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Effect of IX dosing on Polypropylene and PVDF membrane fouling control

Darli Theint Myat[1], Max Mergen[2], Oliver Zhao[2], Matthew B. Stewart[1], John D. Orbell[1,3], Tony Merle[4], Jean-Philippe Croué[4], Stephen Gray[1]

1. *Institute for Sustainability and Innovation (ISI), Victoria University, Melbourne, VIC 8001, Australia,*
2. *Orica Watercare, Melbourne, Vic 3000, Australia*
3. *College of Engineering and Science, Victoria University, Melbourne, VIC 8001, Australia*
4. *Water Reuse and Desalination Center, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Kingdom of Saudi Arabia*

Abstract:

The performance of ion exchange (IX) resin for organics removal from wastewater was assessed using advanced characterisation techniques for varying doses of IX. Organic characterisation using liquid chromatography with a photodiode array (PDA) and fluorescence spectroscopy (Method A), and UV_{254}, organic carbon and organic nitrogen detectors (Method B), was undertaken on wastewater before and after magnetic IX treatment. Results showed partial removal of the biopolymer fraction at high IX doses. With increasing concentration of IX, evidence for nitrogen-containing compounds such as proteins and amino acids disappeared from the LC-OND chromatogram, complementary to the fluorescence response. A greater fluorescence response of tryptophan-like proteins (278nm/343nm) for low IX concentrations was consistent with aggregation of tryptophan-like compounds into larger aggregates, either by self-aggregation or with polysaccharides. Recycling of IX resin through multiple adsorption steps without regeneration maintained the high level of humics removal but there was no continued removal of biopolymer. Subsequent membrane filtration of the IX treated waters resulted in complex fouling trends. Filtration tests with either polypropylene (PP) or polyvinylidene fluoride (PVDF) membranes showed higher rates of initial fouling following treatment with high IX doses (10 mL/L) compared to filtration of untreated water, while treatment with lower IX doses resulted in decreased fouling rates relative to the untreated water. However, at longer filtration times the rate of fouling of IX treated waters was lower than untreated water and the relative fouling rates corresponded to the amount of biopolymer material in the feed. It was proposed that the mode of fouling changed from pore constriction during the initial filtration period to filter cake build up at longer filtration times. The organic composition strongly influenced the rate of fouling during the initial filtration period due to competitive adsorption processes, while at longer filtration times the rate of fouling appeared to depend upon the amount of biopolymer material in the feed water.

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

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). Many researchers have sought to understand the effect of NOM composition on MF/UF fouling and the impact of pre-treatments on reducing membrane fouling (Shon et al., 2004; Guo et al., 2004; Galjaard et al., 2005; Tran et al., 2006; Gray et al., 2007). Water pre-treatment prior to membrane filtration can improve the final quality of water and membrane fouling rates, and a variety of pretreatment processes for membrane filtration have been investigated (Kabsch-Korbutowicz et al., 2006). Treating NOM by coagulation is commonly practised and activated carbon adsorption has also been investigated (Fabris et al., 2007). IX has also been used to remove organic compounds and reduce membrane fouling, and several researchers have shown the potential of magnetic ion exchange (MIEX™) in combination with conventional coagulation for improved NOM removal and reduced low-pressure membrane fouling (Humbert et al., 2012, Drikas et al., 2011).

While IX treatment may remove organic compounds, there are several studies with both surface waters (Fabris et al., 2007; Humbert et al., 2007; Huang et al., 2012) and wastewaters (Fan et al., 2008; Filloux et al., 2012) that have found this removal to have not affected membrane fouling rates during short term laboratory studies. This has been attributed to the removal of low to medium MW humic compounds by IX (Bolto et al., 2002; Croué et al., 1999, Allpike et al., 2005; Humbert et al., 2007; Mergen et al., 2008; Huang et al., 2012), and an inability to remove high molecular weight compounds. A recent study (Huang et al., 2012) has shown partial removal of biopolymers with IX pre-treatment, and that the degree of biopolymer removal increased with higher doses of IX. However, they also found no improved membrane fouling outcomes for short term fouling trials. Filloux et al., 2012 also reported that pre-treatment with IX did not improve the permeate flux for either MF (0.04 μm PVDF) and UF (150 kDa PES) hollow fibre membranes when filtration experiments were performed with wastewater effluent. Conversely, Myat et al. (2012) have shown improved membrane fouling performance with IX treated wastewater for a hydrophobic membrane in laboratory trials performed with regular backwashing over several days. Additionally, a 2-year pilot study (Dixon et al., 2010) has demonstrated improved ultra-filtration (UF) fouling outcomes following IX pre-treatment, while Galjaard et al., 2005 demonstrate near zero UF fouling for IX pre-treated canal water prior to a pilot scale UF membrane.

The aim of this investigation was to explore the effect of IX pre-treatment and the concentration of IX on membrane fouling of both hydrophobic (PP) and hydrophilic (PVDF) membranes in laboratory trials with regular backwashing over a number of days. Batch experiments were conducted with a secondary effluent to evaluate the efficiency of IX resin for DOC removal and to identify the class of organic compounds removed as a function of resin dose. IX treated wastewaters were subsequently filtered through two types of membranes and their fouling rates determined.

2. Materials and methods

2.1. Source water

Water from Melbourne Water's Eastern Treatment Plant (ETP) was used for this investigation. ETP treats approximately 400 ML/day 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 (86 PCU) and a relatively high DOC (14.3 mg/L). The raw water before treatment is referred to as ETP water in the following discussion.

2.2. Ion exchange (IX) treatment (Jar-test procedure)

Magnetic ion-exchange resin (MIEX^{TM}), which consists of 150-180 μm beads of a macroporous, polyacrylic structure, contains quaternary ammonium strong-base functional groups (Mergen et al., 2008). The resin, manufactured by Orica Watercare, was evaluated in this work. This resin is designed for use by continuous dispersion and settling rather than in a static column. Particulate matter was removed from untreated ETP wastewater by vacuum filtration through a 1.2 µm pore size filter (Whatman GF/C). Preliminary experiments with IX were performed on raw water to evaluate the impact of IX treatment on DOC, ultra-violet absorbance at 254 nm (UV_{254}) and colour removal. IX doses in the range of 1-10 mL/L were tested, corresponding to Bed Volumes (BV) in the range of 1000-100 BV (Bed Volumes = Volume treated/IX dose). Resin doses were prepared by adding the required resin dose to measuring cylinders and allowing it to settle for 1 h. Adjustments to the required resin dose were made by adding or removing resin using a plastic pipette. Resin was added to a 1 L square glass jar and mixed on a jar tester with a 60 mm x 20 mm paddle at 180 rpm for 15 minutes. After each jar test, the resin was settled from the treated water for 5 min. Supernatant water was decanted and vacuum filtered through a 1.2 µm pore size filter (Whatman GF/C) to move resin fines. Samples were analysed after each jar test for DOC, UV_{254}, and colour removal and via liquid chromatography without further filtration. Bulk IX experiments using different IX concentrations were conducted to treat 10 L of raw water for each of the fouling experiments. The 10L of treated water was divided into two samples, with one used for the PP fouling studies and the other for the PVDF fouling studies.

Using fresh or regenerated resin in batch tests before analysis of the treated water does not reflect how the resin will be used at full scale, although useful information can be obtained from single use IX tests (Mergen et al., 2008). Therefore, in this work, a separate experiment was carried out in which IX resin was contacted with raw water in jar tests for 5 consecutive occasions (i.e., repeated 5 times using the same IX resin) without regeneration to give an equivalent to treating overall 1000 bed volumes (BV) of water (5 L water treated with 5 mL of resin). 10 L of raw water was treated in this way for fouling studies. The mixing speed and contact time were kept at 180 rpm and 15 minutes. Samples were analysed for DOC, UV_{254} and colour removal, and using liquid chromatography, after each adsorption cycle and for the combined water.

2.3. Water quality analyses and characterisation

The quality of wastewater samples before and after pre-treatment were analysed for pH, conductivity, UV_{254}, DOC and true colour. DOC was measured using a total organic carbon analyser (TOC-V $_{CPH/CPN}$) (Shimadzu, Japan). Both colour and UV_{254} were measured using a HACH DR 5000 spectrophotometer. True colour was measured using a 5 cm quartz cell at 456 nm and converted to Pt-Co units following calibration against a Platinum/Cobalt standard. UV_{254} was measured through a 1 cm quartz cell.

