

# Removal of disinfection by-product precursors by coagulation and an innovative suspended ion exchange process

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## Abstract

This investigation aimed to compare the disinfection by-product formation potentials (DBPFPs) of three UK surface waters (1 upland reservoir and 2 lowland rivers) with differing characteristics treated by (a) a full scale conventional process and (b) pilot scale processes using a novel suspended ion exchange (SIX) process and inline coagulation (ILCA) followed by ceramic membrane filtration (CMF). Liquid chromatography-organic carbon detection analysis highlighted clear differences between the organic fractions removed by coagulation and suspended ion exchange. Pretreatments which combined SIX and coagulation resulted in significant reductions in dissolved organic carbon (DOC), UV absorbance (UVA), trihalomethane and haloacetic acid formation potential (THMFP, HAAFP), in comparison with the SIX or coagulation process alone. Further experiments showed that in addition to greater overall DOC removal, the processes also reduced the concentration of brominated DBPs and selectively removed organic compounds with high DBPFP. The SIX/ILCA/CMF process resulted in additional removals of DOC, UVA, THMFP, HAAFP and brominated DBPs of 50, 62, 62, 62% and 47% respectively compared with conventional treatment.

25    Keywords: ceramic membrane filtration, disinfection by-products,

26    Ion exchange, natural organic matter

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## Introduction

Optimised coagulation is the standard method for the removal of NOM and is effective in the removal of high molecular weight (HMW), hydrophobic and aromatic NOM compounds (Drikas *et al.* 2003; Fearing *et al.* 2004). NOM that is of low MW (LMW) and hydrophilic in nature is not as amenable to removal by coagulation. It is therefore available to react with chlorine to form unwanted disinfection by-products (DBPs) (Mergen *et al.* 2009), some of which are potentially harmful to human health (Richardson and Ternes, 2014). Water treatment works (WTWs) faced with treating water containing high levels of natural organic matter (NOM), or difficult to remove organic matter, are therefore finding meeting DBP regulatory requirements much more challenging using conventional treatment methods. Various strategies exist for reduction of DBPs in treated waters, such as reducing disinfectant dose, switching disinfection method or reducing DBP levels following disinfection, however, arguably the best method is to reduce the DBP precursor concentration prior to disinfection (Bond *et al.* 2010).

Ion exchange (IEX) is an alternative treatment that has received significant attention recently for removal of DBP precursors. Anionic IEX has been used in fluidised (FIX), suspended (SIX) and magnetic (MIEX) forms for this duty (Boyer & Singer 2005; Mergen *et al.* 2008; Cornellison *et al.* 2009; Gan *et al.* 2013; Watson *et al.* 2015). In many cases it has been shown to achieve very high dissolved organic carbon (DOC), especially relating to charged LMW and hydrophilic organic compounds which can be significant DBP precursors. IEX thus appears to target different organic fractions to coagulation (Bolto *et al.* 2002; Drikas *et al.* 2003; Allpike *et al.* 2005; Mergen *et al.* 2009; Bond *et al.* 2010; Kristiana *et al.* 2010). Furthermore, anionic resins can also remove bromide from water sources (Singer & Bilyk

2002), thereby potentially reducing the propensity for formation of brominated DBPs during disinfection (Hua & Reckhow 2012).

Since IEX and coagulation preferentially remove different organic fractions, combining the processes can enhance reductions in NOM and DBP formation potential (DBPFP) (Watson *et al.* 2015). Implementation of IEX prior to coagulation has also been shown to significantly reduce the coagulant dose required (by 50-60%) as well as increase the floc size and strength (Jarvis *et al.* 2008). IEX as a pretreatment to membrane separation has also been widely investigated. Particularly for high DOC upland water sources, IEX alone has been shown to have little impact on suppressing membrane fouling unless combined with low coagulant doses (Huang *et al.* 2012a and b; Kabsch-Korbutowicz and Urbanowska, 2012).

