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Understanding the potential for selective natural organic matter removal by ion exchange

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ABSTRACT

Dissolved organic carbon (DOC) removal from a river water source was investigated using ion exchange (IEX), coagulation and membrane filtration. This research linked the variable charge characteristics of the organic compounds present in the source water with removal by IEX and coagulation. The raw water charge density fluctuated considerably (between 5.4 and 10.7 meq mg_{DOC}^{-1}) and controlled removal of the charge loading. Importantly, charge density was not correlated with the organic carbon concentration. The combined IEX and coagulation process reduced the specific DBP-FP (sDBP-FP) of the final water, with values as low as 18 μg mg_{DOC}^{-1} for both haloacetic acids and trihalomethanes. IEX removed a particular fraction of NOM that 1) enhanced coagulation efficiency, providing increased removal of overall DOC; and 2) enabled coagulation to subsequently remove higher levels of specific components of NOM that have a high DBP-FP. The component of NOM removed by IEX that had a positive impact on coagulation was identified to be charged low molecular weight organic compounds of all hydrophobicity levels, resulting in a reduced specific DBP-FP compared to coagulation alone.

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1. Introduction

Natural organic matter (NOM) has increased in many surface waters across the world, which has impacted on the effective operation of drinking water treatment systems (Matilainen et al., 2010). In many cases this has increased the organics loading onto the works above its treatment capacity, meaning that existing assets struggle to remove enough NOM. In addition to aesthetic impacts, process fouling, biofilm formation, and bacterial regrowth in the distribution network, residual NOM can cause the formation of disinfection by-products (DBPs) when disinfectants are added to the water (Pramanik et al., 2017; Winter et al., 2018). Some DBPs are potentially harmful to humans and have been linked to cancer (Richardson et al., 2007). Trihalomethanes (THMs) and haloacetic acids (HAAs) are the DBPs which are most routinely studied. These compounds are typically the DBPs that are dominant by mass and are used as indicators of a wide range of other DBPs (Li and Mitch, 2018). Therefore, the concentration of these compounds in drinking water are regulated worldwide. In the US, THMs are limited to 80 μg L^{-1} and HAA5 at 60 μg L^{-1} while in the European Union THMs are regulated at 100 μg L^{-1}, and a recent proposal for HAA9 of 80 μg L^{-1} has been released (European Commission, 2018; USEPA, 1998).

Ion exchange (IEX) is an increasingly applied process for the reduction of NOM, particularly in circumstances where coagulation alone is unable to achieve the required level of NOM removal. In this process, an anionic exchange resin is used to remove negatively charged organic compounds by the exchange of a counter ion, usually chloride, from the resin surface. A large proportion of NOM carries a negative charge, mostly attributed to acidic functional groups mainly present in an ionic form at pH > 4 (Bolto et al., 2004).

IEX resins can be used in fixed columns or mixed in the water in suspended reactors in commercial systems such as suspended ion exchange (SIX) and magnetic ion-exchange (MIEX) processes (Cornelissen et al., 2009; Watson et al., 2015; Metcalfe et al., 2015). For NOM removal applications, suspended systems have proven to be more effective as a pre-treatment prior to coagulation. This configuration allows treatment of waters containing suspended solids and shorter contact times through increased rates of mass transfer (Kishore and Verma, 2006; Bazri and Mohseni, 2016). In the SIX process, the resin is suspended in the raw water and is separated after a defined contact time in a plug flow contactor. The used resin is regenerated before it is reinjected into the system

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(Shorney-Darby et al., 2014). A reduction in DBP formation potential (DBP-FP) in waters treated by IEX has been observed and some studies have found a similar or even superior reduction of DBP-FP compared to coagulation (Boyer and Singer, 2005; Metcalfe et al., 2015). However, reduction in both overall DBP concentration and the specific THM-FP (mg of DBP per g of dissolved organic carbon (DOC)) by IEX alone can be higher or lower than coagulation depending on the raw water composition (Metcalfe et al., 2015).

When IEX processes are used in combination with coagulation, higher removal of NOM and reduced DBP-FP compared to conventional coagulation has been consistently observed (Boyer and Singer, 2005; Shorney-Darby et al., 2014; Watson et al., 2015). This is because different groups of organic compound are being targeted by the two processes to provide higher combined removal of NOM (Mergen et al., 2009). Several studies have also shown that IEX combined with coagulation reduces the specific DBP-FP, and some have found a further reduction than that by optimised coagulation alone (Drikas et al., 2011), in certain cases even when there was no reduction in the specific DBP-FP after the IEX stage (Metcalfe et al., 2015).

Additionally, the amount of coagulant used has been shown to be considerably reduced in a combined IEX coagulation process (Crittenden et al., 2012) and an increase in floc strength was found by Jarvis et al. (2008). This suggests selective removal of organic compounds by IEX that improves coagulation performance. However, this may be occurring in a number of different ways and understanding these mechanisms is an important knowledge gap.

Investigations on DOC removal by IEX often look at MW and hydrophobicity to understand removal behaviour (Grefte et al., 2013). However, information linking NOM removal by IEX the charge characteristics of the organic compounds present in real water sources is often overlooked. This is important given that NOM charge density is seasonally variable and can change rapidly and may not always be coincidental with a change in UV_{254} or DOC concentration, often the main way by which IEX dosing is controlled. In the current work the combined influence of NOM hydrophobicity, MW and charge were investigated to understand the selective removal of organics by IEX to determine the importance of variable charge load and charge density on the removal process.