Molecular weight distributions by liquid chromatography (LC) analyses were performed with a photodiode array (PDA) and fluorescence detector in series (Method A), and with LC coupled with UV_{254}, organic carbon detector (OCD) and organic nitrogen detector (OND) (Method B). Details of Method A are described in Myat et al., (2012). Fluorescence excitation and emission wavelengths of 278 nm/304 nm and 278 nm/343 nm (ex/em) were applied, since such wavelengths are known to be specific for tyrosine and tryptophan like compounds respectively (Coble, 1996). Polystyrene sulphonate (PSS) molecular weight standards were used to calibrate the LC column used for Method A, and allowed the results to be reported as apparent molecular weight (MW). Analyses by Method B were performed with a LC-OCD instrument (DOC-Labor).

2.4. Membrane filtration

A single hollow fibre membrane filtration apparatus was used to examine the fouling rate of the raw and IX treated waters. Hydrophobic polypropylene (PP) membranes and hydrophilic PVDF membranes were used. Tran et al., (2006) has previously determined the contact angle of the PP membrane material to be 160° and the PVDF membrane to be 61˚. The permeability of the membranes was verified to be within a set range (see Table 1) before experimental testing, to ensure the variation between fibres was minimised. Table 1 lists the summary of the membrane properties used for fouling studies.

Water was fed at a constant flowrate equivalent to a flux of 50 kg/m^{2}h and the transmembrane pressure (TMP) recorded. The membranes were backwashed every 30 minutes and the tests performed over 3-4 days. Analysis of membrane performance used the unified membrane fouling index developed by Huang et al., (2008) and Nguyen et al., (2011). The hydraulic irreversible fouling index (HIFI) was derived from this analysis and used for comparison of the results. HIFI is related to the fouling resistance and a low value of HIFI represents low rate of membrane fouling while high HIFI values indicate greater membrane fouling rates. This filtration method precludes the determination of fouling mode directly (eg. pore blocking, cake filtration) as the flux is non-uniform along the fibre length. Greater details of the filtration method and analysis techniques are given in Myat et al., (2012).

Table 1: Membrane properties

3. Results and Discussion

3.1. Raw water characterization

The raw water had a relatively high DOC and high colour as shown in Table 2. LC analyses (Method A) showed that the MW distribution of the UV_{254} absorbing compounds was between retention times of 30-50 minutes, approximately corresponding to the range of 100 Da-3000 Da. A broad range of different MW effluent organic matter (EfOM) was also observed at UV_{210} nm (See Fig. 5 and 6 in SI), including a peak in the biopolymer region (retention time 19 minutes, approximately 50 kDa). Her et al., 2004 suggested that UV_{210} absorbance is characteristic of amino groups, and it is able to detect nitrogen containing compounds such as proteins. Biopolymers, such as proteins and polysaccharides, cannot usually be detected by UV_{254} absorbance, and the lack of a biopolymer peak at this wavelength is commonly observed.

Table 2: Characteristics of ETP secondary effluent and IX-treated wastewaters

3.2. Organic removal with single use IX resin

Table 2 describes water quality after the different IX treatment methods for ETP water. DOC removals of 27%, 33%, 58% and 64% were observed during single adsorption IX treatment for ETP raw water at IX doses of 1, 1.6, 5 and 10 mL/L respectively. Similarly, both UV_{254} and colour improved when a high IX dose was applied (i.e., decreasing number of BV). Table 2 shows that the highest removal of DOC, UV_{254} and colour was achieved when the IX dose was at 10 mL/L while the least removal was observed with 1 mL/L resin dose. A bar graph of percent removal of UV_{254}, colour and DOC for the different IX treatment concentrations for ETP raw water is shown in Fig. 7 in SI, and higher percentage reductions in UV254 and colour over DOC are shown. This is consistent with preferential removal over aromatic substances over other organic compounds.

LC-UV_{254} chromatograms from both Methods A and B gave similar results for each water treated by IX (see Figs.8 and 9 in SI). UV_{210} results for each water treated by IX are also reported in Fig. 10 in SI. Table 3 provides the concentration of each organic fraction as determined by the LC-OCD method.

Table 3:

Distribution of the DOM fractions (Method B: LC-UVD-OCD-OND) for raw water treated using different IX concentrations

High MW structures i.e., biopolymer fraction, led to significant peak response in the DOC chromatograms and smaller peaks in the UV_{254} chromatograms (see Fig. 8 in SI). Biopolymers, such as proteins and polysaccharides, could be detected in both DOC and OND chromatograms. The removal of both the biopolymer fraction and humic components increased with increasing IX doses applied (i.e., with decreasing BV). From Table 3, the results show that biopolymer DOC was the lowest and the humic DOC adsorbed or the percent removed onto the resin was >95% when 10 mL/L resin dose was applied. The biopolymer DOC removal (%) was reduced from 33% at 10 mL/L resin dose to 24% at 5 mL/L resin dose, whereas less than 10% removal was observed with resin doses of 1.66 mL/L and 1 mL/L. The measured biopolymer removals for 1.66 mL/L and 1 mL/L IX doses were within experimental error. The humic DOC removal (%) ranged from >95%, 89%, 45% and 29% at 10, 5, 1.66 and 1 mL/L resin doses, respectively. Similar findings were also reported by Huang et al. (2012), that the removal of biopolymer increased with higher doses of IX.

It was interesting to note that a reduction of the biopolymer fraction was only observed with IX dose applied at 10 mL/L and 5 mL/L respectively. The results also show that with increasing concentration of IX dose applied, evidence for nitrogen containing compounds such as proteins and amino acids disappeared, and that the removal of biopolymers appears consistent when determined either by OCD or OND (see Table 3). From LC-PDA-Fluorescence analysis (Method A), the response of the peaks related to individual amino acids could be detected via fluorescence. The biopolymer peak (retention time of 19 minutes: approximately 50 kDa) was also detected by the fluorescence response wavelengths of 278 nm/304 nm (ex/em) and 278 nm/343 nm (ex/em). The fluorescence responses of each water sample are shown in Figs. 1 and 2.

Fig. 1. LC-Fluorescence response (Ex: 278 nm Em: 304 nm; i.e., tyrosine-like DON) for the different IX treatment methods for ETP water

Fig. 2. LC-Fluorescence response (Ex: 278 nm Em: 343 nm, i.e., tryptophane-like DON) for the different IX treatment methods for ETP water

Both Figs. 1 and 2 indicate that IX treatment removed part of the protein-like substances - removal percentages based on the area under these peaks are given in Table 4. The removal of tyrosine-like substances at 278 nm/304 nm (ex/em) from ETP raw water by IX treatment at 1 mL/L was 56% and, by increasing the IX dose to 10 mL/L, only a slightly higher removal percentage of approximately 60% was suggested. The maximum removal of tryptophan-like substances detected at 278 nm/343 nm (ex/em) was approximately 46%. The removal was only observed with 10 mL/L resin dose while an increase in fluorescence intensity at that excitation/emission was detected following IX treatment with low resin doses (e.g. 1 mL/L).

We have previously reported that an increase in fluorescence response at these higher molecular weights indicates either an increase in fluorescence response of these compounds due to a change in their chemical environment (e.g. aggregation with polysaccharides, see Lee 1997), or aggregation of low MW fluorescing compounds into larger entities. The subsequent decrease in this peak, corresponding to low MW fluorescing compounds, for higher resin doses was assumed to arise because of greater removal of these compounds by IX resin. It should be noted that detection of organic compounds with MW > approximately 50 kDa could not be resolved by the LC techniques used, as these molecular weights corresponded to the minimum retention times within the LC column.

