

MAGNETIC ION EXCHANGE RESIN TREATMENT: IMPACT OF WATER TYPE AND RESIN USE

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Abstract

Three raw waters of fundamentally different natural organic matter (NOM) character were treated by magnetic resin using a bench scale method designed to mimic how the resin is used in continuous operation. Increasing water hydrophobicity resulted in reduced dissolved organic carbon (DOC) removal with removal of 56, 33 and 25 % for waters containing 21, 50 and 75 % hydrophobic NOM respectively. Study of consecutive resin uses showed that the NOM in the hydrophobic water had high affinity for the resin shown by DOC removal of 65 % after the first use of the resin. This dropped to 25 % DOC removal after 15 consecutive resin uses. For the more hydrophilic waters, NOM removal remained consistent after each resin use. The hydrophobic sample contained more high MW NOM that was capable of blocking resin sites that prevented continual adsorption of organics on to the resin. The hydrophilic NOM containing a large proportion of hydrophilic acids were consistently removed to around 60 %. The water containing algogenic derived NOM was poorly removed by magnetic resin. Subsequent coagulation showed higher removal with increasing hydrophobicity.

Keywords

Algogenic, coagulation, hydrophilic, hydrophobic, magnetic ion-exchange resin, MIEX and natural organic matter.

1. INTRODUCTION

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

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

example, Fearing *et al.* (2004) showed better DOC and UV₂₅₄ removals (75 % and 95 % respectively) by reducing the coagulant dose from 14 mg L⁻¹ to 5 mg L⁻¹ as Fe (ferric sulphate) when using magnetic resin pre-treatment (20 mL L⁻¹ for 20 minutes).

Whilst the position with regard to reduced DBP formation using magnetic resin is clear, the current position with regard to the types of organic material preferentially removed by the resin is unclear. This is because NOM is a highly variable matrix that can differ temporally and spatially and is highly dependent on the catchment feeding the water body (Vogt *et al.*, 2004). Some work has shown that the resin is more effective at removing NOM from waters that have a high specific UV₂₅₄ absorbance (SUVA) of > 3.0 L m⁻¹ mg⁻¹ DOC, but is also able to remove hydrophilic fractions of NOM (Johnson and Singer, 2004; Boyer and Singer, 2005). Other work has shown that magnetic resin does not remove very large organic molecules >5000 Daltons (Fearing *et al.*, 2004) or small neutral organics (Kim *et al.*, 2005). Removal analysis of different molecular weight (MW) NOM fractions after resin treatment has shown that high MW compounds (5000-7000 Daltons (Da)) composed of hydrophobic humic and fulvic compounds were poorly removed following resin treatment (Allpike *et al.*, 2005). However, good removal was seen for smaller anionic species, thought to contain carboxylic groups. This is in agreement with Humbert *et al.* (2005), who have shown that intermediate MW organics between 500-1500 Daltons were well removed by the resin.

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

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

2. MATERIALS AND METHODS

2.1 Raw water characterisation

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

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

Raw water was collected and characterised by measuring raw water dissolved organic concentration (DOC) (Shimadzu 500A TOC analyser), ultraviolet absorbance at 254 nm (UV₂₅₄) (Jenway 6505 UV/vis spectrophotometer), turbidity (Hach 2100 turbidimeter) and zeta potential (Malvern Zetasizer). All analytical instruments were calibrated using the associated calibration procedure for the instrument prior to use and have an associated analytical error of approximately $\pm 5\%$. High performance size exclusion chromatography (HPSEC) analysis was carried out using a Shimadzu VP series high performance liquid chromatogram (HPLC) using UV₂₅₄ detection. The mobile phase was 0.1 M sodium acetate flowing at 1 mL min⁻¹. A TSK-gel G3000SW 7.5 mm (internal diameter (ID)) by 30 cm column was used with a TSK gel 7.5 (ID)

mm by 30 mm guard column (Tosoh Biosep GmbH, Stuttgart, Germany). The system was calibrated with 110 mL of source water filtered through ultra filtration membranes at different molecular weight cut-offs (MWCO). Membranes with MWCO values of 0.5, 1, 3, 5, 10 and 30 kDa were used (YM1-YM30, Millipore Pty Ltd., Massachusetts, USA, YC05, Millipore Pty Ltd., Sydney, Australia). Samples were analysed un-filtered for turbidity and zeta potential and were filtered using a glass fibre paper (<1 µm pore size, Munktell, Sweden) for DOC, UV₂₅₄ and HPSEC analysis.

