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Impact of magnetic resin on DOC removal and downstream water treatment processes

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Abstract

Seasonal periods of high rainfall and changes in land management have led to difficulties for UK water companies to remove sufficient natural organic matter (NOM) to stay in compliance with the tightening trihalomethane (THMs) standards. Hence alternative treatment options have come into focus of research and development.

The continuous anion exchange process based on a novel magnetic resin (MIEX® resin) has emerged as a promising method to increase NOM removal and has been compared in this thesis to the most widely spread drinking water treatment method of coagulation with hydrolysing metal salts. Therefore the removal efficiency of both processes was investigated by treating different natural waters sources as well as selected organic model compounds of different hydrophobicity and molecular weight (MW). Magnetic resin was thereby seen to be competitive with coagulation for DOC removal in low SUVA sources dominated by mid to low MW material and to outperform coagulation for the treatment of low MW, hydrophilic acids.

However magnetic resin had to be used in combination with subsequent coagulation using largely reduced Fe doses to ensure high levels of DOC removal in sources dominated by high MW NOM. This was related to a physical blockage mechanism of the easily accessible external resin bead surface by this high MW material. An effect that could be reduced by applying increased resin doses, which provided a larger external surface area for DOC removal.

A combination of magnetic resin treatment with coagulation was nonetheless seen to be able to increase DOC removal as well as to generate enhanced floc properties in terms of strength, settling velocity and size. Beside a reduced THM formation potential, making magnetic resin an effective tool to help meet legislative standards, an increased solid-liquid separation was seen in pilot-scale to result from these effects.

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Finally and most of all to Silvana for supporting me and helping me get through the really difficult times.

All I know is that I know nothing.

But I am pretty sure that I am rather right about what I am supposing.

Benoît Martiny

Luxembourgish musician

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Abbreviations and Notations

AOP	Advanced oxidation processes	
AC	Activated carbon	
BAC	Biologically actived carbon	
BSE	Back scattered electron detection system	
BV	Bed volumes	
$C_{0(A)}$	Concentration of NOM at 0 minutes contact time ($mg.L^{-1}$)	
$C_{(A)}$	Concentration of NOM at n minutes contact time ($mg.L^{-1}$)	
CSIRO	Commonwealth Scientific and Industrial Research Organisation	
DAF	Dissolved air flotation	
DBP	Disinfection by-product	($\mu g.L^{-1}$)
DBPFP	Disinfection by-product formation potential	($\mu g.L^{-1}$)
DI	Deionised water	
DOC	Dissolved organic carbon	($mg.L^{-1}$)
EDX	Energy dispersive x-ray analysis detection system	
EOM	Extracellular organic material	
FAF	Fulvic acid fraction	
G	Mean velocity gradient	(s^{-1})
GAC	Granular activated carbon	
HAA	Haloacetic acids	
HAF	Humic acid fraction	
HPIA	Hydrophilic acid	
HPINA	Hydrophilic non-acid	
HPLC	High performance liquid chromatography device	
HPOA	Hydrophobic acid	
HPSEC	High performance size exclusion chromatography	
HRD	High resolution detector	
HU	Hazen units	
IUPAC	International Union of Pure and Applied Chemistry	
K	Reactivity constant	
M	Mol	
MIEX®	Magnetic ion exchange	

MW	Molecular weight	(Daltons)
MWCO	Molecular weight cut-off	(Daltons)
NPOC	Non-purgeable organic carbon	
NOM	Natural organic matter	
NTU	Nephelometric turbidity units	
pKa	Acid dissociation constant	
PolyDADMAC	Polydiallyldimethylammonium chloride	
RO	Reverse osmosis water	
rpm	Revolutions per minute	
SA	South Australian (Water Corporation)	
SE	Secondary electron detector	
SEM	High-resolution cross-sectional scanning electron microscope	
SUVA	Specific ultraviolet absorbance	($L.m^{-1}.mg^{-1}$ DOC)
t	Time	(seconds, minutes)
THM	Trihalomethanes	($\mu g.L^{-1}$)
THMFP	Trihalomethane formation potential	($\mu g.L^{-1}$, $\mu g.mg^{-1}$ C)
TOC	Total organic carbon	($mg.L^{-1}$)
USEPA	United States Environmental Protection Agency	
UV	Ultraviolet	(m^{-1})
WTW	Water treatment works	

1. Introduction

1.1 Background

Natural organic matter (NOM) is a highly heterogeneous, poorly defined mix of organic substances, originating from the degradation of plant, animal and microbial material in soil and varies both temporally and spatially (Edzwald, 1993; Scott *et al*., 2001; Sharp *et al*., 2005; Park *et al*., 2006). While being harmless in itself, NOM can affect potable water quality by enhancing micro-pollutant transport (Ding and Wu, 1997) and thus lowering the efficiency of treatment processes such as activated carbon filtration for pesticide removal by competing for exchange sites (Li *et al*., 2003), increasing the coagulant demand (Sharp *et al*., 2006a), causing bacterial re-growth in the distribution system (Croué *et al*., 1999) and causing undesirable colour, taste and odour (Kam and Gregory, 2001).

However, the greatest concern regarding NOM and drinking water production arises from the formation of disinfection by-products (DBPs) when residual NOM reacts with oxidising chemicals during disinfection, normally chlorine based. Disinfection is necessary to kill and prevent growth of harmful microbes in drinking water (Krasner *et al*., 1989; Kim and Yu, 2007). The main DBPs of concern are the trihalomethanes (THMs) and the haloacetic acids (HAAs). The THM compounds were first identified in 1974 and have been shown to be potentially harmful to human health and have been shown to cause cancer in animals (Rook, 1974; Trussel and Umphres, 1978; Pomes *et al*., 1999). For this reason DBPs have been regulated in drinking water and the current upper limit for THMs in the UK is 100 $\mu g.L^{-1}$ (Drinking Water Inspectorate UK, 1998). In comparison, in the USA a THM limit of 80 $\mu g.L^{-1}$ has been established as well as a 60 $\mu g.L^{-1}$ limit for HAAs (USEPA, 1998).

