



28

## 1. INTRODUCTION

29 Magnetic ion-exchange (MIEX<sup>®</sup>) resin has emerged as an effective technology for  
30 treating waters containing natural organic matter (NOM). The principle driver for  
31 using the resin has been to increase removal of dissolved organic carbon (DOC) to  
32 reduce the disinfection by-product (DBP) formation of a water when compared to  
33 using conventional coagulation alone. Use of the resin as a pre-treatment before  
34 coagulation has consistently shown a reduction in DBP formation when compared to  
35 conventional coagulation (Singer and Bilyk, 2002; Fearing *et al.*, 2004; Hamann *et*  
36 *al.*, 2004; Son *et al.*, 2005). These studies have shown significant reduction in key  
37 DBPs of between 50-70 % for trihalomethanes (THMs) and >60 % for haloacetic  
38 acids (HAAs) when compared to single coagulation alternatives.

39

40 Magnetic ion-exchange resin is a strong base anion resin with ammonia functional  
41 groups, consisting of 150-180 µm beads of a macroporous, polyacrylic structure  
42 (Slunjski *et al.* 2000; Singer & Bilyk 2002). During the operation of the continuous  
43 resin process, NOM rich raw water is contacted with the resin allowing ion-exchange  
44 of organics onto the resin. The high density and magnetic properties of the resin  
45 provides rapid clarification following the contact stage. Between 90-95 % of the resin  
46 is recycled back in to the contactor, with the remainder regenerated with a  
47 concentrated brine solution (Budd *et al.*, 2003). Depending on specific water  
48 characteristics, magnetic resin pre-treatment can remove from 30 % to over 70 % of  
49 the DOC from the water (Wert *et al.*, 2005; Tan *et al.*, 2005; Kim *et al.*, 2005). The  
50 treated water therefore has a much lower coagulant demand allowing much lower  
51 doses to be applied when compared to conventional coagulation of the same raw  
52 water (Fearing *et al.*, 2004; Allpike *et al.*, 2005; Boyer and Singer, 2005). For

53 example, Fearing *et al.* (2004) showed better DOC and UV<sub>254</sub> removals (75 % and 95  
54 % respectively) by reducing the coagulant dose from 14 mg L<sup>-1</sup> to 5 mg L<sup>-1</sup> as Fe  
55 (ferric sulphate) when using magnetic resin pre-treatment (20 mL L<sup>-1</sup> for 20 minutes).

56

57 Whilst the position with regard to reduced DBP formation using magnetic resin is  
58 clear, the current position with regard to the types of organic material preferentially  
59 removed by the resin is unclear. This is because NOM is a highly variable matrix that  
60 can differ temporally and spatially and is highly dependent on the catchment feeding  
61 the water body (Vogt *et al.*, 2004). Some work has shown that the resin is more  
62 effective at removing NOM from waters that have a high specific UV<sub>254</sub> absorbance  
63 (SUVA) of > 3.0 L m<sup>-1</sup> mg<sup>-1</sup> DOC, but is also able to remove hydrophilic fractions of  
64 NOM (Johnson and Singer, 2004; Boyer and Singer, 2005). Other work has shown  
65 that magnetic resin does not remove very large organic molecules >5000 Daltons  
66 (Fearing *et al.*, 2004) or small neutral organics (Kim *et al.*, 2005). Removal analysis  
67 of different molecular weight (MW) NOM fractions after resin treatment has shown  
68 that high MW compounds (5000-7000 Daltons (Da)) composed of hydrophobic humic  
69 and fulvic compounds were poorly removed following resin treatment (Allpike *et al.*,  
70 2005). However, good removal was seen for smaller anionic species, thought to  
71 contain carboxylic groups. This is in agreement with Humbert *et al.* (2005), who have  
72 shown that intermediate MW organics between 500-1500 Daltons were well removed  
73 by the resin.

74

75 With new magnetic ion-exchange plants being continuously installed, there is a strong  
76 need for further research into the types of organic material that can be removed by the  
77 resin. The objectives of this work were to provide a view on the treatment efficiency

78 of using resin pre-treatment on three different raw waters: (1) an algal laden surface  
79 reservoir water; (2) a hydrophilic lowland river water and (3) a hydrophobic highly  
80 coloured moorland water. These results were compared with other literature removal  
81 performance data to determine which types of water are suitable for resin pre-  
82 treatment. The NOM removal efficiencies using a) conventional coagulation and b)  
83 magnetic resin treatment followed by coagulation were compared for each of the  
84 different waters.

