

# 1      **Removal of disinfection by-product precursors by coagulation** 2                                      **and an innovative suspended ion exchange process**

3                                      David Metcalfe<sup>1</sup>, Chris Rockey<sup>1</sup>, Bruce Jefferson<sup>2</sup>,

4    Simon Judd<sup>2,3</sup> and Peter Jarvis<sup>2\*</sup>.

5                                      *<sup>1</sup>Science and Water Quality Department, South West Water, Exeter, EX2 7HY, England.*

6    *<sup>2</sup>Cranfield Water Science Institute, Cranfield University, Bedford, MK43 0AL.*

7    *<sup>3</sup>Department of Chemical Engineering, Qatar University, Qatar.*

8    \*Corresponding author: [p.jarvis@cranfield.ac.uk](mailto:p.jarvis@cranfield.ac.uk)

## 9      **Abstract**

10      This investigation aimed to compare the disinfection by-product formation potentials  
11      (DBPFs) of three UK surface waters (1 upland reservoir and 2 lowland rivers) with differing  
12      characteristics treated by (a) a full scale conventional process and (b) pilot scale processes  
13      using a novel suspended ion exchange (SIX) process and inline coagulation (ILCA) followed  
14      by ceramic membrane filtration (CMF). Liquid chromatography-organic carbon detection  
15      analysis highlighted clear differences between the organic fractions removed by coagulation  
16      and suspended ion exchange. Pretreatments which combined SIX and coagulation resulted in  
17      significant reductions in dissolved organic carbon (DOC), UV absorbance (UVA),  
18      trihalomethane and haloacetic acid formation potential (THMFP, HAAFP), in comparison  
19      with the SIX or coagulation process alone. Further experiments showed that in addition to  
20      greater overall DOC removal, the processes also reduced the concentration of brominated  
21      DBPs and selectively removed organic compounds with high DBFP. The SIX/ILCA/CMF  
22      process resulted in additional removals of DOC, UVA, THMFP, HAAFP and brominated  
23      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

27

28

## 29 **Introduction**

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

43

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

53 2002), thereby potentially reducing the propensity for formation of brominated DBPs during  
54 disinfection (Hua & Reckhow 2012).

55

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

64

65 Much of the research into the use of IEX for DBPFP control has focussed on the MIEX  
66 process (Singer and Bilyk, 2002; Drikas *et al.*, 2003; Allpike *et al.* 2005; Mergen *et al.* 2009).

67 No similarly rigorous reports of pilot-scale studies of the novel SIX process (PWN  
68 Technologies, Netherlands), combined with coagulation, have been presented. The MIEX  
69 process uses a proprietary resin and typically returns 90-95% of the separated resin to the  
70 process without regeneration (Jarvis *et al.*, 2008). However, the SIX process can use most  
71 commercially available resins and is a single pass plug flow system so as to limit resin  
72 fouling and provide more stable adsorption kinetics. In this research the SIX process has been  
73 assessed upstream of ceramic membrane filtration, a combination which has not been widely  
74 researched (Hofs *et al.* 2011; Meyn *et al.* 2012; Lee *et al.* 2013). The aim of this research was  
75 therefore to compare the removal of DBP precursors from three different source waters using  
76 SIX in combination with coagulation and ceramic membrane filtration at pilot scale, to that  
77 achievable by conventional coagulation, clarification and sand filtration. The research was

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

80

## 81 **Methods and Materials**

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

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

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

96

### 97 *Full Scale WTWs Process*

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

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

107

### 108 *Pilot Plant Process*

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

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

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

131

### 132 *Sample Analysis*

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

146

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

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

167

168 The four THMs (chloroform, bromodichloromethane, dibromochloromethane and  
169 bromoform) were determined by headspace extraction using a Hewlett Packard 6890/5973N  
170 GC-MS system operating in the selected ion mode and fitted with an Agilent 7697A  
171 headspace sampler. Nine haloacetic acids (HAA9) were measured using an Agilent  
172 7890A/5975C GC-MS system.