Much of the research into the use of IEX for DBPFP control has focussed on the MIEX process (Singer and Bilyk, 2002; Drikas *et al.* 2003; Allpike *et al.* 2005; Mergen *et al.* 2009). No similarly rigorous reports of pilot-scale studies of the novel SIX process (PWN Technologies, Netherlands), combined with coagulation, have been presented. The MIEX process uses a proprietary resin and typically returns 90-95% of the separated resin to the process without regeneration (Jarvis *et al.*, 2008). However, the SIX process can use most commercially available resins and is a single pass plug flow system so as to limit resin fouling and provide more stable adsorption kinetics. In this research the SIX process has been assessed upstream of ceramic membrane filtration, a combination which has not been widely researched (Hofs *et al.* 2011; Meyn *et al.* 2012; Lee *et al.* 2013). The aim of this research was therefore to compare the removal of DBP precursors from three different source waters using SIX in combination with coagulation and ceramic membrane filtration at pilot scale, to that achievable by conventional coagulation, clarification and sand filtration. The research was

carried out using a large scale pilot facility over an 18 month period to provide representative results for long term operation of the processes.

## Methods and Materials

Three raw waters were tested on over the trial, either individually or as a blend. These were:

- An upland reservoir (UPRES) with low turbidity and low/moderate DOC (Burrator Reservoir).
- A soft, upland river (UPRIV), prone to rapid changes in quality following rain, with low to high DOC and low to moderate turbidity (River Tavy).
- A lowland river (LORIV) prone to changes in quality following rain with low to high DOC and turbidity (River Tamar).

The water sources were those that supplied the full scale WTWs, against which the pilot plant processes were compared. Three different water sources (low to high DOC) were treated by the ion exchange system and the WTWs (Tests 1-3). The raw water treated by the pilot plant and the WTWs was the same in all tests other than a minor difference in Test 3. This water was dominated by the upland river source, and the IEX received the most challenging water (Table 1). Water quality data for the three sources investigated are shown in Table S1, Supporting Information (SI).

### *Full Scale WTWs Process*

The WTWs (Crownhill WTWs, South West Water (SWW), Plymouth, U.K) treated water using optimised coagulation with aluminium sulphate dosed at 3.18 to 5.09 mg/L as Al (Kemira, U.K) and *Magnafloc LT25* (Ciba, U.K) polyelectrolyte at 0.1-0.2 mg/L (Table 1). When treating river waters, powdered activated carbon (PAC, *Aquasorb BP2*, Jacobi, U.K) was dosed at 2-3 mg/L prior to coagulation. The WTWs coagulant dose was optimised

through jar testing and works operation. Flash mixing, flocculation and sludge blanket clarification was followed by rapid gravity sand filtration (RGSF). RGSF filtrate samples were collected during all tests to allow comparison with the pilot plant process to provide a benchmark for organic matter removal based on optimised coagulation.

### *Pilot Plant Process*

Experimental work was performed using a containerised pilot plant comprising the SIX®, in-line coagulation (ILCA®) and CMF (CeraMac®) processes (PWN Technologies, Netherlands) and have been described elsewhere (Galjaard *et al.* 2011). A simple flowsheet of the pilot plant is shown in SI (Figure S1). The 150 m<sup>3</sup>/day pilot plant comprised:

- SIX – an acrylic quaternary amine, gel-type strongly basic anion exchange resin was used in the chloride form over the duration of the trial (Lewatit S5128, Lanxess, Germany) dosed at 18 ml/L with a contact time of 30 minutes, dosing conditions established as suitable for treatment of the water sources in preliminary bench-scale tests. The resin had been in continuous use for 6-18 months when the tests were performed.
- Resin was settled from the treated flow by a lamella separator. Resin was regenerated with 30 g/L NaCl. SIX treated water samples were collected directly after resin separation.
- ILCA using polyaluminium chloride (Water Treatment Solutions, U.K) was used following SIX treatment. Water was pH corrected with NaOH or HCl and injected with coagulant, mixed by a static mixer and flocculated for 3.9 minutes prior to CMF. The coagulation pH was 6.4 for all tests. The coagulant dose was optimised for NOM removal by jar testing. UV absorbance at 254 nm (UVA) was used as the surrogate for NOM removal.

- CMF was carried out using one vertically mounted 25 m<sup>2</sup> ceramic membrane element (Metawater, Japan, nominal pore size 0.1 µm), operating by dead end filtration. The membrane flux was 112 LMH (L/(m<sup>2</sup>h)) in all tests.

