

28

1. INTRODUCTION

29 Magnetic ion-exchange (MIEX[®]) 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 UV₂₅₄ removals (75 % and 95
54 % respectively) by reducing the coagulant dose from 14 mg L⁻¹ to 5 mg L⁻¹ as Fe
55 (ferric sulphate) when using magnetic resin pre-treatment (20 mL L⁻¹ 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 UV₂₅₄ absorbance
63 (SUVA) of > 3.0 L m⁻¹ mg⁻¹ 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 (UV₂₅₄) (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 UV₂₅₄ detection. The
101 mobile phase was 0.1 M sodium acetate flowing at 1 mL min⁻¹. 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, UV₂₅₄ 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 ± 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⁻¹ for 10 minutes for all of the raw waters with a subsequent coagulant dose of 2
178 mg L⁻¹ Fe for Barcombe and Draycote waters and 4 mg L⁻¹ Fe for Albert water.

179 Conventional coagulation tests used optimum doses of 10 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 mg L⁻¹), the
198 greater UV₂₅₄ absorbance of 60.1 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 m⁻¹ respectively). Both Draycote and Albert were low turbidity waters (<1.8 NTU),
201 whilst Barcombe had a high turbidity of 13.1 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-UV₂₅₄
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⁻¹ 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 UV₂₅₄ 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 UV₂₅₄
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 UV₂₅₄ 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 UV₂₅₄ 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 UV₂₅₄
249 absorbance for Draycote and Barcombe indicated that a large portion of the organics
250 in these waters could not be characterised using UV₂₅₄ detection. For this reason,
251 subsequent discussion of data generated from UV₂₅₄ 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 UV₂₅₄ 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 UV₂₅₄ 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 UV₂₅₄ 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 UV₂₅₄ 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 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 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 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 UV₂₅₄
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

487 6. REFERENCES

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