173

## 174 **Results and Discussion**

### 175 *Overall water quality*

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



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

193

194 The choice between macroporous and gel-type resins for NOM removal is challenged by  
195 conflicting outcomes from various studies of resin performance for different resin types when  
196 treating NOM-laden waters (Bolto *et al.* 2002; Cornelissen *et al.* 2008). In the current study,  
197 the gel-type resin was found to perform well, and was consistent with results reported from  
198 studies based on macroporous resins such as MIEX (Drikas *et al.* 2003; Boyer & Singer,  
199 2005; Mergen *et al.*, 2009). In Tests 1 and 2, respectively low (1.1 mg/L) and moderate (4.0  
200 mg/L) DOC water sources, the SIX resin dose (18 ml/L) alone was sufficient to provide  
201 comparable DOC removal to coagulation. Both water sources were hydrophobic, with SUVA  
202 values of 4.2 and 3.7 L/(mg.m) for the low and moderate DOC waters respectively. The DOC

203 removal by SIX was slightly higher than conventional treatment in Test 1 (58 vs. 53%) and 2  
204 (62 vs. 59%). However, removal of the UV-absorbing NOM and organic fractions clearly  
205 differed between the processes and for each water source (Figure 1). The removal of UVA in  
206 comparison to DOC removal by SIX was variable with an additional removal of 10% in Test  
207 1, whilst in Test 2 the removal was -2%. Coagulation gave 25% and 19% more UVA removal  
208 compared to DOC in Test 1 and 2, as expected due to the preferential removal of HMW,  
209 aromatic NOM noted by previous work (Drikas *et al.* 2003). Combining SIX and ILCA led to  
210 significant reductions in UVA with the CMF permeate having less than a third of the UVA of  
211 the conventionally treated water in both tests. For some water sources IEX has been found to  
212 preferentially remove UV absorbing compounds (Drikas *et al.* 2003; Boyer & Singer, 2005;  
213 Shorrock & Drage, 2006), whilst in other cases a neutral or even negative preference for UV  
214 absorbing compounds, similar to Test 2, has been reported (Allpike *et al.* 2005; Boyer &  
215 Singer, 2006). The variation in reported outputs relate to differences in the NOM  
216 composition, the IEX resin type and the available resin surface area, highlighting the need for  
217 empirical testing of waters given the complex geographical and temporal variability in  
218 organic matter.

219

220 In Test 3, SIX removed a smaller proportion of the DOC and UVA than for the other source  
221 waters (Figure 1) which was in part due to the low resin dose for the elevated DOC  
222 concentration. Other likely factors, such as competition from inorganic ions and pore  
223 blocking by HMW NOM contributed to the reduced removal of DOC. Sulphate has been  
224 shown to compete with organic compounds for IEX sites leading to reduced adsorption of  
225 DOC (Boyer & Singer, 2006). In this water, the HMW NOM load was much greater (Figure  
226 1 and S1) and the sulphate concentration was more than double that of previous tests with  
227 26mg/l compared to 3mg/l and 10.3mg/l in Tests 1 and 2 respectively. Fearing *et al.* (2004)

228 recorded reduced removal of DOC by IEX following heavy rainfall attributed to pore  
229 blockage by higher MW organics. Similarly, Mergen *et al.* (2008) found that the HMW  
230 aromatic NOM present in high SUVA waters blocked the surface IEX sites and reduced the  
231 adsorption of lower MW organic compounds being removed by the resin. Despite the reduced  
232 removal of DOC and UVA by SIX in this test, the treated water DOC concentration after the  
233 combined process was half that of the conventionally treated water, with DOC residuals of  
234 0.62 and 1.25 mg/L respectively (similar to that observed in Tests 1 and 2).

235

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

243

244 The SIX process provided only 10-20% removal of the highest MW (>20,000 Daltons)  
245 biopolymer fraction, comprising organic colloids, polysaccharides and protein like  
246 substances. This outcome is consistent with that from other studies which have reported low  
247 removal of the highest MW organics (biopolymers) by IEX (Mergen *et al.* 2009; Huber *et al.*  
248 2011; Grefte *et al.* 2013). This is a phenomenon related to decreasing charge density with  
249 increasing MW and/or size exclusion, where the organics are prevented from entering the  
250 IEX resin pores (Croué *et al.* 1999; Humbert *et al.* 2007). Some studies have, however,  
251 reported high removal of DOC from high MW fractions (Humbert *et al.* 2005; Singer *et al.*  
252 2007; Drikas *et al.* 2011) which may relate to differences in the high MW organic

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

259

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

275

276

277

278 *Disinfection by-product formation*

279 DBPFP was investigated to assess how the improved organic compound removal from the  
280 SIX/ILCA/CMF process preferentially removed DBP precursors in comparison with  
281 conventional treatment. Overall, the removal of DBPFP by this process compares favourably  
282 when compared to previous MIEX/coagulation studies (Singer and Bilyk, 2002; Drikas *et al.*  
283 2002; Drikas *et al.* 2003; Shorrocks and Drage, 2006; Boyer and Singer, 2006; Cromphout *et*  
284 *al.* 2008) and recent work assessing advanced water treatment processes, including  
285 MIEX/coagulation, advanced oxidation processes and activated carbon (Bond *et al.* 2011).