2. Materials and methods

An IEX pilot plant was used consisting of suspended ion exchange (SIX process from PWN Technology, Netherlands), in-line coagulation and ceramic membrane filtration (CCMF) (Supplementary Information, Figure S1). This was compared with a full scale water treatment works (WTW) comprising coagulation and membrane ultrafiltration. Water feeding both plants was from a holding reservoir containing water from the river Dee at Invercannie WTWs. This study was carried out between May and October 2017, following a commissioning and optimisation stage. Fresh resin was added to the SIX at the start of the study to enable understanding of the change in treatment performance as the resin was used multiple times. In this period, the pilot plant was operated with both units (SIX + CCMF). For a period of three weeks (14th August till 04th September) no SIX pre-treatment was used and raw water was directly coagulated and treated by the membrane (CCMF).

2.1. SIX and CCMF pilot plant

The process was run with and without the SIX process, enabling understanding of the influence of IEX on NOM removal by coagulation and membrane filtration. The IEX resin was a gel-type, strongly basic anion exchange resin with an acrylic quaternary amine backbone in the chloride form (Lewatit S5128, Lanxess, Germany). The resin was selected based on a previous pre-screening process for the water source. Raw water contacted with the resin under plug flow conditions at a flow rate of 7 $m^3 h^{-1}$. A resin concentration of 25 mL L^{-1} was applied at a contact time of 30 min based on data from a preliminary study for the water. The resin dose, contact time and flow was kept constant for the duration of the study. The resin was separated from the water by a lamella contactor and regenerated with sodium chloride (25 g L^{-1} Cl^-). Following IEX, water was adjusted to pH 6.4 using caustic soda and sulphuric acid. Polyaluminium chloride (PACl) was added as a coagulant at a dose based on the UV transmittance (UVT) of the water from an online solids-compensated UVT unit (Spectro:lyser, S:CAN, Austria). The PACl had a specific gravity of 1.22, a basicity of 37.9% and an aluminium content of 5.3%. The coagulant dose was calculated from algorithms developed from jar testing of the water (Table S1). The average coagulant dose for SIX + CCMF was 2.13 mg L^{-1} or 0.47 mg_{Al3+} mg_{DOC}^{-1} (range 0.19–6.04 mg L^{-1} or 0.07–0.82 mg_{Al3+} mg_{DOC}^{-1}) and for CCMF 3.73 mg L^{-1} or 0.75 mg_{Al3+} mg_{DOC}^{-1} (range 1.58–6.06 mg L^{-1} or 0.44–1.19 mg_{Al3+} mg_{DOC}^{-1}). After in-line coagulation (ILCA), the water was filtered through a ceramic membrane (pore size 0.1 μm, surface area 25 m^2) at a flux of 150–250 L m^{-2} h^{-1} (LMH). The membrane was backwashed (BW) after loading between 50 and 167 L m^{-2} and underwent an enhanced BW (EBW) after 500–1500 L m^{-2}. The EBW was carried out using NaOCl (100 mg L^{-1} free Cl_2) or H_2O_2 (100 mg L^{-1}, pH 2) (details in Table S1). Samples were taken after treatment by IEX and then following membrane treatment.

2.2. WTW

The WTWs operated at an average of 39 ML day^{-1}. Raw water was adjusted to pH 6.9 using lime. PACl was added as the coagulant and had the same properties as that used in the pilot plant. PACl dose was automatically optimised based on raw water colour, approximately 1.2 mg L^{-1} Al^{3+} per 20 hazen, resulting in an average of 1.62 mg L^{-1} or 0.37 mg_{Al3+} mg_{DOC}^{-1} (range 0.35–3.34 mg L^{-1}; 0.22 to 0.70 mg_{Al3+} mg_{DOC}^{-1}). The coagulated water was filtered from out-to-in, using polyvinylidene difluoride S10V Evoqua membranes with a pore size of 0.04 μm. A total membrane surface area of 11,048 m^2 was available (6 cells, containing 396 elements each) allowing a flux of 21.4–30.2 LMH. Samples of raw water and permeate were taken for analyses.

2.3. Sample analysis

Samples for UVA_{254} measurement were pre-filtered with a 0.45 μm syringe filter and analysed using a Hach DR6000 spectrophotometer (Hach Lange, Germany, 5 cm quartz cuvette cell). DOC was measured using a non-purgable organic carbon method on a Shimadzu TOC-L analyser (EQS 24H) or a Skalar Formacs HT TOC analyser. All samples were passed through a 0.45 μm filter prior to analysis. A series of XAD7 and XAD4 resin were used to separate the DOC into hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI) fractions using adapted methods described in Bond et al. (2010). HAA- and THM-FP were determined from pre-filtered (0.45 μm) samples diluted to 1 mg L^{-1} DOC. Water was spiked with NaOCl to give 5 mg L^{-1} free chlorine and stored for 7 days in the dark at 25 °C. After quenching with thiosulfate, the samples were analysed with Gas chromatography–mass spectrometry. Liquid chromatography-organic carbon detection (LC-OCD) was carried out to determine the relative molecular weight distribution of organic compounds in water as it passed through various treatment stages. Samples were analysed by Het Water

Laboratorium (Haarlem, Netherlands) according to the methods described in Huber et al. (2011).