85

86

## 2. MATERIALS AND METHODS

### 87 *2.1 Raw water characterisation*

88 Three raw waters from across the UK of fundamentally different character were  
89 analysed, these were:

- 90 1) Barcombe – an algae laden reservoir water
- 91 2) Draycote – a hydrophilic lowland river water
- 92 3) Albert – a hydrophobic moorland surface water

93 Raw water was collected and characterised by measuring raw water dissolved organic  
94 concentration (DOC) (Shimadzu 500A TOC analyser), ultraviolet absorbance at 254  
95 nm (UV<sub>254</sub>) (Jenway 6505 UV/vis spectrophotometer), turbidity (Hach 2100  
96 turbidimeter) and zeta potential (Malvern Zetasizer). All analytical instruments were  
97 calibrated using the associated calibration procedure for the instrument prior to use  
98 and have an associated analytical error of approximately  $\pm 5\%$ . High performance size  
99 exclusion chromatography (HPSEC) analysis was carried out using a Shimadzu VP  
100 series high performance liquid chromatogram (HPLC) using UV<sub>254</sub> detection. The  
101 mobile phase was 0.1 M sodium acetate flowing at 1 mL min<sup>-1</sup>. A TSK-gel G3000SW  
102 7.5 mm (internal diameter (ID)) by 30 cm column was used with a TSK gel 7.5 (ID)

103 mm by 30 mm guard column (Tosoh Biosep GmbH, Stuttgart, Germany). The system  
104 was calibrated with 110 mL of source water filtered through ultra filtration  
105 membranes at different molecular weight cut-offs (MWCO). Membranes with  
106 MWCO values of 0.5, 1, 3, 5, 10 and 30 kDa were used (YM1-YM30, Millipore Pty  
107 Ltd., Massachusetts, USA, YC05, Millipore Pty Ltd., Sydney, Australia). Samples  
108 were analysed un-filtered for turbidity and zeta potential and were filtered using a  
109 glass fibre paper (<1 µm pore size, Munktell, Sweden) for DOC, UV<sub>254</sub> and HPSEC  
110 analysis.

111

112 Further characterisation work was carried out by fractionating raw waters using  
113 published methods (Malcolm and MacCarthy, 1992; Goslan *et al.*, 2002). During this  
114 process, 2 L of raw water was filtered through 0.45 µm glass fibre papers and  
115 acidified to pH 2. The water was then passed through two fractionation columns, the  
116 first containing 60 mL of XAD-8 resin and the second containing 60 mL of XAD-4  
117 resin. Effluent passing through both of the columns was the hydrophilic non-acid  
118 fraction (HPINA). Both the ion-exchange columns were back eluted with 250 mL of  
119 0.1 M NaOH. The eluate from the XAD-8 column was the hydrophobic fraction. The  
120 pH of this sample was adjusted to 1 using concentrated HCl and allowed to settle for  
121 24 hours before being centrifuged. The supernatant was decanted; this was the fulvic  
122 acid fraction (FAF). The residual was dissolved in 100 mL of 0.1 M NaOH; this was  
123 the humic acid fraction (HAF). The eluate from the XAD-4 resin was the hydrophilic  
124 acid fraction (HPIA). The fractions were filtered and analysed for DOC.

125

126 The charge density of raw and treated water was measured using a methodology as  
127 described in Sharp *et al.* (2006). Briefly, the charge of water was determined using the

128 Malvern Zetasizer and 0.1 % polyDADMAC (Sigma-Aldrich, UK). 1 L of water was  
129 stirred with a magnetic stirrer and varying amounts of polyDADMAC were added to  
130 the water until the point of zero charge had been reached (as measured by the  
131 Zetasizer). This was then repeated twice. The volume of polyDADMAC added was  
132 used to determine raw water charge and normalised to the charge density per g of  
133 DOC in the water.