### *Sample Analysis*

Samples were collected from the pilot plant and WTWs during stable operation of both systems for the conditions under test. Samples were taken from the pilot plant and WTWs within an hour of one another to ensure direct comparison of the processes treating the same water. UVA was measured using a Hach DR6000 spectrophotometer after samples were filtered through a 0.45 µm filter. Bicarbonate alkalinity was measured by titration using a Metrohm ‘Titrandise’ system at SWW Laboratories (Exeter, U.K). Bromide was analysed by direct injection ion chromatography (Metrosep A Supp 7-250/4.0 column with a sodium carbonate eluent), using a Metrohm Compact IC Pro at ALS laboratories, Wakefield, U.K. Dissolved organic carbon was measured and characterised using liquid chromatography – organic carbon detection (LC-OCD) at Het Water Laboratorium (Netherlands). This analysis determines the DOC concentration and classifies the CDOC (chromatographable DOC) into a series of different MW fractions classified as biopolymers, humic substances, building blocks, LMW neutrals and LMW acids as described by Huber *et al.* (2011).

THM and HAA formation potential tests (THMFP, HAAFP) were performed at SWW Laboratories using an adapted version of the Standard Method 5710B from the American Public Health Association (APHA) (Eaton *et al.* 2005). All glassware was prepared to ensure it was organic free, PTFE lined caps were used and samples were stored in either amber glass or bottles covered with tin foil. Samples were refrigerated overnight at 4°C and chlorine demand tests were carried out the following day. The N-N-diethyl-p-phenylenediamine

(DPD) colourimetric method was used for chlorine measurements and the samples were incubated at 20 °C. Following chlorine demand determination, sample aliquots were buffered at pH 7, dosed with chlorine (ultra-low bromate sodium hypochlorite 14-15%, Brentagg, U.K) and incubated for 7 days at 20 °C. Sample aliquots were tested for residual chlorine and those containing between 3-5 mg/L free chlorine residual were processed for THM and HAA analysis. Triplicate replicates were performed on selected raw water and CMF permeate samples to give an indication of accuracy for the range of waters analysed. All blanks, quality control samples and replicates were well within accepted levels. THM samples were immediately dechlorinated with sodium thiosulphate. HAA samples were immediately preserved with ammonium chloride. Samples were adjusted to a pH <0.5 by the addition of sulphuric acid followed by extraction in 3 ml of methyl tert-butyl ether. The acids were converted to their methyl esters through the addition of acidic methanol and heating for 2 hours at 50 °C. The extract was neutralised by adding a 10% sodium sulphate solution and the solvent layer was analysed for nine HAAs.

The four THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were determined by headspace extraction using a Hewlett Packard 6890/5973N GC-MS system operating in the selected ion mode and fitted with an Agilent 7697A headspace sampler. Nine haloacetic acids (HAA9) were measured using an Agilent 7890A/5975C GC-MS system.

## **Results and Discussion**

### *Overall water quality*

SIX followed by ILCA was compared with conventional treatment for the removal of DOC and DBP precursors from each of the 3 different raw water sources (Tests 1-3). Up to 0.9

mg/L more DOC was removed for SIX/ILCA/CMF compared to that from conventional treatment. Similarly, between 0.007-0.022 cm<sup>-1</sup> more UVA removal was observed (Figure 1). It was observed that no NOM was being removed directly by the membrane itself and that all removal was being achieved by either the SIX or coagulation processes. This was seen from UVA measurements taken from either side of the membrane; in all cases the membrane feed and permeate UVA were almost identical with a less than 0.0009 cm<sup>-1</sup> difference. Membrane fouling and its amelioration through optimising operation and maintenance forms the subject of another study. However, the flux was kept constant at 112 LMH and as a result of the optimised pre-treatment membrane fouling was negligible at <3.64 kPa/day. Coagulant dose reductions of >50% were applied following SIX compared to the full-scale WTWs. Preliminary testing showed that an inline coagulation contact time of 2 minutes was sufficient for the flocculation of the residual DOC after the SIX stage. This corroborates the conclusions of Meyn *et al.* (2012) who found an inline flocculation time between 10 and 240 seconds exerted no influence on DOC removal and that 60 s was sufficient to generate flocs of low membrane fouling propensity.