Zeta potential and charge density experiments were determined using a zetasizer (Malvern Nano Series, Worcestershire, UK). For zeta potential measurements, samples were filled in a polystyrene latex folded capillary cell, equilibrated to 25 °C and measured three times with a minimum of 10 and a maximum of 100 runs. Charge determinations were carried out using an adapted method of Kam and Gregory (2001). Polydiallyldimethyl ammonium chloride (PDADMAC) was purchased from Sigma-Aldrich (Dorset, UK) and diluted to obtain a concentration of 416 mg L^{-1}. For SIX treated samples of DOC ≤1.3 mg L^{-1} a further dilution to 8.32 or 41.6 mg L^{-1} was applied. The solution was delivered stepwise to a stirred 15 mL sample adjusted to pH 7 by an autotitrator MPT-2 with a 3-ch degasser (Malvern), resulting in PDADMAC concentrations between 1.0 and 20.0 mg L^{-1} for raw water and 0.04–15.0 mg L^{-1} for SIX treated water. After each addition the solution was pumped into a folded capillary cell and zeta potential was measured. The point of zero charge (PZC) was determined by fitting a linear regression through the data points of at least three measurements and the PDADMAC concentration was converted into charge load using a charge density of 6.2 meq g^{-1} for PDADMAC. Charge density was calculated by normalising the meq L^{-1} concentration to the DOC of the sample to give meq per g DOC. Charge measurements of the final water were not performed because particulates were removed from the water through the micro- and ultrafiltration processes used.

3. Results and discussion

The raw water was of low turbidity, 0.2–1.4 NTU, and low alkalinity, ranging between 10 and 29 mg_{HCO3} L^{-1}, with nitrate and sulphate concentrations from 0.50 to 1.28 mg_{NO3-} L^{-1} and 1.9–4.5 mg_{SO42-} L^{-1}, respectively (Table 1). The raw water entering the WTWs and the pilot plant fluctuated between 1.5 and 10.1 mg L^{-1} for DOC and 4.7 to 42.0 m^{-1} for UVA (Fig. 1). The SIX process removed an average of 1.5 mg L^{-1} of DOC and 6.8 m^{-1} of UVA, with a maximum removal of 2.4 mg L^{-1} of DOC and 12.1 m^{-1} UVA. The removal of NOM generally tracked the pattern of the raw water, indicating that under the operating conditions, the DOC concentration did not influence the removal capacity of the resin. The DOC concentration in the final water after SIX + CCMF had a mean of 0.7 mg L^{-1}, with values as low as 0.2 mg L^{-1} and a maximum of 1.4 mg L^{-1} (UVA 0.2 to 2.6 m^{-1}). This was considerably lower than the concentrations found in the final water for both the CCMF and the WTWs, which had a mean DOC concentration of 1.3 mg L^{-1} (range 0.5–2.2 mg L^{-1}) and 2.1 mg L^{-1} (range 1.4–2.8 mg L^{-1}), respectively.

A cumulative probability plot showed that 82% of all DOC measurements were below 1 mg L^{-1} for SIX + CCMF while only 17% of the DOC measurements were below this value for CCMF and only 46% were below 2 mg L^{-1} for the WTW (Fig. 2).

Table 1
Raw water physico-chemical characteristics.

Parameter	Unit	Minimum	Maximum	Average
DOC	(mg_C L^{-1})	1.5	10.1	4.4
UVA	(m^{-1})	4.7	42	18.1
Turbidity	(NTU)	0.2	1.4	0.6
Conductivity	(μS cm^{-1})	33	74	51
pH	Hydrogen ion	6.8	7.9	7.3
Alkalinity	(mg_{HCO3-} L^{-1})	10	29	20
Chloride	(mg_{Cl-} L^{-1})	4	8	6
Nitrate	(mg_{NO3-} L^{-1})	<0.5	1.28	0.74
Sulphate	(mg_{SO4-} L^{-1})	1.9	4.5	3.1

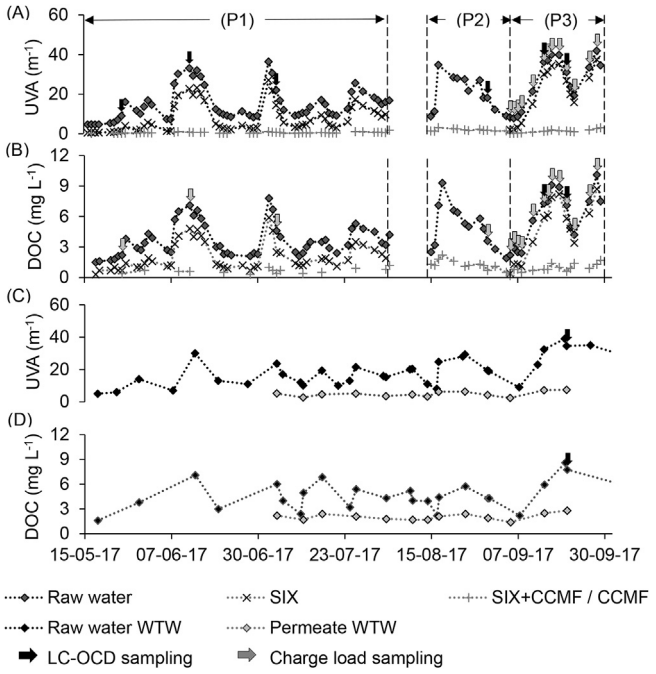


Fig. 1. Time series data for DOC and UVA removal for the pilot plant in (A) and (B) before treatment (raw water), after SIX treatment (SIX effluent) and after coagulation with membrane filtration (final water). Period (P1) operation with SIX and coagulation with membrane filtration (SIX + CCMF); P2 operation with CCMF only (no SIX pre-treatment); P3 operation with SIX + CCMF. UVA_{254} (C) and DOC (D) of samples from Invercannie WTW before treatment and after coagulation and membrane filtration (permeate WTW).