134

### 135 *2.2 Magnetic resin dosing*

136 A new bench scale approach was used to assess the performance of magnetic resin as  
137 described in Mergen *et al.* (2006) in order to more appropriately mirror how the resin  
138 is used operationally. In most bench scale magnetic resin testing protocols, fresh or  
139 regenerated resin has been used singularly in batch tests before analysis on the treated  
140 water is carried out. Whilst useful information can be found from these tests, this does  
141 not reflect how the resin will be used at full scale. Given that between 5-10 % of used  
142 resin is replaced with regenerated resin during the continuous operation of a magnetic  
143 resin unit, used resin is continuously in contact with untreated water with only a small  
144 fraction of fresh/regenerated resin added (Slunjski *et al.*, 2000). In this way, the resin  
145 achieves service runs equivalent to 1250-2500 bed volumes (BV). In these  
146 experiments, resin was contacted with raw water in individual jar tests for 15  
147 consecutive times without regeneration to give an equivalent resin BV of 1500. Resin  
148 doses were prepared by adding the required resin doses in to measuring cylinders and  
149 allowed to settle for 2 hours. Any adjustments to the required resin dose were made  
150 by adding or removing resin using a plastic pipette. Resin was added to 1 L of raw  
151 water and mixed on a jar tester at 150 rpm. After each jar test, the treated water was  
152 settled from the resin for 5 minutes and the supernatant poured-off and combined in to  
153 one large sample containing water from each consecutive jar test. Subsequent jar tests

154 were carried out with the same used resin with further 1 L samples of raw water added  
155 to the settled resin and mixed on the jar tester as before. Analysis and further  
156 experimentation was carried out on both the combined water and the separated water.  
157 The combined water was then considered as being equivalent to that produced from  
158 an operational magnetic resin works.

159

160 Samples were analysed after each separate jar test and for the combined water for  
161 DOC removal and HPSEC. Quality assurance of these results was confirmed by  
162 noting good agreement between the prediction of the DOC in the combined sample  
163 from the individual jar tests and that given by the measured DOC in the combined  
164 sample: 88 % of predictions were within  $\pm 5$  % of the observed DOC removal. The  
165 remaining 12 % of samples were 5.2, 5.5 and 8.0 % different.

166

167 The combined water sample was then coagulated using ferric sulphate (Ferrisol XL,  
168 EA West) on a jar tester. During coagulation, raw or resin pre-treated water was  
169 stirred at 200 rpm for 1.5 minutes following the addition of ferric sulphate and the pH  
170 adjusted using 1 M NaOH. After the rapid mix, the jars were stirred at 30 rpm for 15  
171 minutes followed by a 15 minute settling period before water samples were taken for  
172 analysis. The efficacy of coagulation after resin pre-treatment was compared to direct  
173 coagulation of the raw water under optimised coagulation conditions.

174

175 The magnetic resin and coagulant doses reported were found as the optimums during  
176 preliminary experiments using standard jar testing procedure. Resin was dosed at 10  
177 mL L<sup>-1</sup> for 10 minutes for all of the raw waters with a subsequent coagulant dose of 2  
178 mg L<sup>-1</sup> Fe for Barcombe and Draycote waters and 4 mg L<sup>-1</sup> Fe for Albert water.

179 Conventional coagulation tests used optimum doses of  $10 \text{ mg L}^{-1}$  Fe for all three  
180 waters.

181

### 182 *2.3 Comparison of magnetic resin removal data*

183 The removal of NOM using magnetic resin observed in this work was compared to  
184 other data to determine if general water quality parameters could be used to identify  
185 the potential of removing DOC from a water using the resin. The studies used in this  
186 comparison have been summarised in Table 1. Studies using resin in batch scale  
187 studies were differentiated from studies using the resin in continuous operation  
188 (including full-scale, pilot scale and the methodology used here). The NOM removal  
189 using magnetic resin was normalised to a percentage removal of DOC and plotted  
190 against raw water parameters of DOC, SUVA, hydrophobicity from XAD  
191 fractionation and alkalinity. It was assumed that optimum resin operating conditions  
192 were used in the data extracted from other sources.