A recent increase in NOM levels in UK water has been reported and related to events of increased surface run-offs coinciding with heavy rainfall but also to changes in land management (Eikebrokk *et al*., 2004; Hurst *et al*., 2004). The consequence of such increased NOM was that water companies that traditionally use hydrolysing metal salts for water treatment have struggled to stay in compliance with the THM regulations

(Parsons *et al*., 2005; Sharp *et al*., 2005a). By lowering the pH and increasing the applied coagulant doses, the amount of removed NOM removed during coagulation can be increased and the subsequent DBP formation reduced (Singer and Bilyk, 2002). However this approach of enhanced coagulation does not efficiently improve the elimination of hydrophilic low molecular weight (MW) NOM, which has shown to be largely recalcitrant to removal by coagulation and leads to reduced NOM removal in different sources (Carroll *et al*., 2000) (Table 1.1). In addition, the increased chemical doses used during enhanced coagulation result in both higher chemical costs and increased volumes of sludge that require disposal.

There has been considerable research and development focus into finding additional and/or alternative methods for improving NOM removal. Advanced oxidation processes (AOP) have received a considerable amount of attention as a potential tool for NOM removal (Goslan *et al*., 2004). This is because AOPs are strong oxidants that can potentially mineralise recalcitrant NOM. AOPs include a wide variety of different processes. The most commonly studied AOPs include: Fenton's reagent ($Fe(SO_4)_2$ and hydrogen peroxide), the photoFenton's process (Fenton's reagent ($Fe(SO_4)_2$, hydrogen peroxide and ultraviolet (UV) irradiation), ozone and UV irradiation, and titanium dioxide photocatalysis (TiO_2 and UV irradiation). Research carried out on AOPs have reported varying DOC removal levels of between 35 to 95 % with an increased effectivity when using a combination of different processes described above (Murray *et al*., 2004). While being able to compete with coagulation in terms of DOC reduction, the application of AOPs in full-scale has remained very limited for a number of reasons. Firstly, there has been a lack of full scale operational experience with these processes. Secondly, these technologies often have high associated chemical costs and high energy demand, particularly for the processes involving UV. Therefore AOPs have until now only been recommended as a pre-treatment to coagulation to reduce the NOM load to a level that the water treatment works can cope with adequately. Thereby the reduced NOM loads after AOP treatment were expected to result in lower coagulant doses allowing a reduction of the process costs (Goslan *et al*., 2004; Kitis and Kaplan, 2007).

Other processes used for NOM removal are adsorption by activated carbon (AC) and membrane filtration. These processes have been shown to be competitive with coagulation giving DOC removal levels of anywhere between 10 to 80 % for AC and 10 to 100 % for membrane filtration. However, high concentrations of NOM have been shown to quickly blind and foul the pores in both AC and in membranes. This results in high regeneration costs or even replacement of the AC and the membranes (Othman *et al.*, 2000; Li *et al.*, 2003; Chen *et al.*, 2007). These processes have been more commonly used as post-treatments after coagulation (Dong *et al.*, 2007). Additional DOC removals of between 10-15 % have been observed (Snoeyink and Chen, 1985; Tomaszewska and Mozia, 2002). The hydrophilic, low MW material recalcitrant to coagulation adsorbs onto the membrane surfaces and creates a gel layer that fouls the membranes, as well as to clog the micro and mesopores on AC, which resulted in reduced process efficiency (Li *et al.*, 1997; Gray *et al.*, 2007).

Macroporous anion exchange resins have been widely described as an efficient method for removal of NOM (Odegaard *et al.*, 1989; Fettig *et al.*, 1999; Bolto *et al.*, 2002). This is because a large fraction of NOM can be characterised as being anionic polyelectrolytes because they contain carboxylic and phenolic functional groups. However, NOM removal by anion exchange has never been widely used at full-scale, for a number of reasons (Hongve *et al.*, 1999):

1. *High capital costs*. Anion exchange is normally used in fixed bed columns. This has a high associated capital cost resulting from the necessity to install several columns to avoid process interruption during regeneration of the anion exchange resin (Van der Hoek and Klapwijk, 1989).

2. *Requirement for pre-treatment*. Anion exchange resins have been shown to require a pre-treatment step to remove suspended solids in the water before treatment in fixed bed columns in order to prevent plugging of the upper resin bed (Dorfner, 1972; Bolto *et al.*, 2004). Processes such as coagulation are used for the removal of suspended solids in waters with turbidity values above 5 nephelometric turbidity units (NTU) (Clifford, 1990).

3. *Resin fouling*. Macroporous resins experience fouling as prolonged operation time allows deep diffusion of NOM inside the bead pores. This fouling NOM inside the beads cannot be totally removed by regeneration due to slow diffusion of these

organics on resins (Slunjski *et al*., 1999). Aromatic NOM has been shown to be able to make the resin itself more hydrophobic. This can lead to a reduced water content in the resin preventing optimal diffusion of NOM into the pores (Gönder *et al*., 2006).

4. *Conduit forming*. A non-homogeneous flow of the water through the columns results in different parts of the resin bed being used (Danes, 1971).

Table 1.1 Existing process options for NOM removal and their ability to remove DOC.