Table 4: Method A (LC-PDA-Fluorescence) biopolymer data for different IX treated waters (calculated by peak area units at circa 50 kDa from Figs. 1 and 2)

3.3. Organic removal by consecutive magnetic resin uses

Commercially, a side stream of MIEX™ resin is regenerated so that the resin is cycled through adsorption steps a number of times before it is regenerated and treated water is exposed to resin that has a variety of adsorption histories. To understand what is taking place during this process, the removal of organic matter fractions by IX resin following a number of successive adsorption cycles was assessed by analysing the removal performance via LC Method B. Table 5 presents the percentage of each DOC fraction removed by adsorption onto the resin following the first and 5th adsorption cycles, and LC-OCD chromatograms are reported in Fig. 11 in SI. Also shown is the percentage removal for the average of the five adsorption cycles as measured by combining the resin treated water for all five adsorption cycles. The overall number of bed volumes after the five adsorption cycles with no regeneration was overall 1000 BV.

Table 5: Method B (LC-UVD-OCD-OND) data for raw water treated using cycled resin with no regeneration between adsorption cycles

Analysis of LC-OCD (Method B) data showed that removal of humic DOC ranged from 88% after the first use of resin to 71% after 5 resin uses (see Table 5), and that the variation in adsorption efficiency between adsorption cycles was small. Similarly, the adsorption efficiency of low molecular weight acids and neutrals did not vary substantially between adsorption cycles. The biopolymer DOC adsorbed onto the resin after 1st resin use was 24%. The adsorption rate reduced during subsequent adsorption cycles to less than 1% removal in the final combined water. A similar trend was also observed with OND biopolymer results.

Similar observations were reported by Mergen et al. (2008). In their study, the water dominated by hydrophobic NOM showed good removal efficiency of high MW NOM during the first few adsorption cycles, but the removal efficiency declined with subsequent uses of resin. The decreasing of adsorption efficiency was explained due to size exclusion/blockage of the exchange sites by high MW NOM rather than exhaustion of ion-exchange sites. It was supported by the observation that initially good removal of all organics was observed, however the removal efficiency of high MW organics decreased with increased cycling of the resin.

Similar phenomenon can also be seen with the particular water used in this work, as the highest resin concentration gave the highest removal of biopolymer fraction (see Table 3) and biopolymer adsorption decreased as the resin passed through adsorption cycles. High MW organics will have a reduced number of adsorption sites compared to smaller molecular weight compounds because their size limits access to small pores. The functional groups associated with the organic compounds will also greatly affect their removal efficiency, and the anionic exchange character of the IX resin would adsorb organic acids in preference to amine functional groups. It is interesting to note that both the biopolymers and building blocks fractions displayed reduced adsorption efficiency with number of adsorption cycles and potentially negative adsorption by the 5th cycle (i.e. compounds released from the resin). Both these groups of organic compounds are considered to contain elevated amine functionalised compounds in comparison to the other organic fractions, and such differences in functionalization would support the reduced adsorption of biopolymers and building blocks as competition for sites is increased. Release of compounds in favour of stronger adsorbing compounds may also be possible.

3.4. Membrane fouling results

3.4.1. Fouling experiments using PP and PVDF membranes

Figs. 3 and 4 show the rate of increase in resistance (1/J’s) as a function of specific mass for filtration of ETP and treated ETP wastewaters using polypropylene and PVDF membranes at a constant flux of 50 kg/m^{2}h. Expanded views of the fouling trends are also shown in the left hand corner of the Figs 3 and 4.

Fig. 3. Plot of (1/J's) versus specific mass (kg/m^2) for a) ETP and overall 1000 BV treated water (5 mL/L – 5 cycles, see Table 5) b) 1mL/L and 10 mL/L IX treated wastewaters with PP membranes

Fig. 4. Plot of (1/J's) versus specific mass (kg/m^2) for a) ETP and overall 1000 BV treated water (5 mL/L – 5 cycles, see Table 5) b) 1mL/L and 10 mL/L IX treated wastewaters with PVDF membranes

Fouling rates (m^2/kg) were calculated from the data represented in Figs. 3 and 4, and the values are given in Table 6. The 2-point method described by Nguyen et al. (2011) was applied to compare fouling rate at equal time intervals, corresponding to equal permeate mass or specific mass.

Table 6: Hydraulic irreversible fouling indices (HIFI) of ETP and IX treated waters with PP and PVDF membranes

From Table 6, when filtration tests were carried out with PP membranes, the initial fouling rates were greater than the longer term fouling rates for all waters. After 12 hours of filtration, a high IX dose of 10 mL/L increased the HIFI value compared to ETP and 1 mL/L treated water, indicating that high doses of IX initially led to increased fouling rates compared to no treatment or lower IX doses. This effect was also observed for overall 1000 BV IX treated water. Conversely, lower IX doses (1 mL/L) initially reduced the fouling rate compared to no treatment, but a peak appeared in the fouling rate at approximately 24 hours (1100 kg/m^2) and it was approximately the same or slightly higher than the fouling rate for no treatment. For longer term filtration, ETP filtered water only displayed a moderate decrease in fouling rate as the HIFI value decreased from 1.40 m^2/kg to 0.88 m^2/kg after 24 h of filtration time (after 41 backwash cycles). Interestingly, the HIFI value of overall 1000 BV IX treated water decreased to approximately 22% of its initial value. Such a finding was also reported in a previous paper (Myat et al., 2012) for overall 1000 BV IX treated water. Longer term fouling of polypropylene membrane (>1100 kg/m^2 or 24 hours) by IX treated water was lower than the fouling rate for untreated water, and the fouling rates for both high and low doses of IX doses approached similar values as filtration proceeded (see Fig 12 in SI).

This complex fouling behaviour demonstrates that the effect of IX treatment cannot be determined by short term fouling studies as is often conducted in many laboratory experiments, and that longer term trends may be quite different to the initial fouling characteristics. These results also showed that the fouling kinetics were not uniform and that several mechanisms might take place in the overall process.

A possible explanation for these complex fouling trends is that the fouling mechanism is time dependent. It is proposed that pore constriction occurs in the early stages of fouling due to adsorption of organic compounds on the membrane surface, leading to high fouling rates. The extent of adsorption reduces quickly as the membrane becomes coated with organic material and filter cake fouling becomes the dominant mechanism. Biopolymers are responsible for the majority of the filter cake (Laîné et al., 1989, Taniguchi et al., 2003) and the order of long term fouling rates would support this hypothesis. The initial fouling rates would be determined by adsorption of organic substances within the membrane pores. ETP water is dominated by humics and these compounds would be expected to be the dominant foulant via adsorption. However, humics are preferentially removed with IX resin and competing compounds such as biopolymers, building blocks, low molecular weight acids and neutrals are able to adsorb to the membrane to a greater extent. At 10 mL/L IX dose, there was negligible humic material in the treated water (below detection: see Table 3) and therefore internal pore constriction arises predominantly from compounds other than humics. This change in composition of competing adsorption compounds could lead to the unusual initial fouling trends, however further work is required to confirm this hypothesis.

Table 6 also shows a similar trend for fouling of the PVDF membrane as the PP membrane, with the initial rates of fouling for the IX treated waters being quite different to their long term fouling trends. Again, 10 mL/L treated water had the highest initial fouling rate, followed by ETP and 1 mL/L treated water (see Fig 13 in SI). A similar fouling mechanism to that proposed for the PP membrane could also explain the PVDF fouling trends. At longer filtration times, the extent of fouling may be due to the concentration of biopolymers in the feed solutions. This was supported by the relationship between the fouling rate and the amount of biopolymer present as determined by the OCD (see Table 3), where removals of approximately 9% and 32% of the biopolymers were obtained for the 1 mL/L and 10 mL/L waters respectively. Fig. 14 in SI showed SEM images of the surface on the PVDF membranes, in which images taken from similar positions on the membrane fibres in relation to the potting position. These images also support this hypothesis as the thickness of the cake layer appeared to decrease following IX dose pretreatment.