193

## 194 3. RESULTS

### 195 *3.1 Raw water characterisation*

196 The three raw waters investigated showed very different physico-chemical properties  
197 (Table 2). Whilst all waters were of similar DOC content ( $9.4 - 10.7 \text{ mg L}^{-1}$ ), the  
198 greater  $\text{UV}_{254}$  absorbance of  $60.1 \text{ m}^{-1}$  for Albert water reflected the more highly  
199 coloured nature of this water in comparison to Barcombe and Draycote ( $16.5$  and  $13.9$   
200  $\text{m}^{-1}$  respectively). Both Draycote and Albert were low turbidity waters ( $<1.8 \text{ NTU}$ ),  
201 whilst Barcombe had a high turbidity of  $13.1 \text{ NTU}$  as a result of this water containing  
202 high concentrations of algae. Microscopic examination identified that the dominant  
203 species in this water were green algae (*Chlorella* and *Scenedesmus*).

204

205 Water hydrophobicity was measured in two ways. Firstly, the SUVA provides a quick  
206 indication of the nature of the organics present in the raw water. The high SUVA of  
207 Albert water ( $6.4 \text{ L m}^{-1} \text{ mg}^{-1} \text{ DOC}$ ) was indicative of a hydrophobic water whilst the  
208 low SUVA values of  $<1.8 \text{ L m}^{-1} \text{ mg}^{-1} \text{ DOC}$  for Barcombe and Draycote were  
209 indicative of containing mostly hydrophilic organics.

210

211 More detailed hydrophobicity characterisation was made using XAD resin  
212 fractionation (Figure 1). This showed that the high SUVA Albert water contained a  
213 high proportion of hydrophobic substances (humic and fulvic fractions) with over 75  
214 % of the total DOC determined to be hydrophobic. The water having the lowest  
215 SUVA (Draycote) was confirmed to contain mostly hydrophilic compounds  
216 (hydrophilic acid and non-acid fractions) with over 75 % of the total DOC  
217 hydrophilic. However, whilst the SUVA of Barcombe water suggested that there was  
218 a low hydrophobic content, 50 % of the water was determined to be hydrophobic after  
219 fractionation, indicating that this water contained a large proportion of non-UV<sub>254</sub>  
220 absorbing hydrophobic compounds that the SUVA measurement was not able to  
221 identify.

222

223 The charge density of the raw waters tracked the fractionation hydrophobicity data,  
224 with the more hydrophobic waters containing more highly charged material per mass  
225 of organic in the water. The very hydrophobic Albert water had the highest  
226 concentration of negatively charged organics ( $6.4 \text{ meq g}^{-1} \text{ DOC}$ ) whilst the part  
227 hydrophilic/hydrophobic Barcombe water had an intermediate charge density of  $1.9$   
228  $\text{meq g}^{-1} \text{ DOC}$ . The hydrophilic Draycote water had a low charge density of only  $0.3$

229 meq g<sup>-1</sup> DOC. As a result of the high proportion of hydrophilic acids determined from  
230 fractionation in Draycote water, it may have been expected that this water would have  
231 had a higher charge density. However, this result was observed on repetition of the  
232 measurement.

233

234 The MW distribution of the UV<sub>254</sub> absorbing compounds also showed a relationship  
235 with the hydrophobicity and charge density data (Figure 2). The highly charged and  
236 coloured hydrophobic Albert water contained organics with much greater UV<sub>254</sub>  
237 absorbance with an area under the curve over four times that of Draycote and  
238 Barcombe. Albert water had a higher MW distribution of UV<sub>254</sub> absorbing organics  
239 compared to Barcombe and Draycote with two major peaks at 6 and 8 minutes elution  
240 time. Calibration of the column with source water filtered through ultra filtration  
241 membranes at different molecular weight cut-offs, approximated these peaks as being  
242 >5000 Daltons (Da). The part hydrophobic/hydrophilic Barcombe water had more  
243 high MW UV<sub>254</sub> organic compounds than Draycote with a dominant peak between  
244 8.5-9 minutes, representing organics between 2000-5000 Da. The hydrophilic  
245 Draycote water had the lowest MW with a more even distribution of organics around  
246 a main peak at 9.5 minutes, approximating to organics of 2000 Da.

247

248 Given that the DOC content of the three waters was similar, the low level of UV<sub>254</sub>  
249 absorbance for Draycote and Barcombe indicated that a large portion of the organics  
250 in these waters could not be characterised using UV<sub>254</sub> detection. For this reason,  
251 subsequent discussion of data generated from UV<sub>254</sub> detection has been limited to the  
252 strongly absorbing Albert water.