Method	DOC removal (%)	Disadvantages	References
Coagulation	25-85	High coagulant demand and sludge volume, source dependant removal	Edzwald, 1993; Edzwald and Tobiason, 1999; Fearing *et al*., 2004; Pikkarainen *et al*., 2004; Shorrock and Drage, 2006; Uyak and Toroz, 2007
Advanced oxidation processes	35-95	High chemical demand, expensive, post-treatment to reduce energy costs	Goslan *et al*., 2004; Murray *et al*., 2004; Chin *et al*., (2005); Kitis and Kaplan, 2007
Granulated activated carbon	10-80	Pre-treatment to avoid clogging, expensive	Sketchell *et al*., 1995; Ribas *et al*., 1997; Othman *et al*., 2000; Babi *et al*., 2007
Membrane filtration	10-100	Pre-treatment to avoid clogging, expensive	Jacangelo *et al*., 1995; Schäfer *et al*., 2001; Wittmann *et al*., 2002; Kennedy *et al*., 2005; Kim and Yu, 2005
Macroporous Anion Exchange	30-95	Expensive, extra waste stream	Symons *et al*., 1995; Afcharian *et al*., 1997; Fettig *et al*., 1999; Hongve *et al*., 1999; Bolto *et al*., 2004

Magnetic ion exchange resin (MIEX$^{®}$ resin) has been developed to overcome the many problems associated with traditional ion exchange processes in fixed bed columns. The premise of the development of the resin process was based on the excellent NOM removal capacity of macroporous anion exchange resins, while changing the operational process to eliminate the disadvantages of fixed bed columns (Slunjski *et al*., 1999).

The resin process has been designed to take place in a continuous stirred contactor where NOM exchanges onto the resin, which is homogenously dispersed in the water. In the process, between 5-10 % of the resin is constantly recycled and regenerated. This configuration allows short service times of the resin (due to the constant regeneration) to prevent NOM from diffusing deep inside the pores and become recalcitrant to regeneration. This advantage was further enhanced by designing the beads 2-5 times smaller than conventional resins providing a much greater surface available for ion-exchange. This reduces the dependence on slow NOM diffusion in and out of the resin pores (Bourke *et al*., 1999; Slunjski *et al*., 1999). In addition, the continuous process based on a stirred contactor allows the treatment of high turbidity levels in the water (up to 55 NTU) thereby making any pre-treatment step unnecessary (Nguyen *et al*., 1997; Dahlke *et al*., 2006).

In terms of removal efficiency the magnetic resin was shown to be able to reduce the DOC in different water sources between 35 and 95 % (Johnson and Singer, 2004; Wert *et al*., 2005). When compared to coagulation, magnetic resin was however observed to give a higher level of DOC reduction in low specific ultraviolet absorbance (SUVA) sources and also results in the lower THM formation (Drikas *et al*., 2003; Boyer and Singer, 2005). Coagulation after the treatment with magnetic resin was still shown to be necessary to remove turbidity naturally occuring in the water and from resin carryover, however the doses can be reduced by up to 80 % (Hamm and Bourke, 2001; Slunjski *et al*., 2000a). Furthermore, coagulation was shown to be necessary in order to remove any residual NOM in high SUVA waters (Jefferson *et al*., 2004a). It was observed that this combined treatment broadens the removal range in terms of MW and resulted in lower THM formation potential (THMFP) values than coagulation only (Fearing *et al*., 2004).

1.2 Project development

Since its first implementation in 1996, magnetic resin has been used in a wide range of studies to remove NOM from different water sources with different properties (Slunjski *et al.*, 2002; Allpike *et al.*, 2005; Zhang *et al.*, 2006). The DOC removal ranges achieved by magnetic resin were however shown to vary independently of the properties of NOM.

To date much of the research published on treatment with magnetic resin focused on the removal level of DOC and UV_{254} absorbance, whilst other descriptors of NOM that are likely to play an important role in its removal have been given little or no attention. For example, the impact of the molecular size of NOM has been studied for other anion exchange resins, but not in connection with magnetic resin (Lee *et al.*, 1997; Gönder *et al.*, 2006). The charge density of NOM resulting from the functional groups of the organic molecules (Collins *et al.*, 1986) has not been investigated in any study on magnetic resin. Thus, there is scarce knowledge of the characteristics of NOM ideally suitable for removal by magnetic resin. In addition, it is believed that an approach based on the individual characteristics of NOM for each water source should be used when considering magnetic resin as an alternative process (Drikas *et al.*, 2003). The manufacturers of the magnetic resin therefore strive to understand the characteristics of NOM which influence its removal.

To achieve this goal a range of waters containing different types of organic material were characterised and treated using magnetic resin. This included two high SUVA waters dominated by high MW material and two low SUVA waters of a moderate MW. Solutions containing well defined model organic compounds were also investigated to allow us better understanding which specific characteristics of organic compounds controlled their removal. To simulate continuous usage of magnetic resin at full scale, and in contrast to previous bench-scale studies where one-off uses of virgin or freshly regenerated resin is normally studied (Johnson and Singer, 2004; Humbert *et al.*, 2005), a new continuous bench-scale method that re-uses the same resin dose several times was employed in this work.

Further subjects of this study was the investigation of the effect of magnetic resin on any subsequent coagulation step in order to remove NOM (Slunjski *et al*., 2000a; Fearing *et al*., 2004; Boyer and Singer, 2005) and to investigate the impact of such combined treatment (magnetic resin followed by coagulation) on floc characteristics such as size, strength and settling rate.

1.3 Aims and objectives

The aim of this thesis was to assess and understand:

- The efficiency of magnetic resin to remove NOM from different types of source waters.
- The nature and characteristics of NOM preferentially removed by magnetic resin.
- The downstream impact of magnetic resin pre-treatment on coagulation using hydrolysing metal salts.