The choice between macroporous and gel-type resins for NOM removal is challenged by conflicting outcomes from various studies of resin performance for different resin types when treating NOM-laden waters (Bolto *et al.* 2002; Cornelissen *et al.* 2008). In the current study, the gel-type resin was found to perform well, and was consistent with results reported from studies based on macroporous resins such as MIEX (Drikas *et al.* 2003; Boyer & Singer, 2005; Mergen *et al.*, 2009). In Tests 1 and 2, respectively low (1.1 mg/L) and moderate (4.0 mg/L) DOC water sources, the SIX resin dose (18 ml/L) alone was sufficient to provide comparable DOC removal to coagulation. Both water sources were hydrophobic, with SUVA values of 4.2 and 3.7 L/(mg.m) for the low and moderate DOC waters respectively. The DOC

removal by SIX was slightly higher than conventional treatment in Test 1 (58 vs. 53%) and 2 (62 vs. 59%). However, removal of the UV-absorbing NOM and organic fractions clearly differed between the processes and for each water source (Figure 1). The removal of UVA in comparison to DOC removal by SIX was variable with an additional removal of 10% in Test 1, whilst in Test 2 the removal was -2%. Coagulation gave 25% and 19% more UVA removal compared to DOC in Test 1 and 2, as expected due to the preferential removal of HMW, aromatic NOM noted by previous work (Drikas *et al.* 2003). Combining SIX and ILCA led to significant reductions in UVA with the CMF permeate having less than a third of the UVA of the conventionally treated water in both tests. For some water sources IEX has been found to preferentially remove UV absorbing compounds (Drikas *et al.* 2003; Boyer & Singer, 2005; Shorrock & Drage, 2006), whilst in other cases a neutral or even negative preference for UV absorbing compounds, similar to Test 2, has been reported (Allpike *et al.* 2005; Boyer & Singer, 2006). The variation in reported outputs relate to differences in the NOM composition, the IEX resin type and the available resin surface area, highlighting the need for empirical testing of waters given the complex geographical and temporal variability in organic matter.

In Test 3, SIX removed a smaller proportion of the DOC and UVA than for the other source waters (Figure 1) which was in part due to the low resin dose for the elevated DOC concentration. Other likely factors, such as competition from inorganic ions and pore blocking by HMW NOM contributed to the reduced removal of DOC. Sulphate has been shown to compete with organic compounds for IEX sites leading to reduced adsorption of DOC (Boyer & Singer, 2006). In this water, the HMW NOM load was much greater (Figure 1 and S1) and the sulphate concentration was more than double that of previous tests with 26mg/l compared to 3mg/l and 10.3mg/l in Tests 1 and 2 respectively. Fearing *et al.* (2004)

recorded reduced removal of DOC by IEX following heavy rainfall attributed to pore blockage by higher MW organics. Similarly, Mergen *et al.* (2008) found that the HMW aromatic NOM present in high SUVA waters blocked the surface IEX sites and reduced the adsorption of lower MW organic compounds being removed by the resin. Despite the reduced removal of DOC and UVA by SIX in this test, the treated water DOC concentration after the combined process was half that of the conventionally treated water, with DOC residuals of 0.62 and 1.25 mg/L respectively (similar to that observed in Tests 1 and 2).

The LC-OCD results show the preferences of SIX and coagulation for different organic fractions (Figure 1 - original chromatogram traces shown in SI Figure S2). Whereas SIX preferentially removed LMW compounds, coagulation favoured the HMW compounds, which is consistent with previous work conducted using MIEX combined with coagulation for DOC removal (Humbert *et al.* 2007). The coupling of the process therefore gave much better overall removal than the single processes due to their differing selectivities for organic fractions.

The SIX process provided only 10-20% removal of the highest MW (>20,000 Daltons) biopolymer fraction, comprising organic colloids, polysaccharides and protein like substances. This outcome is consistent with that from other studies which have reported low removal of the highest MW organics (biopolymers) by IEX (Mergen *et al.* 2009; Huber *et al.* 2011; Grefte *et al.* 2013). This is a phenomenon related to decreasing charge density with increasing MW and/or size exclusion, where the organics are prevented from entering the IEX resin pores (Croué *et al.* 1999; Humbert *et al.* 2007). Some studies have, however, reported high removal of DOC from high MW fractions (Humbert *et al.* 2005; Singer *et al.* 2007; Drikas *et al.* 2011) which may relate to differences in the high MW organic

characteristics (such as charge density), resin use (virgin resin) or the analytical technique used. On the latter, it should be noted that biopolymers do not usually strongly absorb UV light (Huber *et al.* 2011) and therefore are not detected by high performance size exclusion chromatography using UV detection (Aslam *et al.* 2013). Coagulation was very effective at removing biopolymers (72-80%) but the combined process resulted in even greater removal of this fraction (75-95%).