253

254 3.2 *Removals*

255 DOC removals of 56, 33 and 25 % were observed during consecutive magnetic resin  
256 treatment for Draycote, Barcombe and Albert waters respectively in the final  
257 combined water (Figure 3).

258

259 When resin treated water was subsequently combined with coagulation using low  
260 coagulant doses, the combined resin + coagulation systems gave between 2-8 %  
261 improved DOC removal when compared to conventional coagulation. The small  
262 increase in removal was close to the limit of error on the instrument used for DOC  
263 analysis, therefore some uncertainty was assigned to the conclusion that the combined  
264 system led to improved NOM removal. The benefit of coagulation after resin pre-  
265 treatment was greatest for increasing water hydrophobicity, with increased DOC  
266 removal of 8, 45 and 63 % seen for Draycote, Barcombe and Albert respectively.

267

268 Analysis of the HPSEC traces of UV<sub>254</sub> absorbing organics for Albert water showed a  
269 small reduction in the peak at 6 minutes elution time after resin treatment, identified  
270 by a 14 % decrease in curve area for organics eluted between 5-6.5 minutes (Figure  
271 4). This material was the high MW organics that were >5000 Da. Most organic  
272 material was removed by the resin for NOM eluted between 7-9 minutes, with a  
273 reduction of 43 % over this range, indicating organics of around 5000 Da. This  
274 represented removal of a broad range of different MW organics for this water.

275

276 Subsequent coagulation removed significantly more UV<sub>254</sub> absorbing organics for the  
277 very hydrophobic Albert water compared to resin treatment alone. For the residual  
278 NOM after magnetic resin treatment, over 95 % of the curve area was removed ,

279 leaving a residual of small MW compounds representing NOM of <2000 Da. In  
280 comparison to coagulation alone, the combined resin and coagulation treatments  
281 showed 46 % less relative curve area for residual UV<sub>254</sub> absorbing organics for Albert  
282 water.

283

#### 284 *3.4 Consecutive magnetic resin uses*

285 Further investigation in to the removal of different organics using magnetic resin was  
286 assessed by analysing the removal performance of DOC after consecutive resin uses  
287 for single and combined waters (Figure 5). For the combined sample (solid line), this  
288 represents the DOC of the combined water from the preceding individual jar tests.  
289 The organic removal from the algal laden Barcombe water remained consistently  
290 around 30 % after consecutive resin uses resulting in a final DOC removal in the  
291 combined water of 33 %. A similar pattern was seen for the hydrophilic Draycote  
292 water with only a slight drop in the removal of DOC from 64 % after the first use of  
293 the resin to 55 % after 15 resin uses, giving an overall DOC removal of 56 % in the  
294 final combined water. The behaviour of Albert water was very different. The removal  
295 capacity was initially very high (65 %), but rapidly dropped until only 4 % of the  
296 DOC was removed after the fifteenth use (1500 BV) of the resin resulting in a  
297 removal of 25 % in the final combined water. This represents a total load of 90.2,  
298 47.5, and 35.3 mg of DOC on to the magnetic resin for Draycote Barcombe, and  
299 Albert respectively.

300

301 Analysis of HPSEC profiles for consecutive resin uses was again restricted to Albert  
302 water because this was the only water that was dominated by UV<sub>254</sub> absorbing  
303 compounds (Figure 6). There was a rapid decrease in the removal of MW material

304 over the elution range between 7-10 minutes, indicating mostly organics between  
305 2000-5000 Da. After a single use of the resin when 65 % of the total DOC had been  
306 removed, over 86 % of the curve area had been removed over this elution range. This  
307 was reduced to 20 % removal after 15 uses of the resin (1500 BV).