Robustness of DOC removal was evaluated using an adjusted method described by Jarvis et al. (2008). The steepness of the slope in the linear region of the cumulative probability curve between 15 and 85% was used to evaluate robustness, where a steeper slope indicates a more robust system (Fig. 2). Comparison of the slopes identified that SIX + CCMF was 34% more robust than CCMF and 69% more robust than the WTW, showing that the SIX + CCMF process had a much narrower range around this lower mean value.

Additionally, the coagulant dose was 30% lower when SIX + CCMF was used compared to CCMF. This is in agreement with previous results where reductions of coagulant of up to 50–60% have been seen when IEX was used upstream of coagulation (Grefte et al., 2013).

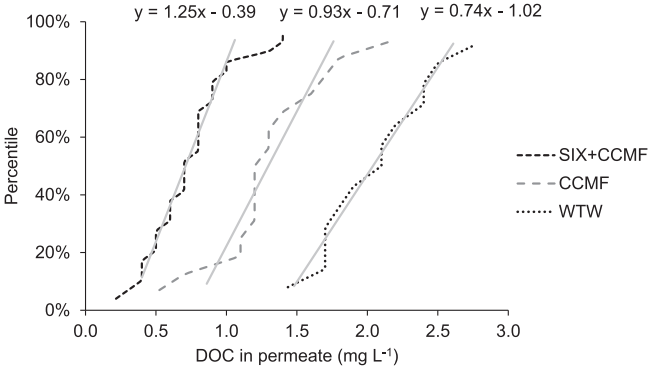


Fig. 2. Robustness of the different treatment methods shown as linear regressions (between 15 and 85%iles) in the cumulative frequency plot of the DOC in final water of SIX + CCMF, CCMF and permeate from the WTW.

The reduction in DOC in the treated water was generally concurrent with a decrease in the DBP-FP. While the proportion of the SIX-removed NOM decreased with increasing NOM load due to limitations in the capacity of the resin for a consistent resin dose, the overall improvements in DOC and sDBP-FP were still observed following subsequent coagulation. There was a strong positive linear relationship between the raw and SIX treated water THM and HAA-FP (Fig. 3A and B). For example, raw water HAA- and THM-FP of 260 and 196 μg L^{-1} were reduced to 30 and 32 μg L^{-1} while a raw water DBP-FP of 2677 and 1525 μg L^{-1} for THMs and HAAs were reduced to 2210 and 1366 μg L^{-1}. This can be attributed to the lower relative NOM removal at higher initial concentrations, which were 2.4 and 8.6 mg L^{-1} DOC for the described cases. For the SIX + CCMF, a weaker but positive relationship was seen between the raw and treated water. However, overall the concentration of DBPs was lower than for all of the other treatment processes, regardless of the incoming DBP-FP. HAA- and THM-FP were measured as low as 9 and 7 μg L^{-1} with an average of 30 and 33 μg L^{-1}, respectively. Comparatively, the DBP-FPs obtained in the final water for CCMF and WTW as a function of the raw water DBP-FPs were consistently higher than for the final water of SIX-CCMF, demonstrating the benefit of the pre-treatment. This was particularly evident since the downstream coagulant dose to DOC ratio was much lower for the IEX treatment compared to CCMF: 0.47 and 0.75 mg_{Al3+} mg_{DOC}^{-1} respectively. The lowest HAA- and THM-FP values observed for CCMF were 52 and 57 μg L^{-1} and for the WTW 347 and 269 μg L^{-1}, respectively.

IEX treatment alone was not shown to reduce the sDBP-FP for variable incoming water quality with both the sHAA-FP and sTHM-FP being similar to the incoming water quality (Fig. 3C and D). However, the final water from the SIX + CCMF had much lower sHAA and sTHM-FP than all treatments. For example, the treated water from SIX + CCMF had sHAA and sTHM-FP of 18–68 μg mg_{DOC}^{-1} (mean 39 μg mg_{DOC}^{-1}) and 18–65 μg mg_{DOC}^{-1} (42 μg mg_{DOC}^{-1}) respectively. The mean sHAA-FP concentration was 41 and 79% lower compared to CCMF and SIX while the average sTHM-FP was 35 and 65% lower, respectively. Comparatively, the average permeate sHAA-FP and sTHM-FPs from the WTWs were 107 ± 16 μg mg_{DOC}^{-1} and 80 ± 7 μg mg_{DOC}^{-1}.