5. Conclusion

It is known that when IX resin is used in water treatment for the removal of humic material that increased removal of humics occurs at higher resin doses and that sustained humics removal can be achieved with resin recycling. Furthermore biopolymer removal can be achieved at high resin doses but the removal rate of biopolymers declines as resin is recycled through multiple adsorption stages. This behaviour has been attributed to the adsorption of biopolymers onto the exterior or within the larger pores as a result of size exclusion mechanisms, whereas the smaller humics have a greater available surface area for adsorption. However, this work also provides evidence that differences in functional groups may also explain the reduced adsorption of biopolymers and building blocks upon recycling of resin due to competitive adsorption with humic compounds, as there was some indication biopolymers and building blocks where released when resin had passed through 5 recycling cycles. Biopolymers and building blocks may contain elevated levels of amine functional groups compared to other organic components via higher concentrations of proteins and amino acids, and these groups are expected to have less affinity for adsorption by anion exchange membranes. Therefore, with an increasing number of adsorption cycles, the biopolymers and building blocks are displaced by humic substances.

Filtration tests with PP and PVDF membranes identified increased rates of initial fouling following treatment with high IX doses (10 mL/L) while treatment with lower IX doses resulted in decreased fouling rates relative to the untreated water. Fouling at longer filtration times, after approximately 24 hours, lead to a change in fouling rates with the rate of fouling of IX treated waters being lower than untreated water. The complex fouling behaviour was attributed to a change in fouling mode - from pore constriction to filter cake build up. It was proposed that during pore constriction, the rate of fouling was strongly influenced by the composition of adsorbing species and their molecular weights which varied following IX treatment. Untreated water was composed primarily of humics, while treatment with high IX doses resulted in little or no humics being present in the feed. At longer filtration where cake filtration was assumed to be the dominating fouling mechanism, the rate of fouling appeared to depend upon the amount of biopolymer material in the feed water.

This mechanism may explain inconsistencies in results between laboratory studies and pilot plant trials for the effect of IX for organics removal on membrane fouling. Laboratory studies generally use new membranes in short term fouling tests and this is likely to correspond to the region were both pore blocking and cake filtration occur. The fouling response will not be indicative of long term fouling trends under such conditions. Pilot plant trials however, generally operate for extended periods of time with the same membranes and have shown reduced fouling following IX pre-treatment as has this study when extended filtration times are considered.

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Highlights

- A step change in membrane fouling mechanism occurred after 24 hours of filtration
- Initial membrane fouling was determined by the mix of organic compounds
- Longer term fouling appeared to be the result of biopolymer concentration
- IX change resin capability to remove biopolymers reduced with continuous use
- Associations between organic compounds was indicated by changes in fluoresence

Tables

Table 1
Membrane properties

Membrane	Fibre dimensions		Pore size, µm	Permeability, kg/m^{2}hbar	Surface charge mV	Contact Angle (˚)
	Outer diam., mm	Inner diam., mm				
PP	0.50	0.25	0.2	1000 ± 226	-19.5 ± 0.1	160
PVDF	0.65	0.48	0.1	875 ± 116	-8.9±0.2	61

Table 2
Characteristics of ETP secondary effluent and IX-treated wastewaters

IX (mL/L)	UV_{254} (cm^{-1})	pH	DOC (mgC/L)	% DOC removal	SUVA (L/m-mgC)	Colour (Pt-Co)
0	0.365	7.81	14.3±0.3	-	2.6±0.1	86
1	0.261	7.48	10.5±0.1	27%	2.5±0.1	62
1.66	0.224	7.52	9.6±0.2	33%	2.3±0.1	50
5	0.112	7.45	6.1±0.4	58%	1.8±0.1	21
10	0.084	7.34	5.2±0.1	64%	1.6±0.1	12

Table 3
Distribution of the DOM fractions (Method B: LC-UVD-OCD-OND) for raw water treated using different IX concentrations

				IX adsorption			
			ETP	**1mL/L**	**1.66mL/L**	**5mL/L**	**10mL/L**
Biopolymers	DOC	ppb	1091	991	1048	826	732
	Removal	*%*	-	*9.2*	*3.9*	*24.3*	*32.9*
	DON	ppb	154	124	153	116	104
	Removal	*%*	-	*19.5*	*0.6*	*24.7*	*32.5%*
Humics	DOC	ppb	6967	4918	3818	791	n.a.
	Removal	*%*	-	*29.4*	*45.1*	*88.6*	*>95%*
	DON	ppb	885	370	327	73	n.a.
	Removal	*%*	-	*58.2*	*63.1*	*91.8*	*>95%*
building blocks	DOC	ppb	2215	1971	1981	1809	1797
	Removal	*%*	-	*11.0*	*10.6*	*18.3*	*18.9*
LMW acids	DOC	ppb	604	542	549	519	551
	Removal	*%*	-	*10.2*	*9.1*	*14.1*	*8.8*
Neutrals	DOC	ppb	2130	1711	1635	1562	1433
	removal	*%*	-	*19.7*	*23.2*	*26.7*	*32.7*

Table 4
Method A (LC-PDA-Fluorescence) biopolymer data for different IX treated waters (calculated by peak area units at circa 50 kDa from Figs. 1 and 2)

	Protein-like substances (Biopolymer fraction)			
	278-304 nm (Tyrosine-like)		278-343 nm (Tryptophan-like)	
	Peak area	% removal	Peak area	% removal
ETP	183		977	
1 mL/L	80	56%	4772	-388%
1.66 mL/L	80	56%	2217	-127%
5 mL/L	75	59%	1446	-48%
10 mL/L	74	59%	525	46%

Table 5
Method B (LC-UVD-OCD-OND) data for raw water treated using cycled resin with no regeneration between adsorption cycles

				IX adsorption		
			ETP	**5 mL/L 1st use**	**5 mL/L 5th use**	**Overall 1000 BV***
Biopolymers	DOC	ppb	1091	827	1146	1085
	Removal	*%*	-	*24.2*	*-5.0*	*0.5*
	DON	ppb	154	122	168	137
	removal	*%*	-	*20.8*	*-8.3*	*11.0*
Humics	DOC	ppb	6967	816	2042	1482
	removal	*%*	-	*88.3*	*70.7*	*78.7*
	DON	ppb	885	101	168	198
	removal	*%*	-	*88.6*	*81.0*	*77.6*
building blocks	DOC	ppb	2215	1867	2444	2394
	removal	*%*	-	*15.7*	*-10.3*	*-8.1*
LMW acids	DOC	ppb	604	522	509	515
	removal	*%*	-	*13.6*	*15.7*	*14.7*
Neutrals	DOC	ppb	2130	1539	1621	1534
	removal	*%*	-	*27.7*	*23.9*	*28.0*

*also termed as ‘mixed of the 5 treated water’

Table 6
Hydraulic irreversible fouling indices (HIFI) of ETP and IX treated waters with PP and PVDF membranes

	PP_HIFI ($m^2/kg \times 10^{-3}$)								PVDF_HIFI ($m^2/kg \times 10^{-3}$)							
	ETP		Overall 1000 BV		1mL/L		10 mL/L		ETP		Overall 1000 BV		1mL/L		10mL/L	
Time (h)	HIFI	%	HIFI	%	HIFI	%	HIFI	%	HIFI	%	HIFI	%	HIFI	%	HIFI	%
12	1.403	100%	1.640	100%	0.915	100%	1.655	100%	0.756	100%	1.212	100%	0.674	100%	0.970	100%
24	0.877	63%	0.364	22%	1.006	110%	0.644	39%	0.614	81%	0.692	57%	0.421	62%	0.390	40%
48	0.855	61%	0.456	28%	0.735	80%	0.493	30%	0.813	108%	0.697	58%	0.403	60%	0.570	59%
72	0.903	64%	0.547	33%	0.504	55%	0.462	28%	0.703	93%	0.407	34%	0.569	84%	0.330	34%
96	0.989	70%	0.638	39%	0.589	64%	0.480	29%	0.618	82%	0.318	26%	0.583	86%	0.310	32%