Humic substances were removed more effectively by SIX (68-78% removal) than conventional treatment (65-68%) for the low to moderate DOC waters and combining the processes led to almost complete removal of this fraction for all sources (>94%). The removal of building blocks (weathering products of humic substances) by SIX (65-75%) was much greater than conventional treatment for the low to moderate DOC waters (39-46%). IEX is very effective at removing humic compounds and their breakdown products due to both groups containing similar acidic, negatively charged functional groups. Coagulation alone was less effective at removing building blocks because these compounds are more hydrophilic. LMW neutrals compounds were removed to a similar degree by SIX and conventional treatment (~35%). However, following the combined process, their removal was increased for all raw waters (35-53%) showing the clear benefits of combining SIX with coagulation. Neutral compounds have been shown to be removed by IEX through surface adsorption onto the resin surface (Cornelissen *et al.* 2008). Similarly, adsorption onto floc surfaces during conventional coagulation is likely, such that coupling the process evidently benefits removal of these fractions.

## Disinfection by-product formation

DBPFP was investigated to assess how the improved organic compound removal from the SIX/ILCA/CMF process preferentially removed DBP precursors in comparison with conventional treatment. Overall, the removal of DBPFP by this process compares favourably when compared to previous MIEX/coagulation studies (Singer and Bilyk, 2002; Drikas *et al.* 2002; Drikas *et al.* 2003; Shorrock and Drage, 2006; Boyer and Singer, 2006; Cromphout *et al.* 2008) and recent work assessing advanced water treatment processes, including MIEX/coagulation, advanced oxidation processes and activated carbon (Bond *et al.* 2011).

The DBPFP of SIX-treated water was similar to that achieved by conventional treatment for the low and moderate DOC source waters, with THMs between 50-60 µg/L and HAAs at 60-70 µg/L in Test 1 and THMs at 100-130 µg/L and HAAs 90-100 µg/L in Test 2 (Figure 2). For the high DOC water (Test 3), the DBPFP of the SIX treated water was much higher due to the reduced DOC and UVA removal achieved. However, when SIX was combined with coagulation the DBPFP was very low and, as for all the waters sources investigated, much less than that achieved with coagulation alone. The combined process reduced the raw water DBPFP by 83-97% resulting in 58-67% lower THMFP and HAAFP in the treated water when compared to conventional treatment (Figure 2).

The specific reactivity (or yield) of the residual organic compounds in (µgTHMs/mgDOC) from each process was investigated to determine the extent of the impact of treatment on reactivity compared with overall DBPFP (Figure 3). For treatment of low and moderate DOC waters (Test 1 and 2), SIX alone led to slightly lower THM specific reactivity than conventional treatment (93 and 96 µgTHMs/mgDOC in Test 1 and 75 and 82 µg/mg in Test 2). The addition of coagulation following IEX further reduced the reactivity in the low DOC

water to 70  $\mu\text{g}/\text{mg}$  but the reactivity didn't change in Test 2. These differences reflect the specific organic compounds found in the two water sources. For Test 1, the water was from an upland reservoir and contained relatively more hydrophobic and  $\text{UV}_{254}$  absorbing NOM than for the lowland river water. These organic compounds are very amenable to coagulation, while having a high THMFP (Liang and Singer, 2003; Bond *et al.* 2010). For water sources that contain more hydrophobic NOM, pre-treatment by IEX reduces the NOM load passing on to downstream coagulation, while not significantly changing the reactivity of the remaining organic compounds to chlorine. The probable consequence is that the reduction in NOM load enables the coagulant to remove more of the hydrophobic NOM that has a high reactivity than is the case for conventional coagulation without IEX pre-treatment. For the higher DOC water, the SIX treated water showed only a small reduction in reactivity for THM formation compared to the raw water, likely because of the high load of NOM in the water. However, the combined treatment resulted in much lower reactivity of 54  $\mu\text{g}/\text{mg}$  compared to 75  $\mu\text{g}/\text{mg}$  for conventional treatment.