The results suggest that IEX plays a number of roles in

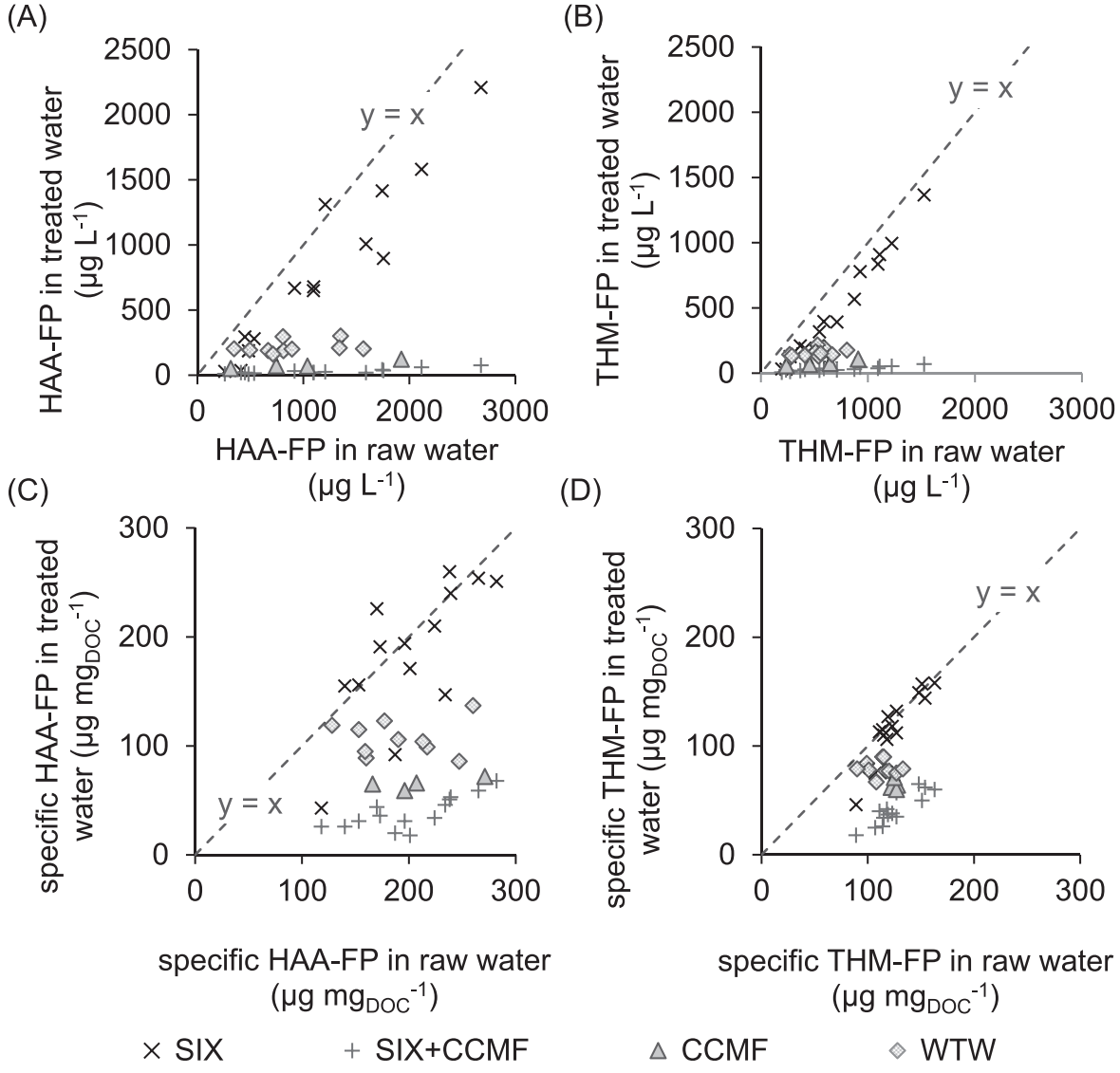


Fig. 3. DBP-FP of the water treated by different steps/methods as a function of their raw water DBP-FP for HAAs (A) and THMs (B), and DBP reactivity expressed as specific formation potential of the water treated by different steps/methods as a function of their raw water sDBP-FP for HAAs (C) and THMs (D).

improving NOM removal by eliminating a particular fraction of NOM that 1) enhances coagulation efficiency, providing increased removal of overall DOC; and 2) enables coagulation to subsequently remove higher levels of specific components of NOM that have a high DBP-FP. The following section investigates the key features of NOM that controls its removal and the DBP-FP dealing in turn with NOM hydrophobicity, MW and charge.

With respect to hydrophobicity (Figs. S2A and S2B), the hydrophobic compounds (HPO) represented the largest fraction in the raw water (62 ± 6%), consistent with results reported in previous studies for similar types of NOM dominated water sources (Boyer and Singer, 2005; Sharp et al., 2006). The transphilic (TPI) fraction accounted for 22 ± 4% and the hydrophilic (HPI) fraction 16 ± 3% of the overall DOC. After SIX treatment, the proportions of NOM fractions did not change considerably. This was also found when other NOM specific suspended IEX resins have been investigated (Boyer and Singer, 2005), suggesting that no preferential removal of any of the fractions occurred. When the SIX effluent was treated with CCMF, the proportion of the HPI fraction increased to 43 ± 6%, while the HPO fraction was reduced to 35 ± 4%. This was a result consistent with other coagulation studies that have shown preferential removal of hydrophobic NOM by coagulation (Watson et al., 2015). Similar results to the overall DOC removal were seen for the DBPs, with no correlation between the removed DOC of the different fraction and a reduction in the sDBP-FP (Fig. S3). This is in line with researchers who have reported that all fractions contribute to the DBP-FP (Hua and Reckhow, 2007).

Removal of NOM by IEX is primarily driven by charge, which is present to differing degrees in all of the hydrophobicity fractions (Sharp et al., 2006). Removal of these organic compounds, or a fraction of, may be important in reducing significant DBP precursors. However, these results show that fractionation does not have sufficient sensitivity to show the NOM which is selectively removed by IEX.

Molecular size is important in controlling removal by IEX due to size-exclusion effects (Bazri and Mohseni, 2016). The importance of the relative MWs of NOM on removal across the SIX and CCMF processes was investigated using LC-OCD. The LC-OCD chromatogram profiles for the different processes before and after treatment show 4 peaks (Fig. 4). Peak 1 represents molecules >10 kDa and peak 2, 3 and 4 are associated with molecular weights of ~1 kDa, 0.3–0.5 kDa and <0.35 kDa, respectively (Huber et al., 2011). For all raw water samples, peak 2 was dominant, showing that the bulk of the DOC to be of medium molecular weight, around 1 kDa. The profile presented in Figure A shows a raw water with a DOC concentration of 6.5 mg L^{-1}, while the profiles in Figure B–D were from samples ranging between 2.3 and 7.4 mg L^{-1} DOC.