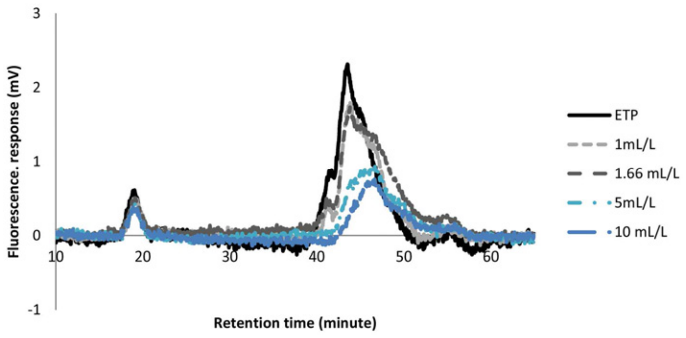
Figure Captions

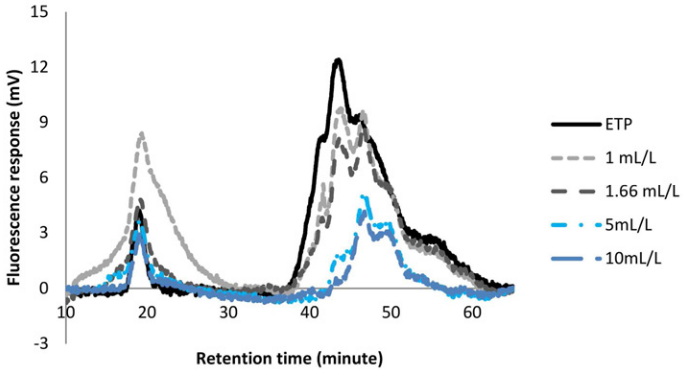
Fig. 1. LC-Fluorescence response (Ex: 278 nm Em: 304 nm; i.e., tyrosine-like DON) for the different IX treatment methods for ETP water

Fig. 2. LC-Fluorescence response (Ex: 278 nm Em: 343 nm, i.e., tryptophane-like DON) for the different IX treatment methods for ETP water

Fig. 3. Plot of (1/J's) versus specific mass (kg/m^2) for a) ETP and overall 1000 BV treated water (5 mL/L – 5 cycles, see Table 6) b) 1mL/L and 10 mL/L IX treated wastewaters with PP membranes

Fig. 4. Plot of (1/J's) versus specific mass (kg/m^2) for a) ETP and overall 1000 BV treated water (5 mL/L – 5 cycles, see table 6) b) 1mL/L and 10 mL/L IX treated wastewaters with PVDF membranes


3
2
1
0
-1
10
20
30
40
50
60
Fluorescence. response (mV)
Retention time (minute)
ETP
1mL/L
1.66 mL/L
5mL/L
10 mL/L


15
12
9
6
3
0
-3
Fluorescence response (mV)
10
20
30
40
50
60
Retention time (minute)
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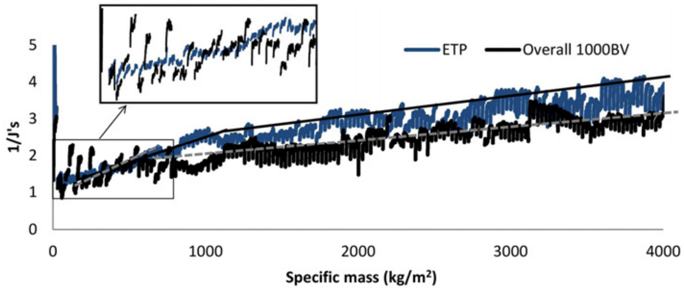
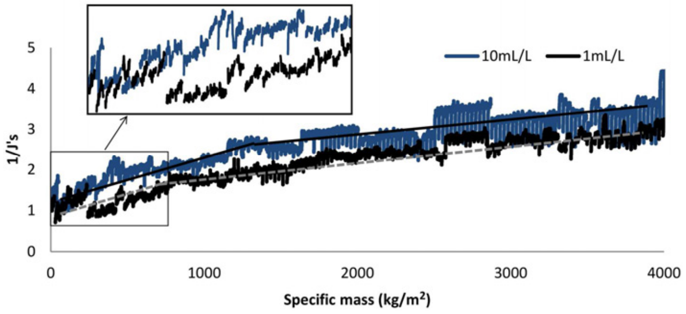
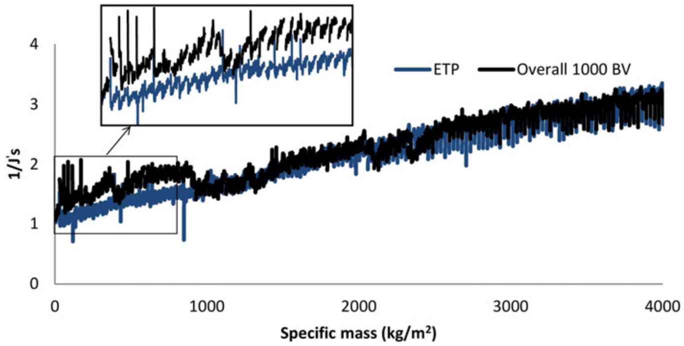
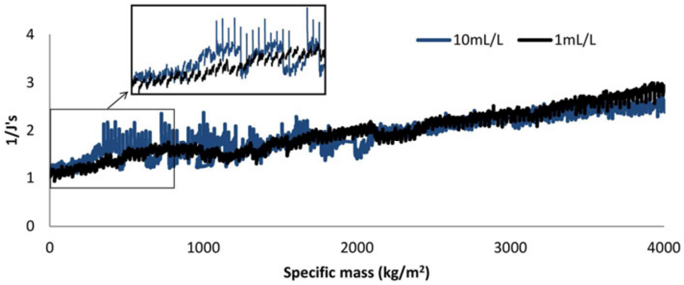
1.66 mL/L
5mL/L
10mL/L


ETP
Overall 1000BV
1/J's
0
1
2
3
4
5
0
1000
2000
3000
4000
Specific mass (kg/m²)


5
4
3
2
1
0
1/J's
0
1000
2000
3000
4000
Specific mass (kg/m²)
10mL/L
1mL/L


ETP
Overall 1000 BV
1/J's
Specific mass (kg/m²)
0
1
2
3
4
0
1000
2000
3000
4000


10mL/L
1mL/L
1/J's
0
1
2
3
4
0
1000
2000
3000
4000
Specific mass (kg/m²)

SUPPORTING INFORMATION

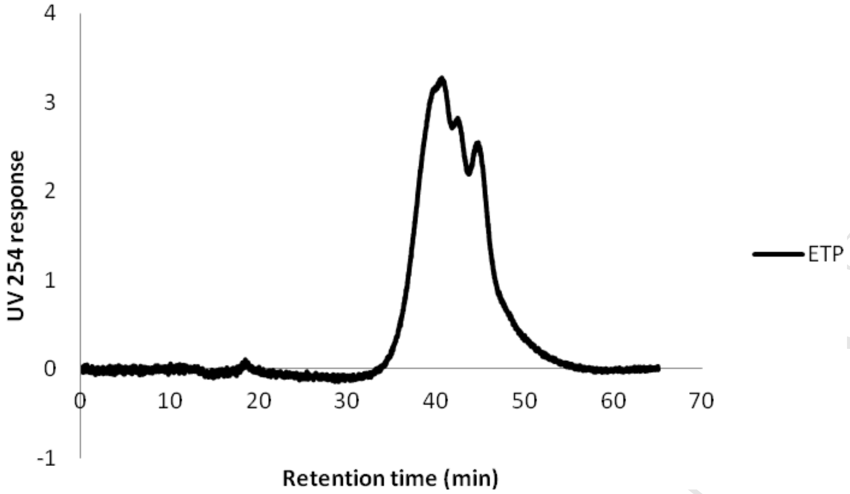
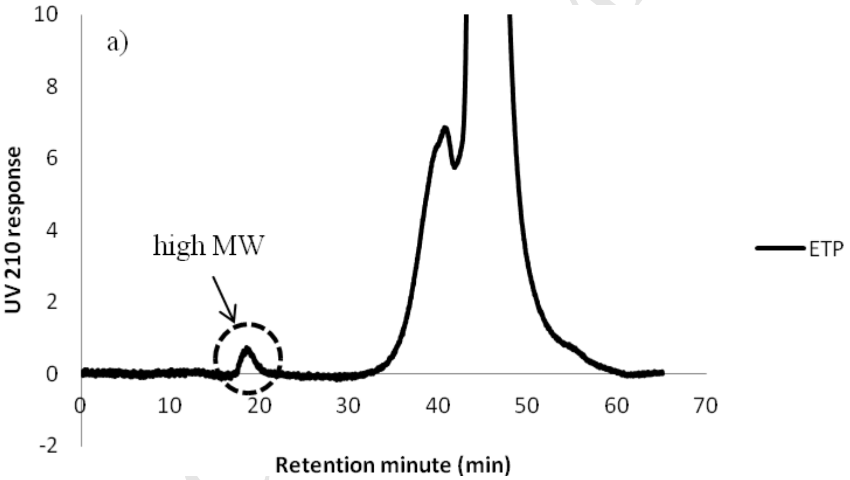