The specific reactivity of NOM for HAA formation was reduced following IEX treatment, but the reduction following coagulation was much more significant. Coagulation significantly reduced the HAA reactivity (27-58%) in all of the waters, with the highest reductions found when treating the moderate and high DOC waters (Tests 2 and 3). These findings are consistent with the conclusions of studies which have determined that the majority of reactive HAA precursor compounds are aromatic, hydrophobic NOM. Many of these compounds are also of high molecular weight, which may exclude them from removal by IEX. However, as discussed, these compounds are very well removed by coagulation processes meaning that overall IEX followed by coagulation gave the lowest HAA reactivity levels.

328 A comparison of the current data with previous laboratory, pilot and full-scale studies of IEX  
329 pre-treatment (all based on MIEX) prior to coagulation, compared with conventional  
330 treatment, shows good agreement with reported data (Figure 4). Most of the data, including  
331 that from the current study, shows THM and HAA levels to be reduced by 40% or more  
332 compared with conventional coagulation. Reductions in HAA recorded for the  
333 IEX/coagulation process aligned with the highest of those reported, a positive result given  
334 that most of the bench scale testing has been performed using virgin resin. The DOC and  
335 UVA removal efficiency of virgin IEX resin has been shown to decrease significantly with  
336 use (Shorrock and Drage, 2006; Walker and Boyer, 2011). The resin in this study had been in  
337 continuous use for between 6 – 18 months therefore providing representative results for long  
338 term operation. In general, the reduction in DBP concentrations for the combined treatment  
339 appears to be due to improved removal of DOC and, to a lesser extent, selective removal of  
340 highly reactive organic species, with some correlation between the two. The selective  
341 removal of precursors is not always observed and is more likely when overall THM/HAA  
342 reductions are low. In the current study, all three of the conditions tested yielded reductions  
343 in THMs and in DOC reactivity; two out of three conditions revealed the same trend for  
344 HAAs. In the exceptional case, HAAs were reduced whilst the reactivity did not change.

345

346 The LC-OCD results (Figure 1) indicate that most of the additional NOM removed by the  
347 advanced process compared to conventional treatment was of low MW. Previous research has  
348 shown that these lower MW NOM fractions can contribute significantly to overall DBPFP  
349 (Kitis *et al.* 2002; Kristiana *et al.* 2010). The improved overall removal of the lower MW  
350 humic substances and building block fractions by the combined process significantly reduced  
351 the DBPFP as these more hydrophobic fractions have been shown to be the most reactive  
352 DBP precursors (Bolto *et al.* 2002; Kitis *et al.* 2002; Wassink *et al.* 2011). Improved removal

of LMW acids and neutral compounds by IEX was also observed. These compounds have previously been shown to be poorly removed by coagulation and, although generally at low concentrations, are nonetheless significant THM precursors (Hua & Reckhow, 2007). The preferential removal of LMW compounds by SIX further explains the reduced DBPs recorded for the combined process.

#### *Reduction of Brominated DBPs*

The combined process led to apparent synergistic removal of reactive DBP precursors, which resulted in significantly reduced reactivity of the residual organics. For example, in Test 3, when the removal of DBP precursors by SIX was reduced, the combined process lead to reductions in specific reactivity (47% for THMs and 76% for HAAs) which were higher than the sum of the removals attainable from each process individually (SIX 6% and 9%, conventional 3% and 58% for THM and HAA respectively). In addition to the removal of reactive DBP precursors, IEX can also remove bromide which, in turn, may lead to reduced concentrations of brominated DBPs (Br-DBPs) and so the specific reactivity, given that bromide is a heavier ion than chloride. Reduction of Br-DBPs is also important because they are thought to be more toxic than their chlorinated analogues (Singer & Bilyk 2002; Hua & Reckhow 2012). The removal of Br-DBPs was therefore further investigated to establish the removals possible with each process.