286

287 The DBPFP of SIX-treated water was similar to that achieved by conventional treatment for  
288 the low and moderate DOC source waters, with THMs between 50-60 µg/L and HAAs at 60-  
289 70 µg/L in Test 1 and THMs at 100-130 µg/L and HAAs 90-100 µg/L in Test 2 (Figure 2).  
290 For the high DOC water (Test 3), the DBPFP of the SIX treated water was much higher due  
291 to the reduced DOC and UVA removal achieved. However, when SIX was combined with  
292 coagulation the DBPFP was very low and, as for all the waters sources investigated, much  
293 less than that achieved with coagulation alone. The combined process reduced the raw water  
294 DBPFP by 83-97% resulting in 58-67% lower THMFP and HAAFP in the treated water when  
295 compared to conventional treatment (Figure 2).

296

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

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

317

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

327

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

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

358

### 359 *Reduction of Brominated DBPs*

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

372

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



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

385

386 Despite the CMF permeate having by far the lowest concentration of Br-DBPs, these  
387 compounds represented a higher proportion of the total DBP concentration in this water  
388 (Figure 5c). This arises because of the very high removal of DOC provided by the combined  
389 process which leads to a reduced chlorine demand. Thus, when the removal of DOC is  
390 greater than the removal of bromide, the ratio of bromide to chlorine and DOC both increase,  
391 causing a shift towards the formation of a greater proportion of brominated THM and HAA  
392 compounds (Singer *et al.* 2007). The reductions in Br-DBP seen in water treated by  
393 coagulation is attributable to the removal of organic precursors which have a higher  
394 preference for bromine incorporation during disinfection. Previous studies reported a general  
395 trend for increased reactivity of bromine with lower MW, more hydrophilic compounds, for  
396 which the removal has been shown in the current study to be significantly higher with SIX  
397 than with coagulation (Hua & Reckhow 2012; Farré *et al.* 2013). However, Kristiana *et al.*  
398 (2010) found that the highest MW fraction (>20000 Daltons) had the highest  
399 brominated/chlorinated DBP ratio; these compounds have been shown to be much more  
400 effectively removed by coagulation than SIX in this study.

401

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

417

418

## 419 **Conclusions**

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

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

429

430 The specific reactivity of the residual organics with chlorine was reduced to a greater degree  
431 by the combined process, using a reduced coagulant dose, than by either individual process.

432 This was in part related to the SIX/ILCA/CMF process significantly reducing Br-DBP  
433 concentrations in comparison to conventional treatment. The enhanced BR-DBP removal can  
434 be attributed to reductions in bromide concentration and enhanced removal of reactive LMW  
435 organics by SIX, and the removal of HMW biopolymers by coagulation. Removal of bromide  
436 by SIX was found to be strongly related to bicarbonate alkalinity. The SIX/ILCA process  
437 provided mean additional reductions in DOC, UVA, THMFP, HAAFP and Br-DBP of 50,  
438 62, 62, 62 and 47% respectively when compared with conventional treatment which was  
439 based on coagulation and media filtration.

440

## 441 **Acknowledgments**

442 The authors would like to acknowledge: South West Water, Exeter, U.K who funded and  
443 supported the work and South West Water Laboratories, Exeter, U.K for the provision of  
444 water analysis; Gilbert Galjaard, Holly Shorney-Darby, Jumeng Zheng and Harry Scheerman  
445 from PWN Technologies, Netherlands for the design and build of the pilot plant and for  
446 ongoing technical support throughout the project; RWB Water Services, Almelo, Netherlands  
447 for the design, build and ongoing assistance with maintenance of the pilot plant; Het Water  
448 Laboratorium, Haarlem, Netherlands who provided LC-OCD analysis; ALS Laboratories,  
449 Wakefield, U.K for bromide and HAA analysis.

450

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