Fig. 5. Chromatogram of UV response at 254 nm for ETP wastewater (Method A)



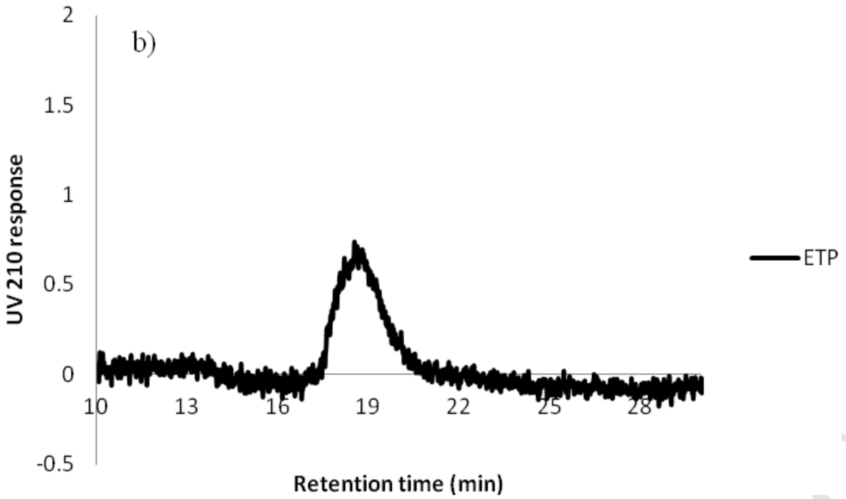


Fig. 6. Chromatograms of UV response at 210 nm showing a) at all retention times b) highlighting the high MW at approximately 19 minute retention time (Method A)

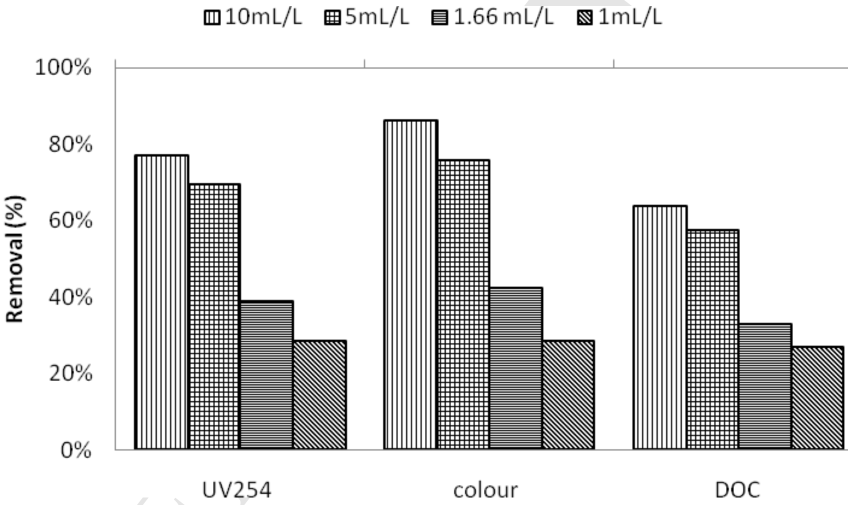


Fig. 7. Percent removal of UV_{254}, Colour and DOC for the different IX treatment concentrations for ETP raw water

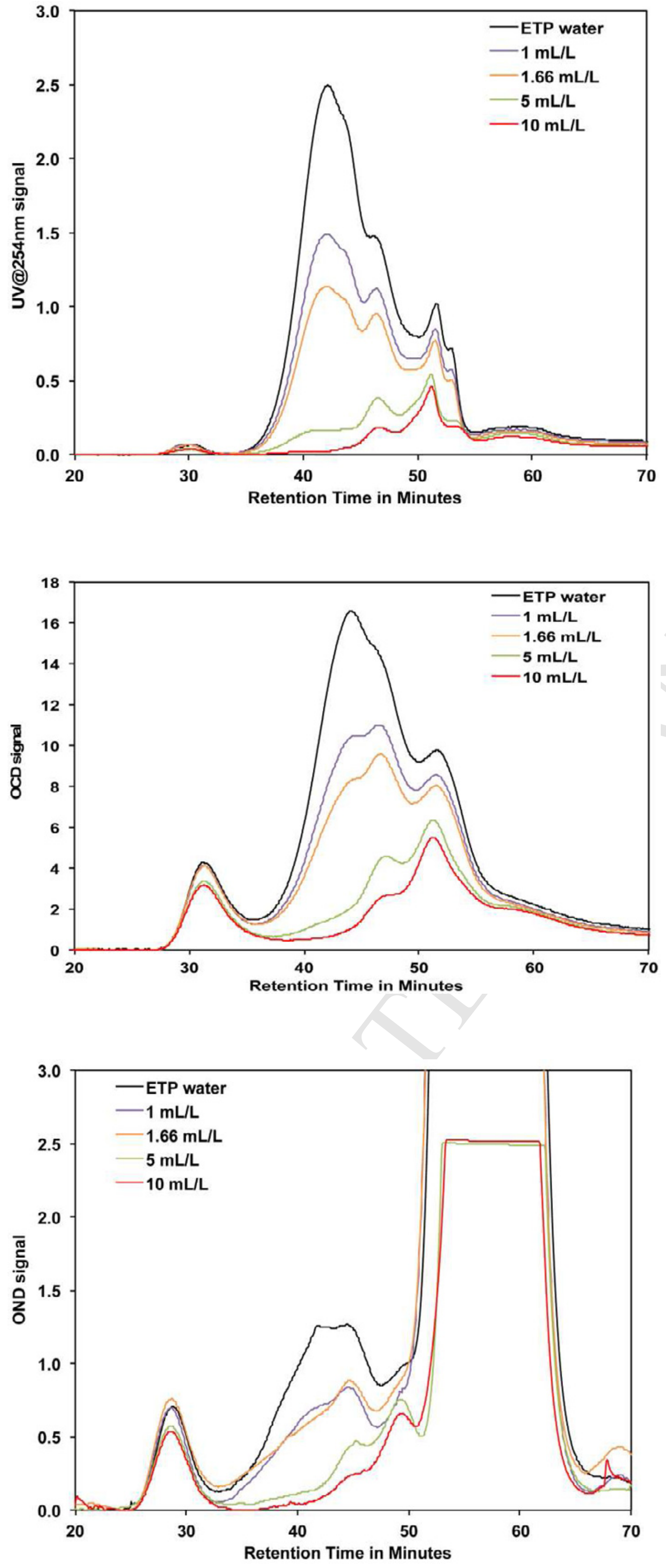


Fig. 8. LC-OCD/UV/OND chromatograms following organic matter adsorption by IX resin (single use) at different doses

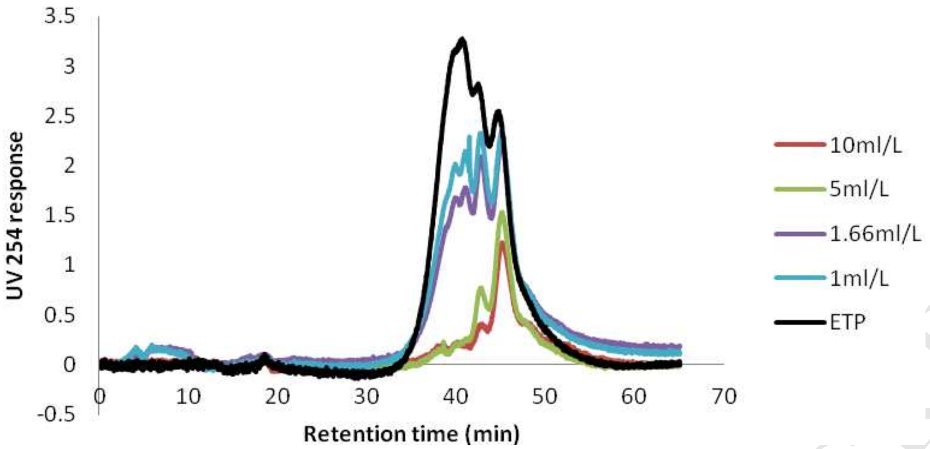


Fig. 9. The removal of UV_{254}-absorbing compounds for the different IX doses applied for ETP wastewater (Method A)