308

309

#### 4. DISCUSSION

310 The results of this work have been compared with other work to determine which  
311 variables control NOM removal using magnetic resin. The removal efficiency of  
312 NOM for the final combined water seen here has been compared to other single batch  
313 resin studies for extremes of SUVA investigated in each study (Table 3). The data  
314 contained in this table is for one-off uses of resin in stirred reactors between 1 and 15  
315 L. Whilst there have been an appreciable range of different water qualities  
316 investigated, it can be seen that the removal of NOM after resin treatment was  
317 generally lower than that seen previously, this was particularly the case for high  
318 SUVA waters. This was unlikely to be related to the resin dose or contact time given  
319 that the resin dose used ( $10 \text{ mL L}^{-1}$ ) was as high as that used in the comparable work,  
320 whilst contact times above 10 minutes have been shown to offer little increased NOM  
321 removal (Humbert *et al.*, 2005; Kim *et al.*, 2005). One-off uses of resin for treatment  
322 of hydrophobic type waters resulted in high DOC removal of between 64-93 % (Table  
323 3). For example Fearing *et al.* (2004) looked at the same hydrophobic Albert water  
324 source as used in this work. Using virgin resin, they achieved 66-82 % DOC removal;  
325 a result similar to that achieved in this work after 1 use of the resin (65 % DOC  
326 removal), but well above the final removal of 25 % in the combined water. For Albert  
327 water, the methodology adopted in this work gave a better indication of how much  
328 NOM could be removed for more realistic resin loadings likely during continuous

329 operation. For the hydrophilic waters, one-off use of the resin has resulted in more  
330 variable DOC removal ranging from 43-79 % depending on the water investigated  
331 (Table 3). It was shown in this work that consecutive uses of the resin resulted in  
332 more consistent NOM removal for hydrophilic water types. Therefore, for these  
333 waters, one-off jar tests will give an indication of the likely removal using magnetic  
334 resin in continuous operation.

335

336 Further comparison of removal data was made with magnetic resin studies where  
337 more detailed water characteristics were given (Figure 7). These figures were  
338 generated from the studies listed in Table 1. There was no significant relationship  
339 between raw water DOC and removal: for raw water DOCs of  $>6 \text{ mg L}^{-1}$  the mean  
340 DOC removal was  $67.6 \pm 15.1 \%$  whilst for waters of  $\text{DOC} < 6 \text{ mg L}^{-1}$  the mean DOC  
341 removal was  $60.0 \pm 22.1 \%$  for single resin use investigations. In continuous systems  
342 raw water DOCs of  $>6 \text{ mg L}^{-1}$  the mean DOC removal was  $47.5 \pm 19.1 \%$  whilst for  
343 waters of  $\text{DOC} < 6 \text{ mg L}^{-1}$  the mean DOC removal was  $60.5 \pm 15.9 \%$ . This indicated  
344 that due to the spatial and temporal variation in NOM from different sources, a bulk  
345 water variable such as raw water DOC is an unsuitable measure to determine water  
346 treatability using magnetic resin.

347

348 There were no clearly defined relationships between removal of NOM with magnetic  
349 resin and water hydrophobicity (from SUVA or fractionation), but there was some  
350 indication that increasing removal was seen with increasing hydrophobicity for single  
351 use resin studies, whilst in continuous testing, this order was reversed. Waters  
352 containing SUVA values of  $<4 \text{ L m}^{-1} \text{ mg}^{-1}$  DOC have previously been defined as  
353 being dominated by hydrophilic compounds (Edzwald, 1993). For one-off use of the

354 resin, when the SUVA of the raw water was  $>4 \text{ L mg m}^{-1}$  removal was  $75.6 \pm 10.2 \%$   
355 compared to  $56.8 \pm 19.7 \%$  when the SUVA was  $<4 \text{ L m}^{-1} \text{ mg}^{-1}$  DOC. The large  
356 standard deviation of the lower SUVA waters indicated that there was a wider  
357 variation in removals seen in these water types when compared to the higher SUVA  
358 waters. For the continuous systems, there were only two instances when the SUVA  
359 was  $>4 \text{ L m}^{-1} \text{ mg}^{-1}$  DOC, so comparison of the removals was not made.

360

361 There was a similar distinction between the average removals for single use resin  
362 investigations and waters that contained greater or less than 50 % hydrophobic NOM  
363 from fractionation as was seen for high and low SUVA waters. When more than 50 %  
364 of the raw water DOC was hydrophobic, DOC removal with magnetic resin was  $71.0$   
365  $\pm 7.8 \%$  compared to  $49.6 \pm 20.5 \%$  for  $<50 \%$  hydrophobic DOC. For continuous use  
366 of the resin, the relationship between the DOC removal and the hydrophobicity  
367 decreased with increasing hydrophobicity from 55 to 25 % (however, these three  
368 points were generated from the continuous bench scale methodology used in this  
369 study). There was no relationship between the alkalinity of the raw water and the  
370 removal seen with the resin for all of the studies investigated.