Consequently, a series of objectives were identified:

- Investigation of the physico-chemical properties of magnetic resin.
- Comparison of NOM removal by magnetic resin in high SUVA waters, dominated by high MW aquatic humics of high aromaticity as well as in low SUVA sources containing NOM of lower MW and aromaticity.
- Provide a bench-scale and pilot-scale comparison between treating raw water and magnetic resin pre-treated water with conventional coagulation.
- Investigation of the impact of magnetic resin on strength, size and settling rates of the flocs formed after subsequent coagulation to identify the potential advantages or disadvantages of magnetic resin as a pre-treatment on solid-liquid separation and filtration.
- Analysis of the impact of magnetic resin treatment on the formation of carcinogenic THMs during the disinfection process due to interaction of chlorine with NOM recalcitrant.
- To assess the removal of different organic model compounds by magnetic resin and investigate properties of magnetic resin waste stream to establish a profile of NOM preferentially removed by magnetic resin.

1.4 Thesis plan and publications

A literature review was carried out (Chapter 2) to investigate if the reported preferential treatment of high SUVA sources by magnetic resin can be supported.
The literature review showed that magnetic resin has a preference for UV_{254} absorbing material in general, and furthermore, it is an effective treatment of low SUVA sources. The role that the MW of NOM plays in removal was also investigated. The Materials and Methods are defined in Chapter 3.

The results of the research are presented in 6 topic specific sections (Chapter 4).

In Section 4.1 the physico-chemical properties of magnetic resin were investigated, including the pore size, the water content and the bead size of the resin, which altogether have been described to be important parameters for effective NOM removal by anion exchange resins. The settling velocity of the magnetic resin beads was also investigated since carry-over of resin could be a potential issue at full-scale plants.

Section 4.2 reports an investigation of the efficiency of NOM removal by magnetic resin for both low and high SUVA waters as well as a range of organic model compounds, using bench-scale experiments. The impact of different NOM species in natural waters on the removal efficiency of magnetic resin has been accepted for publication (Mergen, M.R.D., Jarvis, P., Jefferson, B., Parsons, S.A.: *Magnetic resin treatment: Impact of water type and resin use. Water Research* (2008)), in press.

Section 4.3 compares the efficiency of coagulation using hydrolysing metal salts to magnetic resin treatment and links to Section 4.4 which investigates the impact of the pre-treatment with magnetic resin has on the properties of the flocs formed by coagulation.

Section 4.5 covers a laboratory and pilot plant comparison between the coagulation of magnetic resin pre-treated high SUVA water and coagulation alone looking at impacts on solid-liquid separation and the formation of THMs. The pilot scale data has been accepted for publication. (Jarvis, P., Mergen, M.R.D., Jefferson, B., Parsons, S.A.:

Magnetic resin and coagulation/DAF pilot plant trials. Environmental Science and Technology (2008)), in press.

To further investigate the characteristics of the organic material removed by magnetic resin, samples of used regenerant solution from 3 full-scale and 1 pilot-scale sites were collected and analysed (Section 4.6).

The overall implications of this research are pulled together in a final discussion (Chapter 5) and key conclusions are made (Chapter 6).

Final suggestions for further work are made in Chapter 7.

2. Literature review: NOM removal by magnetic resin treatment

2.1 Abstract

Natural organic matter (NOM) can be removed from water by anion exchange resins due to its weak acidic character. However, to date anion exchange resins have not been widely implemented due to their treatment design and recently a magnetic resin process (MIEX® resin), based on a continuous stirred contactor has become the focus of much research and development. The literature is not in agreement when it comes to describing the characteristics of NOM preferentially removed by the resin. For example the impact of different resin concentrations is clear in high SUVA sources where increasing the dose leads to increased NOM removal. The same is not clear for low SUVA waters. One explanation is that higher MW NOM, often related to high SUVA waters, is thought to require an increased number of easily available exchange sites to prevent it from blockage of internal ion-exchange sites. Downstream impacts of using magnetic resin include improved floc characteristics, reduced coagulant doses as well as reduced disinfection by-product formation.

2.2 Introduction

Natural organic matter (NOM) is composed to 70 to 80 % of weak organic acids which are ionised at the natural pH range of water (from pH 6 to 8) (Symons *et al*., 1995; Fettig *et al*., 1999). Functionally the organic material is predominantly phenolic and carboxylic in nature, but also contains alcohol, purine, amine and ketone groups (Dennett *et al*., 1995). The charge can be measured direct as charge density values ranging from 6.4 to 12.2 meq.g^{-1} DOC, reported for river, reservoir and aquifer waters (Collins *et al*., 1986).

NOM is commonly characterised by fractionating it into its hydrophobic and hydrophilic fraction and the hydrophobic fraction of NOM (HPOA) has been reported to have a charge density of 5 to 15 meq.g^{-1} DOC and thus one to three orders of magnitude higher than the hydrophilic acid fraction (HPIA) (Edzwald, 1993; Kam and Gregory, 2003; Sharp *et al*., 2006b). However, Croué *et al*., (1999) reported a charge density of 6.6 meq.g^{-1} DOC for HPIA and of 5.3 meq.g^{-1} DOC for hydrophilic non-acids (HPINA) from river water, whilst Sharp *et al*., (2006b) reported no detectable charge density for HPINA collected from a moorland source. Considering this anionic functionality of NOM, anion exchange based on the replacement of counter ions on the functional groups attached to the resins polymeric matrix with organic acids has been described as an alternative treatment for NOM removal to coagulation (Symons *et al*., 1995; Fettig *et al*., 1999; Odegaard *et al*., 1999; Bolto *et al*., 2002).

The aim of this review is to identify the characteristics of NOM preferentially removed by magnetic resin to define whether a certain water type is most suitable for this novel treatment as well as how the character of NOM can impact on its removal. Thus, the removability of NOM of different UV_{254} absorbance, hydrophobicity and molecular weight (MW) was compared. Furthermore the impact of magnetic resin on downstream coagulation was investigated and compared to conventional coagulation to elucidate the reported beneficial impact on solid-liquid separation and DBP formation.