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

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

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

2.2 Magnetic resin dosing

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

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

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

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

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

Conventional coagulation tests used optimum doses of 10 mg L⁻¹ Fe for all three waters.

2.3 Comparison of magnetic resin removal data

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

3. RESULTS

3.1 Raw water characterisation

The three raw waters investigated showed very different physico-chemical properties (Table 2). Whilst all waters were of similar DOC content (9.4 – 10.7 mg L⁻¹), the greater UV₂₅₄ absorbance of 60.1 m⁻¹ for Albert water reflected the more highly coloured nature of this water in comparison to Barcombe and Draycote (16.5 and 13.9 m⁻¹ respectively). Both Draycote and Albert were low turbidity waters (<1.8 NTU), whilst Barcombe had a high turbidity of 13.1 NTU as a result of this water containing high concentrations of algae. Microscopic examination identified that the dominant species in this water were green algae (*Chlorella* and *Scenedesmus*).

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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

meq g⁻¹ DOC. As a result of the high proportion of hydrophilic acids determined from fractionation in Draycote water, it may have been expected that this water would have had a higher charge density. However, this result was observed on repetition of the measurement.

The MW distribution of the UV₂₅₄ absorbing compounds also showed a relationship with the hydrophobicity and charge density data (Figure 2). The highly charged and coloured hydrophobic Albert water contained organics with much greater UV₂₅₄ absorbance with an area under the curve over four times that of Draycote and Barcombe. Albert water had a higher MW distribution of UV₂₅₄ absorbing organics compared to Barcombe and Draycote with two major peaks at 6 and 8 minutes elution time. Calibration of the column with source water filtered through ultra filtration membranes at different molecular weight cut-offs, approximated these peaks as being >5000 Daltons (Da). The part hydrophobic/hydrophilic Barcombe water had more high MW UV₂₅₄ organic compounds than Draycote with a dominant peak between 8.5-9 minutes, representing organics between 2000-5000 Da. The hydrophilic Draycote water had the lowest MW with a more even distribution of organics around a main peak at 9.5 minutes, approximating to organics of 2000 Da.

Given that the DOC content of the three waters was similar, the low level of UV₂₅₄ absorbance for Draycote and Barcombe indicated that a large portion of the organics in these waters could not be characterised using UV₂₅₄ detection. For this reason, subsequent discussion of data generated from UV₂₅₄ detection has been limited to the strongly absorbing Albert water.

3.2 Removals

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

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

Analysis of the HPSEC traces of UV₂₅₄ absorbing organics for Albert water showed a small reduction in the peak at 6 minutes elution time after resin treatment, identified by a 14 % decrease in curve area for organics eluted between 5-6.5 minutes (Figure 4). This material was the high MW organics that were >5000 Da. Most organic material was removed by the resin for NOM eluted between 7-9 minutes, with a reduction of 43 % over this range, indicating organics of around 5000 Da. This represented removal of a broad range of different MW organics for this water.

Subsequent coagulation removed significantly more UV₂₅₄ absorbing organics for the very hydrophobic Albert water compared to resin treatment alone. For the residual NOM after magnetic resin treatment, over 95 % of the curve area was removed ,

leaving a residual of small MW compounds representing NOM of <2000 Da. In comparison to coagulation alone, the combined resin and coagulation treatments showed 46 % less relative curve area for residual UV₂₅₄ absorbing organics for Albert water.

3.4 Consecutive magnetic resin uses

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

Analysis of HPSEC profiles for consecutive resin uses was again restricted to Albert water because this was the only water that was dominated by UV₂₅₄ absorbing compounds (Figure 6). There was a rapid decrease in the removal of MW material

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

4. DISCUSSION

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

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

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

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

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

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

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

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

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

The dominant hydrophilic compounds in the NOM from Draycote showed more consistent NOM removal on to the resin. The lower MW distribution of the UV₂₅₄ absorbing organics indicated that this type of NOM was able to access more of the available resin surface area (including internal pores) of the resin providing more available area for more consistent NOM removal when compared to the organics in the hydrophobic water. This was consistent with other work that has shown that hydrophilic acids are typically characterised by lower MW compounds that can be effectively removed by anionic ion-exchange resins (Bolto *et al.*, 2002). Hydrophilic acids of this type therefore seem very amenable to treatment using magnetic resin and

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

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

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

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

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

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

5. CONCLUSIONS

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

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

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