371

372 In summary, bulk water properties did not provide a clear indication of the potential  
373 removal of NOM by magnetic resin. This relates to the inherent variability in NOM  
374 composition in different source waters which bulk water measurements, such as those  
375 investigated, are unable to quantify in detail.

376

377 In this work, the NOM that was dominated by hydrophobic NOM showed good initial  
378 removal during the first few uses of resin but subsequently removal efficiency quickly

379 declined. Hydrophobic NOM is regarded as being of high MW consisting of humic  
380 and fulvic acids (Edzwald, 1993). The reduced removal with resin use was explained  
381 by blockage of exchange sites by high MW NOM. This was supported by the HPSEC  
382 profiles from Albert that showed initially good removal of a range of organics, but  
383 this rapidly decreased, particularly the removal of high MW organics. This fraction of  
384 NOM therefore had high affinity for the resin because hydrophobic organics contain  
385 high concentrations of dissociable functional groups that impart negative charge on  
386 the organic material (Ussiri and Johnson, 2004). However, the resin was quickly  
387 saturated or pores of the resin were blocked by the large humic and fulvic acid type  
388 organics that dominated Albert water. This is a phenomenon also seen in carbon  
389 adsorption, where large MW NOM blocks outer pores, reducing adsorption capacity  
390 by preventing smaller organics from adsorbing via smaller internal pores (Ebie *et al.*,  
391 2001; Ding *et al.*, 2006). The operational consequences of this suggest that the resin  
392 needs to be regenerated on a more frequent basis for waters dominated by high MW  
393 NOM to ensure enough sites are available for exchange of organics on to the resin.

394

395 The dominant hydrophilic compounds in the NOM from Draycote showed more  
396 consistent NOM removal on to the resin. The lower MW distribution of the UV<sub>254</sub>  
397 absorbing organics indicated that this type of NOM was able to access more of the  
398 available resin surface area (including internal pores) of the resin providing more  
399 available area for more consistent NOM removal when compared to the organics in  
400 the hydrophobic water. This was consistent with other work that has shown that  
401 hydrophilic acids are typically characterised by lower MW compounds that can be  
402 effectively removed by anionic ion-exchange resins (Bolto *et al.*, 2002). Hydrophilic  
403 acids of this type therefore seem very amenable to treatment using magnetic resin and

404 would provide extended use of the resin during operation when compared to  
405 hydrophobic waters. Given that Draycote water had a very low charge density, it was  
406 unclear whether the principal mechanism for removal of the hydrophilic compounds  
407 was ion-exchange or a non-charge related mechanism. Fettig (1999) concludes that  
408 most NOM is removed by ion-exchange when using anionic ion-exchange resins.  
409 However, for smaller MW compounds, surface adsorption becomes more important. It  
410 is likely that for the lower MW hydrophilic acids, molecular polarity would encourage  
411 exchange and/or adsorption of these compounds. Given the high removals seen, the  
412 use of charge density as determined from the method used in this work was not  
413 considered a good indicator of the potential for NOM removal by magnetic resin.

414

415 The consistently low NOM removals seen for Barcombe water showed that the resin  
416 had a low affinity for NOM in this water. A combination of size exclusion and low  
417 charge may explain the low levels of NOM removal seen using magnetic resin. Given  
418 that this water was dominated by algae it was probable that this water contained high  
419 concentrations of soluble algogenic matter. This is known to include glycolic acids,  
420 carbohydrates, polysaccharides, amino acids, peptides, organic phosphorous,  
421 enzymes, vitamins, hormonal substances, inhibitors and toxins (Her *et al.*, 2004;  
422 Henderson *et al.*, 2006). Many of these compounds tend to be uncharged and are  
423 therefore unlikely to have a strong affinity for exchange on to the resin (Allpike *et al.*,  
424 2005). However, it has been shown that algal derived extra-cellular organic matter  
425 (EOM) is dependent on species. Algae such as *Microcystis aeruginosa* produce EOM  
426 of negligible charge density, whilst *Chlorella vulgaris* has EOM with a charge density  
427  $3.2 \text{ meq g}^{-1} \text{ DOC}$  (Henderson *et al.*, 2006). As *Chlorella* was one of the dominant  
428 algae in the water sampled here, this explains why some charge density was measured