Integration of the peaks enabled a comparison of the removal of NOM by size to be made for the different treatment systems. When the raw water DOC concentration was low (2.3 mg L^{-1}), all peaks were substantially reduced (Fig. 4B). In this case the area of peak 2 and 3 were reduced by 83% and 78% by SIX, respectively, while peak 1 showed a reduction of 19%. Removal of peak 2 and 3 was expected as these smaller molecules diffuse more easily into the pores of the resin and are not restricted to exchange sites on the outside, whereas larger molecules are rejected due to size exclusion (Winter et al., 2018). Lower removal of organic compounds around peak 4 (40%) seems contradictory to this statement. However, as has been noted it is not only size that defines the removal, but also charge is of importance. Huber et al. (2011) reported elution of neutral LMW NOM around peak 4 (elution time of ≥60 min), suggesting these organic compounds carry little charge. However, peaks 2 and 3 have been associated with charged organic compounds (Shorney-Darby et al., 2014). For higher DOC concentrations (6.5 mg L^{-1}, Fig. 4A), the removal for all peaks was much less pronounced. The removal obtained for peaks 2, 3 and 4 were 13%, 20% and 17%, respectively. This can be explained by the limited capacity of the resin and possible blockage of the resin surface by large molecules at high DOC concentrations.

The water profile for SIX + CCMF showed a reduction of peak 1 and 2 by 88 and 100% compared to the SIX effluent showing the preferential removal of HMW fractions by coagulation (Fig. 4A). These results are consistent with those seen in the literature (Metcalfe et al., 2015). Likewise permeate of the WTW (Fig. 4D), showed high removal of the HMW fraction shown in peak 1 (74%) and peak 2 (72%).

Overall, organic compounds represented in peaks 3 and 4 were targeted more effectively by IEX, shown by their consistently lower combined DOC values in SIX + CCMF compared to CCMF treated water, across a broad range of water qualities (2.3–7.4 mg L^{-1}) (Fig. S4). This was further evidenced by determining the proportion of removed DOC for each of the different peaks from the

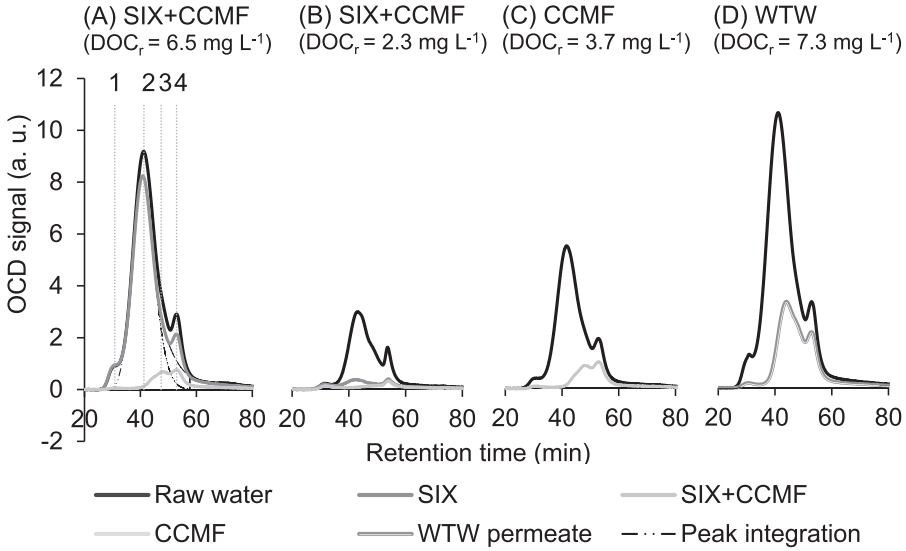


Fig. 4. Selected LC-OCD chromatograms of the waters in the SIX + CCMF process for high (A) and low (B) raw water DOC concentrations; LC-OCD chromatogram of raw and final water for CCMF treatment (C); LC-OCD chromatogram for raw water and permeate of WTW (D); DOC_r = raw water DOC.

chromatographed DOC (CDOC) (Fig. 5). Organic compounds represented in Peak 2 had the highest proportion of the removed CDOC for SIX (76%), while peaks 3 and 4 accounted for 15% and 7%. For CCMF following SIX pre-treatment, 91% of the removed CDOC was from peak 2, while the values for peak 3 and 4 were both only 3%. This confirms that IEX has more specific removal of these LMW compounds compared to coagulation. The profiles for CCMF compared to the WTWs were very similar. This shows that although the combined process had higher overall removal, the compounds being targeted by the coagulation/membrane process was similar, a result consistent with the fractionation data. The relative MW analysis showed better removal of lower MW organic compounds compared to coagulation processes. However, IEX was effective in removing some organic compounds from all MW fractions apart from peak 1, the highest MW NOM as a result of size exclusion of these compounds.

