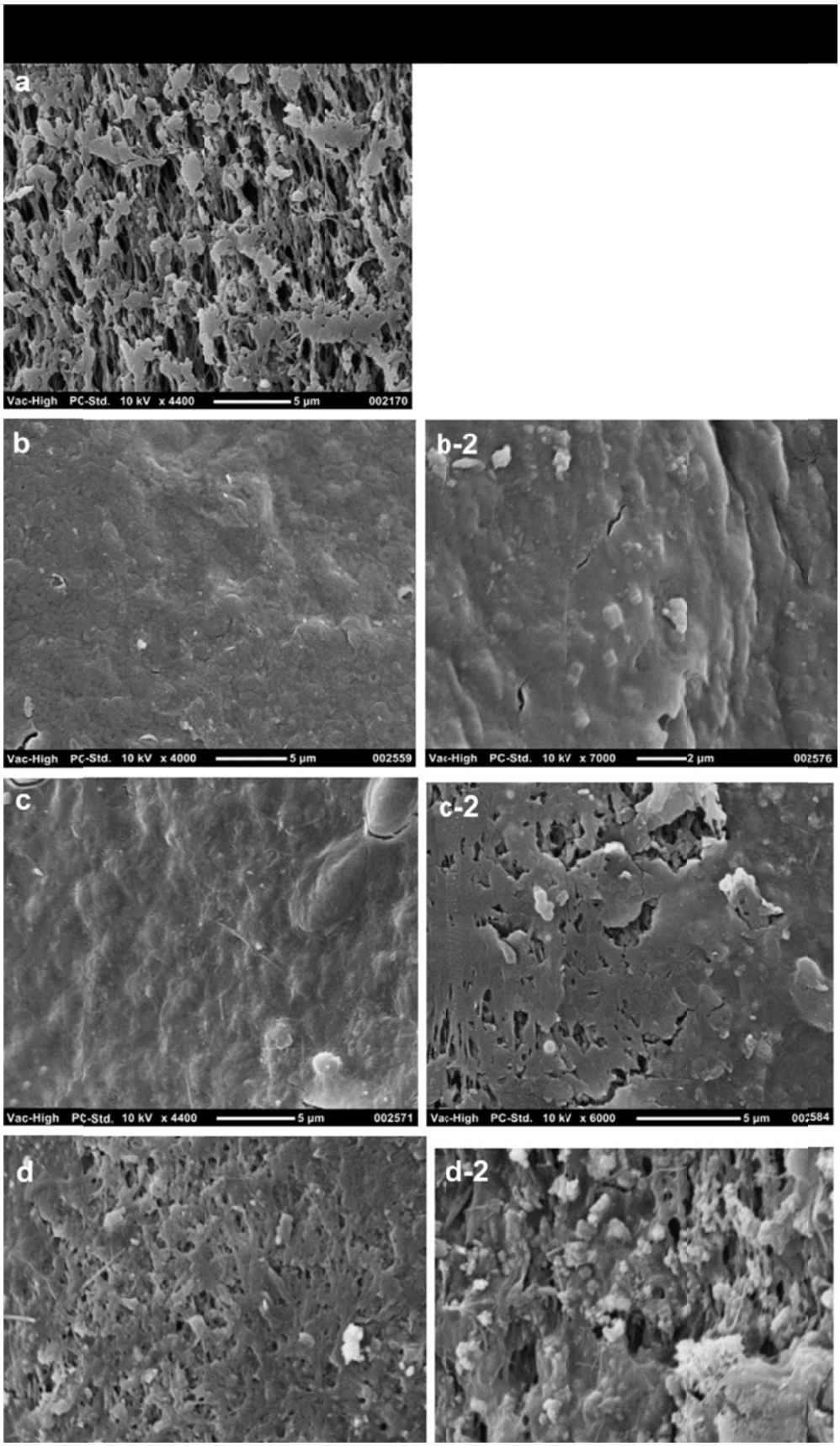
652

653 Fig. 10. Fluorescence spectrum at 278 nm/343 nm for a) feed and b) permeate solutions of

654 ETP, IX and PAC waters

655



656

657 Fig. 11. SEM images representing the membrane surface of a) virgin membrane b) ETP

658 filtered c) IX filtered and d) PACfiltered membranes

659

660 **4. Conclusion**

661 Characterisation of organic MF/UF fouling compounds in wastewater demonstrated that
662 EEM was unable to detect proteins or polysaccharides in a humic/fulvic dominated
663 wastewater. Characterisation based on LC systems (Methods A and B) were able to
664 effectively characterise organic matter in different apparent MW ranges and provided
665 complementary information. Both methods displayed similar UV_{254} responses for the
666 characterisation of humic and fulvic acids. Method A (LC-PDA-fluorescence) was effectively
667 used for analysing the presence of biopolymer fractions using UV absorbance at 210 nm and
668 fluorescence detection in which specific excitation and emission wavelength pairs were
669 applied (278 nm/304 nm and 278 nm/343 nm ex/em).

670

671 Tyrosine-like proteins (278 nm/304 nm) and UV_{210} biopolymers were effectively removed by
672 PAC (70% and 72%) and to a lesser extent by IX (4% and 39%). Residual amounts of
673 tryptophan-like proteins remained in PAC and IX treated waters. Method B (LC-UV_{254}-
674 OCD-OND) indicated similar trends, with proteins not detected in the PAC water although
675 some biopolymer remained, while IX removed biopolymers and proteins to similar extents.
676 PAC removed more biopolymers than IX and preferentially removed proteins, while IX did
677 not display preferential removal for particular biopolymers. Hence, characterisation of the
678 organic composition of waters by LC Methods A and B was a useful approach in identifying
679 potential membrane foulants for which both proteins and polysaccharides (biopolymers) are
680 thought to play a major role, particularly for longer filtration times where cake filtration
681 dominates.

682

683 The greater fluorescence response of tryptophan-like proteins (278 nm/343 nm) following IX
684 treatment was consistent with aggregation of tryptophan-like compounds into larger
685 aggregates, either by self aggregation or with polysaccharides. Selective removal of low MW
686 acids and neutrals by IX appeared to enhance the aggregation process, suggesting these
687 compounds might inhibit aggregation of tryptophan-like proteins.
688
689 In long- term filtration with IX and PAC treated waters, the fouling rates decreased during
690 extended filtration to approximately 15% of the initial fouling rates, whereas the fouling rate
691 of ETP water remained the same throughout the filtration period. Such behaviour was
692 consistent with initial fouling being dominated by pore constriction while at longer times
693 filtration was dominated by filter cake build up.
694
695 Lower rejection of UV_{210} and tryptophan-like proteins were recorded for ETP filtration
696 compared to filtration of IX and PAC waters. This suggests that the increased aggregation
697 tendency of biopolymers following IX and PAC treatments increases rejection of
698 biopolymers.
699
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701
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707

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