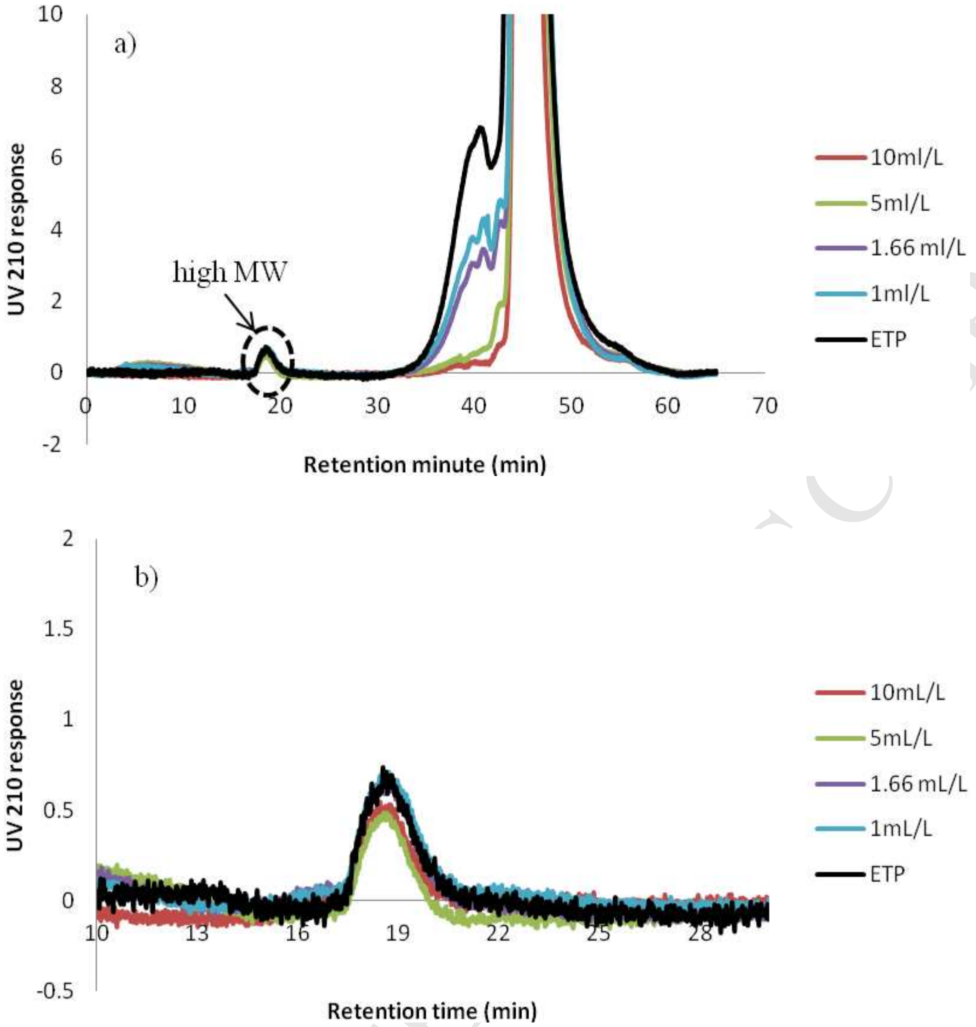


Fig. 10. The removal of UV_{210}-absorbing compounds for the different IX doses applied for ETP wastewater a) at all retention time b) highlighting the high MW at approximately 19 minutes retention time

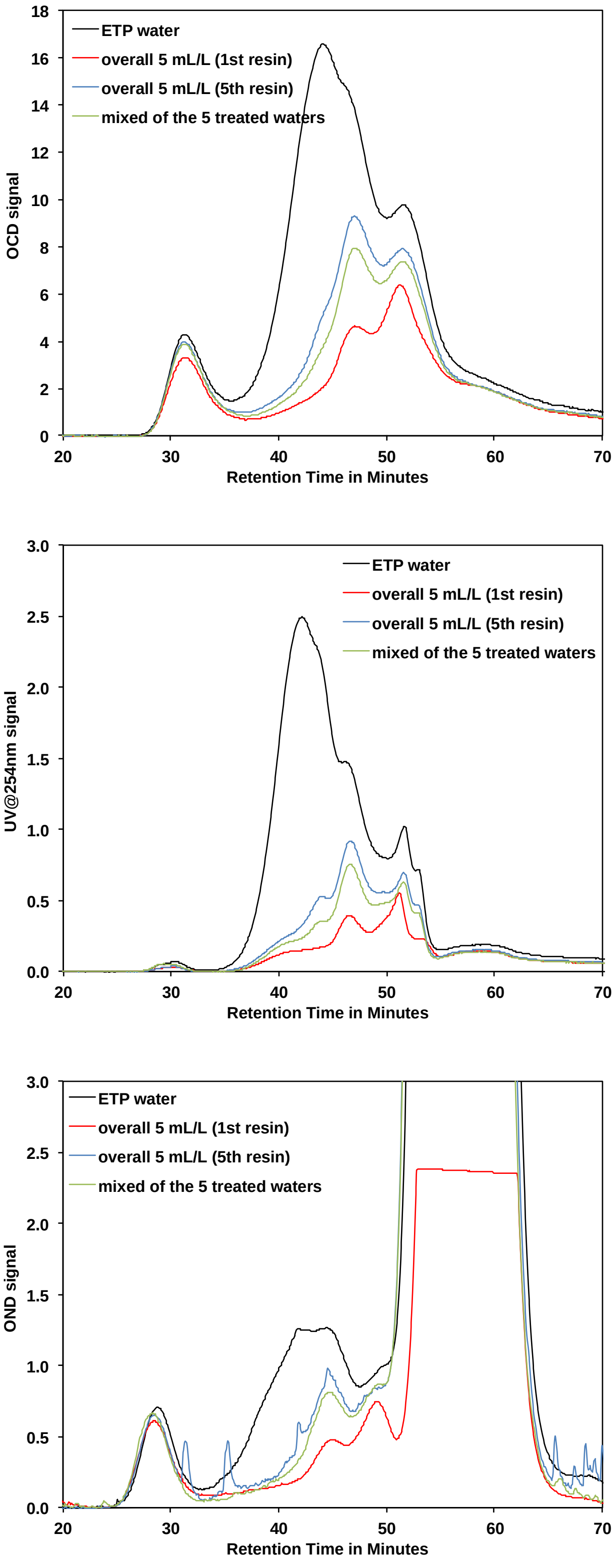


Fig. 11. LC-OCD/UV/OND chromatograms of organic matter adsorption by ion exchange resin at consecutive resin use (overall 1000 BV) for ETP water

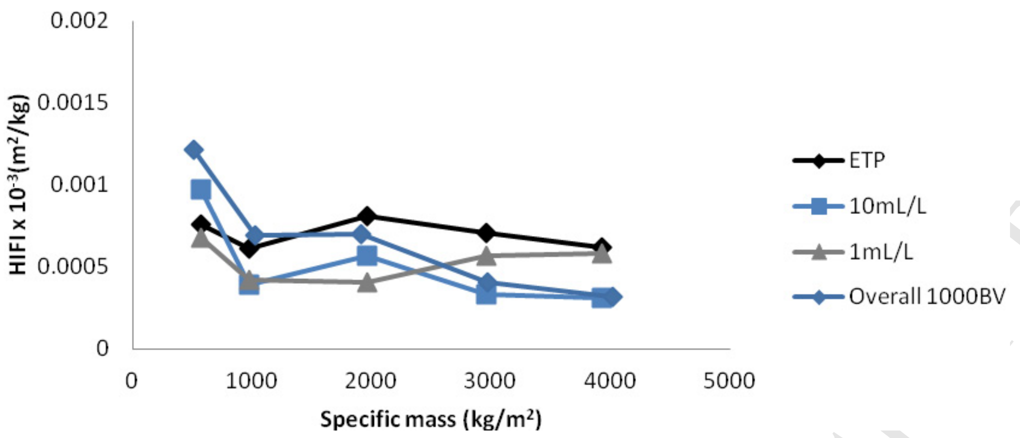


Fig. 12. Plot of HIFI values versus specific mass (kg/m^2) for ETP, 1mL/L, 10mL/L and overall 1000 BV IX treated waters with PP membranes