The charge load (CL) of the raw water was between 15.6 and 82.7 μeq L^{-1} and the charge density (CD) ranged from 5.4 to 10.7 meq mg_{DOC}^{-1} showing variable charge composition of the raw water over the duration of the trial (Fig. 6). These values are in line with CDs measured for other NOM laden water sources ranging from 0.3 to 16.7 meq mg_{DOC}^{-1} (Bazri and Mohseni et al., 2016; Boyer et al., 2008; Mergen et al., 2009). As the CL in the raw water increased, the residual CL in the SIX increased in a linear fashion (Fig. 6). This showed a limit to the amount of charge that could be removed by the resin, less than 0.1% of the theoretical resin capacity (1.25 meq mL^{-1}). Similarly low removal was reported by Mergen et al. (2009), who investigated charge load removal from different waters using magnetic IEX resin (capacity 0.5 meq mL^{-1}) and found charge load removals of up to 31 μeq L^{-1}, utilising 0.6% of the resin capacity. This low utilisation was explained by organic compounds blocking the surface and internal pores of the resin. In addition, some compounds may be missed by the charge density method. For example, small compounds such as glutamic acid have been shown to be difficult to detected using the described titration method. Additionally, anions (sulphate, nitrate, hydrogen carbonate) compete with organic molecules (Boyer et al., 2008; Liu et al., 2017) and the required charge to remove these in the water source investigated here was calculated to be up to 2.9% of the resin capacity.

There was a weak positive correlation between raw water charge load and the removed charge load ($r^2 = 0.41$) (Fig. 6). This showed that when there was more charge in the water, the SIX process was able to remove more of this charge load. As such, when a shift in the concentration of charged molecules and/or charged functional groups on individual molecules occurs in the raw water, this will influence the removal of NOM, even when the DOC concentration of the raw water does not change. It is therefore helpful to normalise the charge in the raw water to DOC and compare this with the amount of charge removed (Fig. 7). There was a stronger relationship between these parameters ($r^2 = 0.67$) with higher charge density showing higher charge removal. For example when the CD in the raw water was 7.7 meq g_{DOC}^{-1} the charge load removal was 13.0 μeq L^{-1}, while for a CD of 10.4 meq g_{DOC}^{-1} the charge load removed was 21.9 μeq L^{-1}. In both cases the raw water DOC was 7.5 mg L^{-1}. This aligns with the fact that more highly charged molecules are preferentially removed due to the stronger affinity to the ion exchange resin.

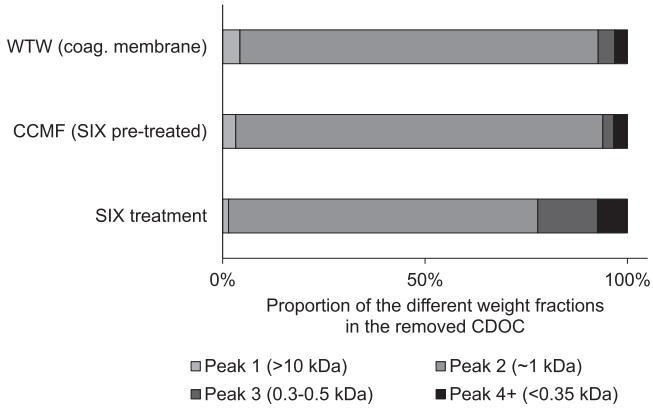


Fig. 5. Comparison of the proportion of the size fractions of the removed CDOC (sum of peak 1 to 4+) for the different treatment steps/methods.

Studies investigating removal of model compounds by IEX have shown strong relationships between high removal and high charge density. For example, small organic acids such as citric and benzoic acids show high levels of removal (Finkbeiner et al., 2017). Given that LMW organic compounds were preferentially removed by IEX, it is plausible to consider that carboxylic acid compounds with high CD are well represented in the LMW fraction. The scatter around the relationship between CD and CL removal was attributed to the influence of the size of organic molecules. Large molecules with significant charge density will be less well removed due to size exclusion effects. This shows the importance of considering both NOM charge and molecular size when considering removal.

However, these results show that measuring charge density in the raw water is a more suitable parameter that can be used to determine removal of NOM by IEX compared to measurements such as DOC and UVA, where there was no correlation with removal (Fig. 7). This was presumably due to the fact that different concentrations of uncharged NOM was present in the water. This is an important observation as many WTWs use online instruments that measure UV or DOC to control IEX resin dose. By using CD it would be possible to more effectively control the IEX dose in response to the change in charge load from the raw water, which as has been shown is not always commensurate with an increase in NOM concentration.

There was no obvious relationship between the DBP-FP and the charge density following the SIX process (Fig. S4). This further supports the view that IEX does not always directly reduce DBP reactivity, but facilitates better removal of the DBP precursors by coagulation. Previous work has shown that small organic acids inhibit the hydrolysis of aluminium coagulants by creating a stable complex between the metal salt and the ligands, particularly dicarboxylates such as citrate and oxalate (Violante and Violante, 1980). More recent work on the removal of humic acid by polyaluminium chloride has shown a detrimental effect when certain counter ions (including oxylate, citrate and malate) were present (Lin and Lee, 2013). Complexation of these anions with the coagulant was the mechanism proposed to explain a deterioration in the polyaluminium cluster structure, reducing the removal of the humic acid. Jarvis et al. (2015) showed that the presence of small acids such as aspartic and oxalic acid reduced coagulation efficiency, and some compounds (including aspartic acid) restricted floc growth. Organic compounds such as these would be effectively removed by IEX, allowing the coagulant to work more effectively on other compounds, such as larger humic acid compounds, which also tend to have higher DBP-FP.