2.3 Efficiency of NOM removal by anion exchange

Anion exchange resins can be characterised by their functional groups into strong-base exchange resins (SBA) and weak-base exchange resins (WBA). SBA resins which contain quaternary ammonium exchange sites can be further differentiated into Type I and Type II resins. The Type II exchange site $(\mathrm{Resin\text{-}CH_2N(CH_3)_2CH_2OH^+Cl^-})$ is differentiated by the presence of an additional hydroxide group from the Type I exchange site $(\mathrm{Resin\text{-}CH_2N(CH_3)_3^+Cl^-})$ (Brattebo *et al*., 1987; Kim *et al*., 1976; Wachinski and Etzel, 1997). During water treatment NOM is exchanged against chloride or hydroxide which are the counter ions on the exchange sites in the following reaction (Wachinski and Etzel, 1997):

$$\mathrm{Resin\text{-}CH_2N(CH_3)_3^+Cl^- + RCO_2^- \rightarrow Resin\text{-}CH_2N(CH_3)_3^+RCO_2^- + Cl^-}$$

During regeneration with either sodium hydroxide or sodium chloride the exchange is reversed in the following reaction (Kishore and Verma, 2006):

$$\mathrm{Resin\text{-}CH_2N(CH_3)_3^+RCO_2^- + Cl^- \rightarrow Resin\text{-}CH_2N(CH_3)_3^+Cl^- + RCO_2^-}$$

It was reported that the use of SBA resins in the chloride form was advantageous for NOM removal due to the higher selectivity coefficient on resin functional groups of chloride when compared to hydroxide, allowing an easier regeneration of the resin (Gottlieb *et al*., 1996; Bae *et al*., 2002).

WBA resins have functional groups that are either secondary $(\mathrm{Resin-CH_2NHR})$ or tertiary amines $(\mathrm{Resin-CH_2NHR_2})$. They operate only at pH levels below 6. Their functional groups operate by adsorbing acids and form amine hydrosalts (Brattebo *et al*., 1987; Wachinski and Etzel, 1997).

Alongside functionality, the nature of the bead matrix was observed to influence NOM removal. Resin beads are crosslinked organic polymers which are made in bead form by dispersion polymerisation of their respective monomers, such as acrylates and styrene and a crosslinking agent such as divinylbenzene (Yang *et al*., 2005; Wang *et al*., 2006). An increase of the crosslinking agent level above 20 % during the production process, gives rise to a permanent macroporous structure, which allows a facilitated diffusion of large molecules inside the particle that contains most functional groups. Crosslinking agent levels below 20 % result in so-called gel resins which micropores depend on the resins swelling ability to allow intraparticular diffusion (Kunin and Yarnell, 1997; Ahmed *et al*., 2004; Badyal *et al*., 2004). Hydrophilic acrylic resin backbones are reported to be more prone to swelling and thereby leading to increased water content, allowing an increased intraparticular NOM diffusion in comparison with hydrophobic styrenic resins (Gottlieb, 1996).

Comparison of different studies on anion exchange resins in fixed bed columns confirms that SBA resins with macropores as well as a polyacrylic backbone allowed the greatest NOM removal (Symons *et al*., 1995; Afcharian *et al*., 1997; Bolto *et a*l., 2004; Tan *et al*., 2005).

Anionic resins are the only suitable ion exchange resins for NOM removal. Afcharian *et al*., (1997) reported a 90 % DOC reduction from a river water by two MP-SBA-St.DVB resins (MP-500®, S6328A®) while two styrenic, macroporous non-ionic resins (VPOC-1062®, VPOC-1064®), designed to remove NOM by adsorption (Ribeiro and

Ribeiro, 2005), reduced the DOC by only 20 %. In comparison a strong acid exchange resin designed to remove cations (SP-112®) did not result in any significant DOC removal.

A comparative study reported by Bolto *et al.*, (2004) showed that styrenic macroporous SBA resins (MP-SBA-St.DVB) were able to remove more UV_{254} absorbing material than styrenic gel SBA resins (Gel-SBA-St.DVB) of similar water content. Macroporous MP-500® which had a 43 % water content removed 20 % of the UV_{254} absorbance, while the gelular IRA-400® with a 45 % water content removed only 14 % of the UV_{254} absorbance (Table 2.1). The same trend was seen for the macroporous IRA-904® (57 % water) and the gelular IRA-401® (56 % water) which removed 43 and 24 % respectively of the UV_{254} absorbance. Tan *et al.*, (2005) confirmed these observation as the gelular resin Marathon A® removed 30 % of DOC, while the macroporous resin DOWEX-22® removed 70 % DOC. The fact that the weak base macroporous, styrenic resin (MP-WBA-St.DVB) DOWEX-M43® also removed 70 % DOC was however unexpected as the pH of the water treated by Tan *et al.*, (2005) was of 6.8 to 8.6. This trend of enhanced NOM removal by macroporous resins was attributed to the enhanced diffusion of NOM molecules inside the rigid styrenic resin beads via the macropores. However the use of a polyacrylic backbone was shown to be able to significantly increase the removal capacity of gelular resins. The gelular acrylic SBA resin IRA-458® (Gel-SBA-Acryl.) was seen to remove 47 % UV_{254} absorbance, while the MP-SBA-St.DVB IRA-900® removed 43 % UV_{254} absorbance. Nonetheless the macroporous polyacrylic SBA resin (MP-SBA-Acryl) IRA-958®,with a 97 % UV_{254} absorbance reduction, allowed the best performance, which was attributed to the combination of macropores and to the increased swelling properties of the resin.