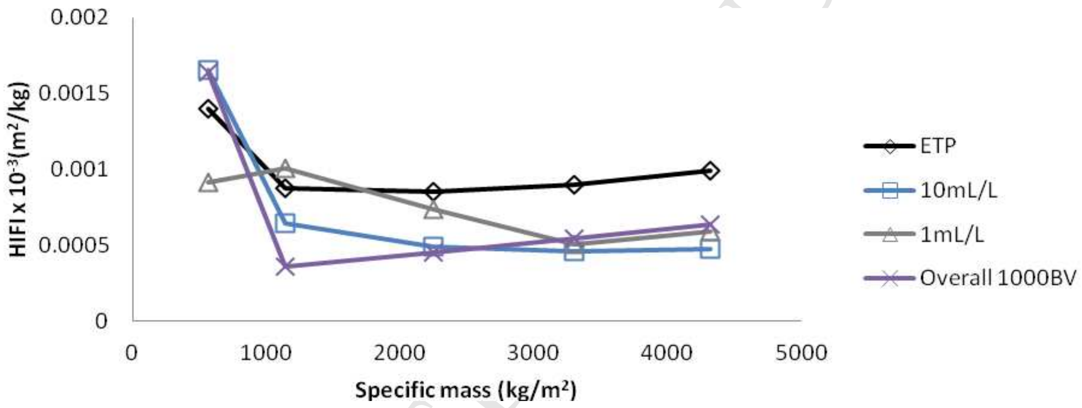
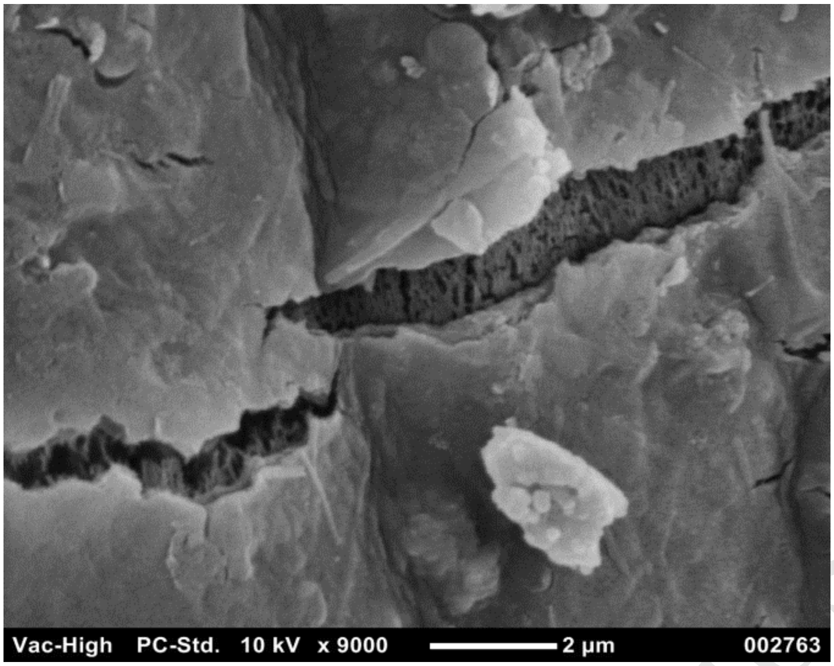


Fig. 13. Plot of HIFI values versus specific mass (kg/m^2) for ETP, 1mL/L, 10mL/L and overall 1000 BV IX treated waters with PVDF membranes

(a)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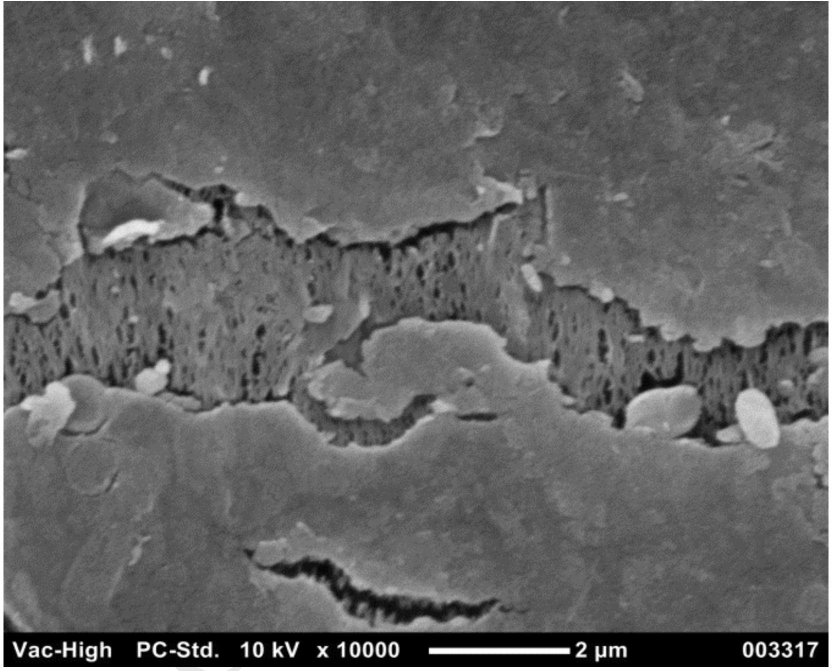
2 µm
002763

(b)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(c)

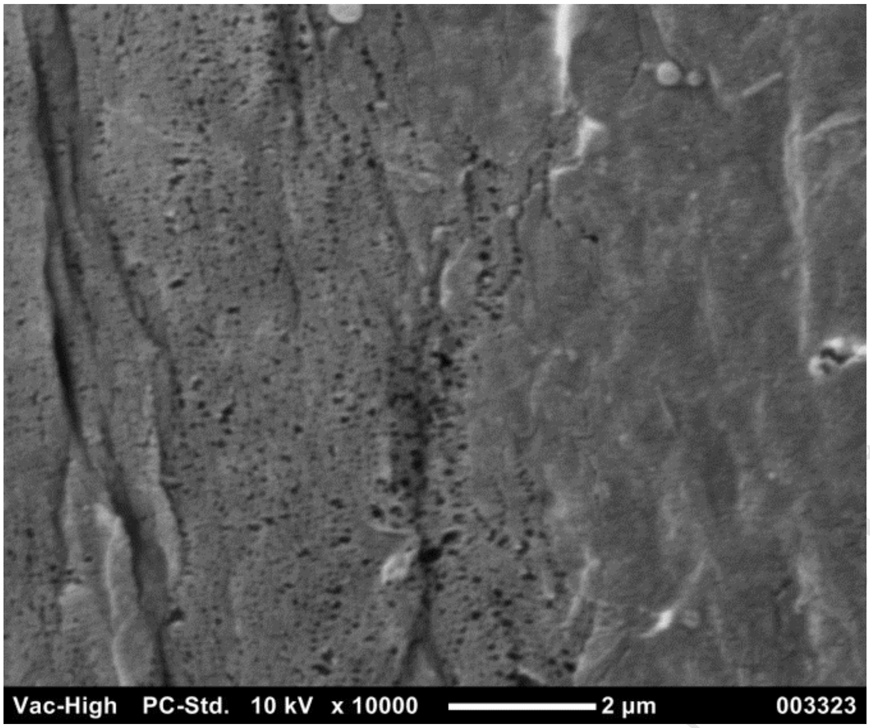

Fig. 14. SEM images representing the membrane surface of a) filtered ETP (b) 1 mL/L IX water filtered (c) 10 mL/L IX water filtered with PVDF membranes