Therefore, the removal or reduction of specific compounds by IEX is believed to be responsible for improved coagulation of the remaining DOC by enhancing the interactions of the coagulant with the remaining organic compounds, improving floc formation and size, and increasing the available surface for adsorption of organic compounds. The present study has extended our understanding further by elucidating that these specific organics are charged compounds of LMW with hydrophilic, transphilic and hydrophobic character. For future investigation, analysis of the charge of the

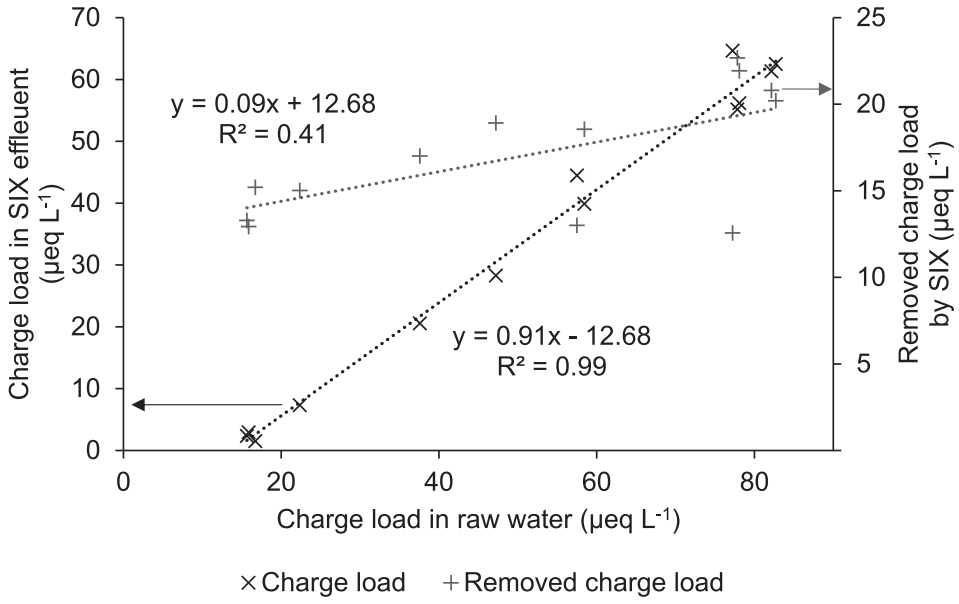


Fig. 6. Relationship between the charge load in the raw water and in the SIX treated water, along with the charge load removed.

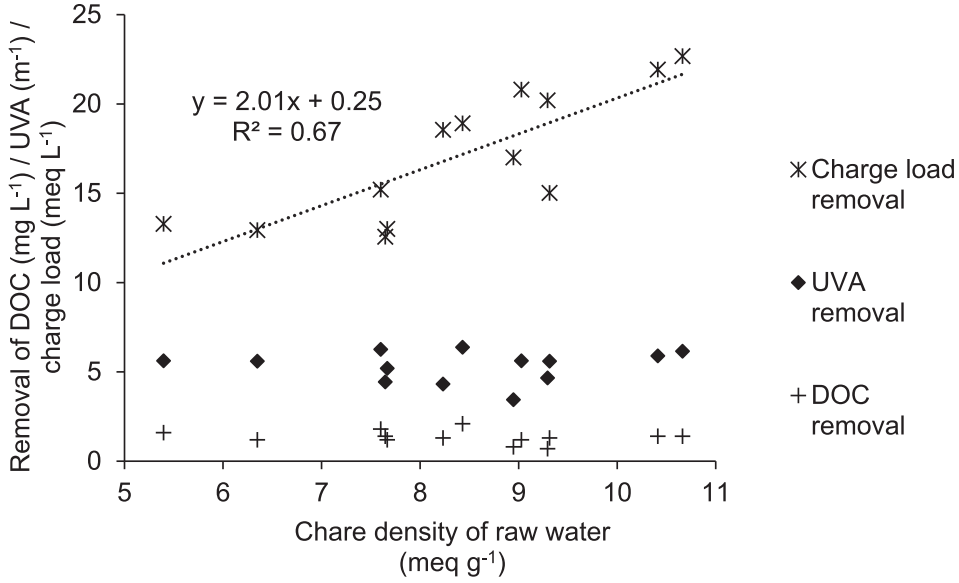


Fig. 7. Relationship between the charge density in the raw water and removed charge load, UVA and DOC by SIX.

different size fractions could give a more detailed view on the interaction between molecular weight and charge density of organic compounds on their removal and the influence on the DBP-FP in the final water. The cost of implementing SIX with in-line coagulation and CCMF has been estimated to be equal or lower than that of building a conventional clarification water treatment system (Metcalfe et al., 2015). Additional operational cost required for chemicals in the regeneration of the resin is compensated by a reduction in the required coagulant dose before the membrane. A smaller footprint is needed for the SIX + CCMF process compared to conventional processes. As a result, the economical case for implementing ion exchange combined with membrane processes makes ion-exchange an attractive option for enhanced removal of DBP precursors.

4. Conclusions

DOC and UVA of a fluctuating water source were successfully reduced using a novel suspended ion exchange technology upstream of coagulation and ceramic membrane filtration. The process gave improved performance compared to coagulation-filtration in both a pilot plant and at full-scale in terms of removal of sum parameters (DOC, UVA) as well as the (specific) formation potential of DBPs. The following conclusions could be drawn about the selective removal of organic compounds by IEX:

- Analysis of hydrophobic, transphilic and hydrophilic fractions revealed that there was no considerable change in the distribution of the fractions after SIX treatment compared to the raw

water. Hydrophobicity was not shown to be contributor to removal by ion exchange.
- IEX preferentially removed compounds with a molecular weight around 1 kDa.
- Higher charge densities improved the removal of charge load. The results showed that charge describes removal behaviour better than other more normally monitored parameters.
- The results of the combined analyses indicate that IEX removes specific charged organics of low molecular weight, regardless of their hydrophobicity and this improves the coagulation process resulting in a reduced sDBP-FP.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2018.09.042.

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