An increase in DOC removal due to a hydrophilic backbone in macroporous as well as gelular resins was confirmed by Symons *et al.*, (1995) who compared the efficiency of IRA-458® to remove total organic carbon (TOC) that was of a MW >10 kDa. They found that the hydrophilic gelular IRA-458® reduced the TOC by 65 % to a higher extent than IRA-402® (Gel-SBA-St.DVB), XE-510® (MP-SBA-St.DVB) and IRA-904® (MP-SBA-St.DVB) with 15 to 60 % TOC reduction. IRA-958® with a polyacrylic, macroporous structure (200 nm pore diameter) was reported to outperform with 80 %

TOC reduction all other resins as already seen by Bolto *et al*., (2004). Nonetheless IRA-938®, which was of styrenic macroporous structure removed 88 % of TOC and thus more than IRA-958®. This resin was reported by Symons *et al*., (1995) to have pore diameters of 7000 nm, which would not obstruct the intraparticular diffusion of NOM molecules, reported of 2 to 50 nm (Collins *et al*., 1986; Thurman and Malcolm, 1986), even if it had low swelling properties.

It can be concluded that the ability of anionic resins to swell and thereby increase the resin water content, as well as having increased pore diameters were key properties for good NOM removal.

Table 2.1 Impact of ion exchange resin properties on efficiency for NOM removal in bench-scale fixed bed column tests (adapted from Afcharian *et al*., 1997; Bolto *et al*., 2004; Symons *et al*., 1995; Tan *et al*., 2005) (NI: Not indicated)

Reference	Resin name	Matrix	Particle size (µm)	Pore diameter (nm)	Water content (%)	Investigated parameter	Reduction of investigated parameter (%)
Afcharian *et al*., 1997	MP-500®	MP-SBA-St.DVB	620	NI	43	DOC	90
	S6328A®	MP-SBA-St.DVB	400-1250	NI	NI	DOC	90
	VPOC-1062®	MP-Nonionic-St.DVB	NI	11	NI	DOC	20
	VPOC-1064®	MP-Nonionic-St.DVB	NI	5	NI	DOC	20
	SP-112®	MP-SAC-St.DVB	650	NI	52-57	DOC	0
Bolto *et al*., 2004	MP-500®	MP-SBA-St.DVB	620	NI	43	UV$_{254}$	20
	IRA-400®	Gel-SBA-St.DVB	300-900	NI	45	UV$_{254}$	14
	IRA-904®	MP-SBA-St.DVB	NI	70	57	UV$_{254}$	43
	IRA-401®	Gel-SBA-St.DVB	NI	NI	56	UV$_{254}$	24
	IRA-900®	MP-SBA-St.DVB	650-820	NI	60	UV$_{254}$	42
	IRA-458®	Gel-SBA-Acryl.	600-900	NI	60	UV$_{254}$	47
	IRA-958®	MP-SBA-Acryl.	700-900	200	69	UV$_{254}$	97
Symons *et al*., 1995	IRA-402®	Gel-SBA-St.DVB	NI	NI	NI	TOC (>10 kDa)	15
	XE-510®	MP-SBA-St.DVB	NI	20	NI	TOC (>10 kDa)	50
	IRA-904®	MP-SBA-St.DVB	NI	70	57	TOC (>10 kDa)	60
	IRA-458®	Gel-SBA-Acryl.	600-900	NI	NI	TOC (>10 kDa)	65
	IRA-958®	MP-SBA-Acryl.	700-900	200	69	TOC (>10 kDa)	80
	IRA-938®	MP-SBA-St.DVB	450	7000	73	TOC (>10 kDa)	88
Tan *et al*., 2005	Marathon A®	Gel-SBA-St.DVB	500-550	NI	50-60	DOC	30
	DOWEX-22®	MP-SBA-St.DVB	NI	NI	48-56	DOC	70
	DOWEX-M43®	MP-WBA-St.DVB	NI	NI	40-50	DOC	70

2.4 Development of magnetic ion exchange resin

Anion exchange resins in conjunction with coagulation treatment have shown to be able to achieve DOC reduction levels from 30 to 95 % in terms of NOM removal efficiency. Nonetheless anion exchange has never been widely applied at full-scale, and to date only few examples can be cited. For example, only 12 out of 160 water treatment works designed for NOM removal in Norway use anion exchange (Odegaard *et al*., 1999). In Germany only one plant has been reported to use anion exchange (Brattebo *et al*., 1987). This low level of application of the process was described to be related to a number of reasons:

1. Several fixed bed columns are required in order to avoid process interruption during regeneration of the resin (Van der Hoek and Klapwijk, 1989).
2. Intolerance of fixed bed columns to turbidity values above 5 NTU (Clifford, 1990). This requires pre-treatment processes to be installed before ion-exchange.
3. Irreversible resin fouling from NOM diffusing deep inside the pores of the resin (Slunjski *et al*., 1999). Significant resin treatment is required in order to remove these organics from the resin.
4. A non-homogeneous flow of the water through the columns (Conduit forming) results in only different parts of the resin bed being used (Danes, 1971).

In order to tackle these problems while maintaining the advantages of anion exchange resins for NOM removal, CSIRO, SA Water Corporation and Orica started to develop the magnetic resin process during the 1960’s. To increase the accessibility of the beads, as well as to increase intraparticular diffusion during NOM removal and regeneration a macroporous, polyacrylic structure able to swell was chosen over a gelular or styrenic structure. Furthermore to reduce slow diffusion rates, magnetic resin with mean particle diameter of 150 to 180 μm was designed (Slunjski *et al*., 2002). Type I quaternary ammonium exchange sites in the chloride form were chosen to allow the resin to operate in a large range of waters of different pH levels as well as to enable a better removal of organic material during regeneration since the affinity of chloride is higher when compared to hydroxide (Gottlieb *et al*., 1996; Wachinski and Etzel, 1997; Bae *et al*., 2002;).