Removal of bromide by IEX resins and subsequent reduction of Br-DBPs has been shown in previous work to be dependent upon the concentration of competing anions such as bicarbonate and sulphate (Walker & Boyer, 2011). In this study bromide removal by SIX was confirmed to be inversely related to raw water alkalinity varying between 9% for the LORIV, which had the highest alkalinity of 35 mg/L as CaCO<sub>3</sub>, and 47% for the UPRES

which had the lowest alkalinity at 4 mg/L as CaCO<sub>3</sub> (Figure 5a). As expected, and demonstrated in previous studies (Boyer and Singer, 2005; Kristiana *et al.* 2010), coagulation did not remove bromide. The concentration of Br-DBPs was lower in the SIX treated water than the conventionally treated water other than for the high DOC load in Test 3 (Figure 5). Br-DBP concentration was reduced significantly by SIX/ILCA/CMF, with a 48-75% reduction in comparison with the raw waters and a 30-67% reduction in comparison with the conventional process.

Despite the CMF permeate having by far the lowest concentration of Br-DBPs, these compounds represented a higher proportion of the total DBP concentration in this water (Figure 5c). This arises because of the very high removal of DOC provided by the combined process which leads to a reduced chlorine demand. Thus, when the removal of DOC is greater than the removal of bromide, the ratio of bromide to chlorine and DOC both increase, causing a shift towards the formation of a greater proportion of brominated THM and HAA compounds (Singer *et al.* 2007). The reductions in Br-DBP seen in water treated by coagulation is attributable to the removal of organic precursors which have a higher preference for bromine incorporation during disinfection. Previous studies reported a general trend for increased reactivity of bromine with lower MW, more hydrophilic compounds, for which the removal has been shown in the current study to be significantly higher with SIX than with coagulation (Hua & Reckhow 2012; Farré *et al.* 2013). However, Kristiana *et al.* (2010) found that the highest MW fraction (>20000 Daltons) had the highest brominated/chlorinated DBP ratio; these compounds have been shown to be much more effectively removed by coagulation than SIX in this study.

The NOM removals observed have shown that the SIX process compares favourably to existing IEX pre-treatment systems before coagulation. Although a detailed cost analysis is beyond the scope of this paper, overall capital costs are lower for the SIX/ILCA/CMF process than for conventional treatment due to the smaller footprint and reduced associated civil and construction costs. ILCA adds very little to the capital costs since it comprises ostensibly only a tank and dosing pump. Operational cost projections are similar to a conventional WTWs due to the impact of the reduced coagulant dose off-setting the supplementary costs of the pumping energy (for the membrane) and chemicals usage/disposal (for the ion exchange and membrane). The main novel feature of SIX is in the single pass nature of the ion-exchange process. This means that only freshly regenerated resin is introduced and contacted with raw water for a known period of time. This provides favourable adsorption kinetics, such that low resin inventories are needed, and reduces the opportunity for resin blinding and bio-fouling. Furthermore, IEX resins can be selected based on the characteristics of the organic compounds present in the water rather than being fixed to a particular supplier.

## Conclusions

A novel combined IEX/coagulation process has been applied to the treatment of raw waters for reducing the DBPFP. The process employs suspended ion exchange (SIX) with in-line coagulation (ILCA), followed by ceramic membrane filtration. SIX and ILCA were shown to remove different organic fractions, with SIX preferentially removing the low-molecular weight fraction and coagulation removing the high molecular weight compounds. The processes were thus complimentary and when combined a broad range of organics were removed resulting in very high DOC and UVA removal thus providing possible benefits in

terms of the efficiency of downstream processes, improved biostability, reduced chlorine demand and better aesthetic treated water quality.

The specific reactivity of the residual organics with chlorine was reduced to a greater degree by the combined process, using a reduced coagulant dose, than by either individual process. This was in part related to the SIX/ILCA/CMF process significantly reducing Br-DBP concentrations in comparison to conventional treatment. The enhanced BR-DBP removal can be attributed to reductions in bromide concentration and enhanced removal of reactive LMW organics by SIX, and the removal of HMW biopolymers by coagulation. Removal of bromide by SIX was found to be strongly related to bicarbonate alkalinity. The SIX/ILCA process provided mean additional reductions in DOC, UVA, THMFP, HAAFP and Br-DBP of 50, 62, 62, 62 and 47% respectively when compared with conventional treatment which was based on coagulation and media filtration.

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