429 in this water. Charged compounds such as uronic acid have been shown to constitute a  
430 portion of the EOM excreted by algae and are therefore likely to be present in such  
431 algae dominated waters (Hoyer *et al.*, 1985). These acids are typical of the charged,  
432 small MW that have strong affinity with magnetic resin and explains why some NOM  
433 was removed from this water (Allpike *et al.*, 2005). In addition, large polysaccharides  
434 and proteins have been shown to be exuded by microbes and algae (Humbert *et al.*,  
435 2007; Henderson *et al.*, IN PRESS). These compounds have a higher MW than humic  
436 and fulvic acids indicating that size exclusion may also play a significant part in the  
437 poor removals seen from this water using magnetic resin.

438

439 More detailed knowledge of the raw water is required other than variables such as  
440 DOC, SUVA or alkalinity to indicate likely removal by magnetic resin. This work has  
441 shown that a key variable for removal in a hydrophobic water source was the MW of  
442 the organics in the water. Removal of NOM of between 2000-5000 Da decreased with  
443 increasing resin use. Size exclusion/blockage was thought to explain the decreased  
444 removal with resin use rather than exhaustion of ion-exchange sites. This was because  
445 10 mL of magnetic resin has a total charge capacity of 5 meq (Bourke, 2006).  
446 However, based on the charge density calculation of the Albert NOM, only 0.39 meq  
447 of DOC was removed indicating that exchange sites were far from exhausted. High  
448 MW organic matter of algal origin may also explain the limited removal seen for  
449 Barcombe water. The consistent removal seen for Draycote water indicated that this  
450 water contained lower MW compounds that could be continuously well removed with  
451 increasing resin use. It is also believed that NOM should be charged for high levels of  
452 removal by magnetic resin, however given the high removals observed for Draycote

453 water an alternative method is required to determine charge in hydrophilic samples  
454 dominated by hydrophilic acids.

455

456 The benefit of adding coagulant after resin pre-treatment was also shown in this work.  
457 An additional 8-63 % DOC was removed following coagulation of the combined  
458 waters. This follows the same trend as pilot/full-scale trials where 15-19 % extra DOC  
459 removal has been seen for coagulation after resin pre-treatment (Allpike *et al.*, 2005;  
460 Shorrocks and Drage, 2006). Increasing additional NOM removal was observed with  
461 increasing hydrophobicity. Sharp *et al.* (2006) gave a hierarchy that showed that the  
462 HPIA and HPINA were the fractions least well removed by coagulation when  
463 compared to hydrophobic compounds. It was therefore unsurprising that the water  
464 with the highest hydrophilic content showed the poorest DOC removal during  
465 coagulation. The refractory NOM that could not be removed by coagulation or  
466 magnetic resin treatment has previously been shown to be small neutral or positively  
467 charged NOM that have fluorescent characteristics similar to proteins (Humbert *et al.*,  
468 2005).

469

470

## 5. CONCLUSIONS

471 Removal of NOM using magnetic resin was water specific. A bench scale protocol  
472 was used that showed hydrophilic dominated waters could be assessed in one-off jar  
473 tests, whilst hydrophobic NOM required consecutive resin uses. General water  
474 parameters such as DOC did not indicate whether a water would be amenable to  
475 treatment using the resin. Both hydrophilic and hydrophobic NOM can be removed by  
476 the resin, however it appeared that high MW NOM (typical of the NOM found in  
477 hydrophobic water sources) quickly saturated or blocked the resin. Therefore MW of

478 the organics in the NOM plays an important role in determining removal efficiency.  
479 Water dominated by hydrophilic acids showed consistently high levels of removal on  
480 to the resin. Algogenic NOM was poorly removed because of the increased presence  
481 of uncharged organics likely to be composed of mainly carbohydrates and proteins.

482

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486

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# Magnetic ion-exchange resin treatment: Impact of water type and resin use

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