To avoid process interruption for regeneration of the resin and to guarantee a homogeneous contact of the resin with water, the process was designed as a continuous process in up to three contactors to avoid short-circuiting (Figure 2.1). Optimum conditions are usually established in preliminary jar tests, typically using resin doses between 5-30 $mL.L^{-1}$ and contact times between 5-30 minutes. The resin is then separated from the treated water in a gravity settling tank where solid-liquid separation is enhanced by the magnetic properties of the beads which contain magnetic iron oxide to promote agglomeration. Due to the rapid separation of the resin, high separator loading rates can be used (10 $m^{-3}.m^{2}.h^{-1}$). As a result of this, the process is resistant to turbidity levels of up to 55 NTU (Nguyen *et al.*, 1997; Slunjski *et al.*, 2002).

Around 90-95 % of the settled resin is recycled back into the contact tank for immediate reuse. The other 5-10 % is diverted and collected in a regeneration tank. The resin is regenerated with a 12-20 w% NaCl regenerant solution on average every 4 to 5 hours. This step is necessary in order to avoid NOM to deeply diffuse into the pores and lead to irreversible fouling of the beads. After regeneration the diverted resin remains in a storage tank until it is re-used (Nguyen *et al.*, 1997; Slunjski *et al.*, 1999; Smith *et al.*, 2002). As the stirred contactors involve a constant recirculation of the resin by pumps it is noteworthy that the chosen macroporous structure of the beads was observed to be of advantage since it makes the beads more resistant to hydraulic pressure (Kunin and Yarnell, 1997). This is due to the higher percentage of crosslinking agents of the macroporous structure.

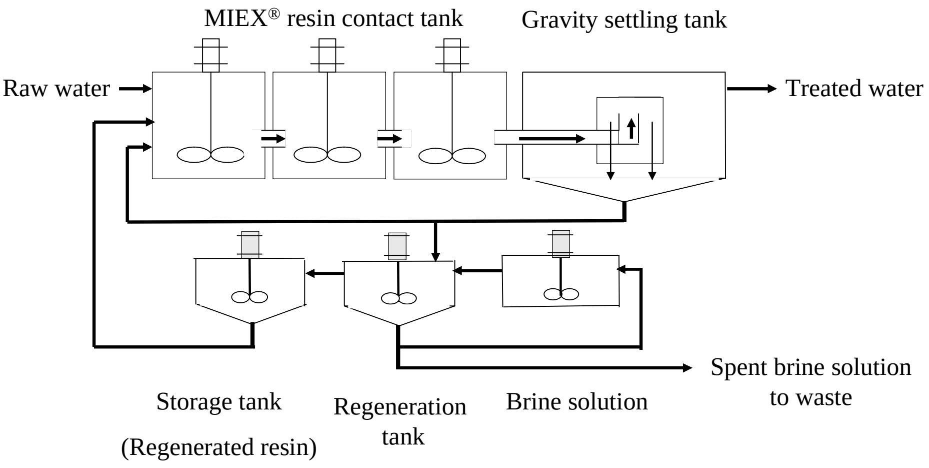


Figure 2.1 Magnetic resin process schematic (adapted from Budd *et al.*, 2004).

The first full-scale magnetic resin plant was installed in Australia in 1996 (Morran *et al.*, 1996) and since then the process has been installed at 9 different water treatment works (WTW) worldwide with capacities ranging from 325 to 110000 m^3 d^{-1} (Table 2.2).

Table 2.2 Existing magnetic resin treatment plants (adapted from: Allpike *et al.*, 2005, MIEX® Press International, 2005; MIEX® Press International, 2007; Nestlerode *et al.*, 2006a; Orica Watercare, 2006a; Orica Watercare, 2006b; Pelekani *et al.*, 2001)

Location	WTW name	Water type	Maximum Capacity (m^3 d^{-1})	Reference
Australia	Aireys Inlet	Reservoir water	2850	Orica Watercare, 2006a
	Mt. Pleasant	River Water	2500	Pelekani *et al.*, 2001
	Wanneroo	Ground water	110000	Allpike *et al.*, 2005
Belgium	Kluizen	Reservoir water	1200	MIEX® Press International, 2005
United States	Big Elk Meadows	River water	325	Orica Watercare 2006b
	Green Valley	Lake water	4500	Nestlerode *et al.*, 2006a
	Palm Springs	Groundwater	45000	Orica Watercare 2005
	Cedar Key	Groundwater	1620	MIEX® Press
	Wedgefield	Ground water	6480	International, 2007

The literature has been inconclusive about the type of NOM preferentially removed by magnetic resin. Boyer and Singer (2005) and Budd *et al.*, (2003) reported good removal in water dominated by aromatic high MW NOM, while Bourke (2001) reported the resin preferentially removed low MW NOM. Drikas *et al.*, (2003) described magnetic resin to be effective for all types of water but that its efficiency was dependant on the character of the organics in each individual source.

2.5 NOM removal by magnetic resin

2.5.1 Comparison of DOC removal efficiency of magnetic resin with other resins

Although there is a range of commercially available anion exchangers, there has been only one comparison of NOM removal by magnetic resin (MIEX®) and other resins (IRA-938®, DOWEX-MSA® and DOWEX-11®) for the same water source (Humbert *et al.*, 2005) in the literature (Table 2.3). This work investigated the DOC and UV_{254}

absorbance removal kinetics in a water containing 6.6 mg.L^{-1} DOC with a SUVA of 2.3 L. m^{-1}.mg^{-1} DOC.

The magnetic resin beads were the smallest to be tested and also the only resin with a hydrophilic, polyacrylic backbone (Table 2.3). IRA-938® has a higher water content (73 %) than DOWEX-11® and DOWEX-MSA® with 48 to 58 and 56 to 66 % respectively. No data was reported for the magnetic resin.

Table 2.3 Description of different resins designed for NOM removal (adapted from: Humbert *et al.*, 2005)

Resin name	Matrix	Particle size (µm)	Water content (%)
Magnetic resin	Macroporous Polyacrylic	150-180	/
IRA-938®	Macroporous Styrenic DVB	450	73
DOWEX-11®	Gel Styrenic-DVB	500-600	48-58
DOWEX-MSA®	Macroporous Styrenic DVB	590-690	56-66

Humbert *et al.*, (2005) compared contact times required for efficient NOM removal and showed that magnetic resin had reached a state of pseudo-equilibrium after only 10 minutes. DOC and UV_{254} absorbance removal of 77 and 90 % respectively could not be significantly increased after 10 minutes contact (Figure 2.2 (A) and (B)). Pseudo-equilibrium was described as the point at which the kinetic reactions become so slow, that sorption and desorption of NOM on the resin is nearly in balance (Dorfner, 1972; Talwalkar and Mahajani, 2006).

IRA-938® resin also reached pseudo-equilibrium after 10 minutes contact time, and removed 73 and 95 % DOC and UV_{254} absorbance respectively. DOWEX-11® and DOWEX-MSA® removed DOC and UV_{254} absorbance by 67-55 % and 82-71 % respectively after 30 minutes contact time and were reported to reach pseudo-equilibrium after 1 hour. Boyer and Singer (2005) and Singer and Bilyk (2002) both evaluated contact time and reported that 20 minutes were required to reach equilibrium at which 70 and 75 % UV_{254} absorbance, respectively, was removed.

When comparing the final SUVA of the treated water, values of 0.9 and 0.5 L.m^{-1}.mg^{-1} DOC were measured for magnetic resin and IRA 938® respectively, while values of 1.3 and 1.5 L.m^{-1}.mg^{-1} DOC were measured for DOWEX-11® and DOWEX-MSA® respectively. It could be seen from this comparison that magnetic resin and IRA-938® removed more of the UV_{254} absorbing organics than DOWEX-11® and DOWEX-MSA®.

Humbert *et al*., (2005) attributed the better performance of magnetic resin to its smaller bead size which, as described by Bolto *et al*., (2004), allows NOM to rapidly attach to the larger and easily accessible external exchange sites. It was also suggested that the macroporous, polacrylic structure of magnetic resin allows the resin to swell to a high extent and facilitates intraparticular NOM diffusion and hence frees the external exchange sites. Both Bolto *et al*., (2004) and Symons *et al*., (1995) have previously shown that the macroporous, polyacrylic IRA-958® ranged in the top end in terms of removal efficiency when compared to styrenic macroporous resins. The high removal for IRA-938® was related to its large macroporous structure (Humbert *et al*., 2005).

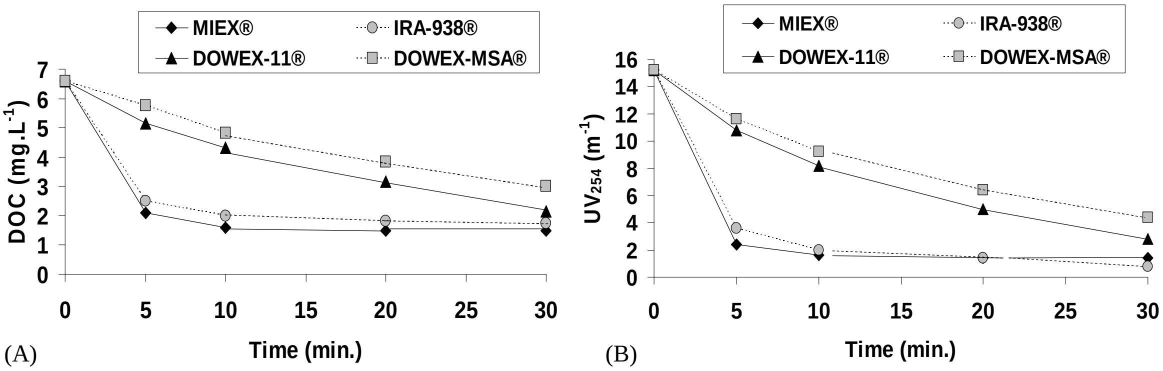


Figure 2.2 DOC (A) and UV_{254} (B) removal kinetics for magnetic resin (MIEX®), IRA-938®, DOWEX-11® and DOWEX-MSA® (adapted from: Humbert *et al*., 2005).

2.5.2 Reduction of DOC and UV_{254} absorbance in different high and low SUVA sources

Data has been collected for comparison of DOC and UV_{254} absorbance reduction from a range of studies on magnetic resin undertaken at full, pilot and bench-scale (Table 2.4). The pH of the source waters ranged from 6.6 to 8.1, at which carboxylic functional groups had been described to be ionised and suitable for anion exchange (Symons *et al*., 1995). Considering that in the literature there have been different opinions whether magnetic resin is more appropriate for treatment of high or low SUVA waters (Bourke, 2001; Boyer and Singer, 2005; Budd *et al*., 2003) removal levels in different water sources were compared to each other.

The full-scale and pilot-scale studies have been presented separately from bench-scale studies, as the bench-scale data is often based on a single resin use, whilst full and pilot-scale have continuous resin use. Full-scale treatment studies such as those reported by Allpike *et al*., (2005); Nestlerode *et al*., (2006b); Drikas *et al*., (2003) and Hamm and Bourke (2001) gave similar 44-60 % DOC or TOC removal from waters with SUVA values of 1.3-5.7 L m^{-1} mg^{-1} DOC. No clear pattern in DOC removal efficiency using the resin for waters of high or low SUVA was observed. Pilot-scale studies typically showed an increase in DOC removal with increasing SUVA values. For example Boyer and Singer (2006), Shorrock and Drage (2006) and Wert *et al*., (2005) treated waters with SUVA values of 3.2, 2.2 and 0.9 L m^{-1} mg^{-1} DOC and removed 73 %, 34 % and 30 % DOC and TOC respectively.

Kitis *et al*., (2007) investigated five different source waters with SUVA values ranging from 2.7 to 5.1 $L.m^{-1}.mg^{-1}$ DOC at bench-scale by re-using the same resin dose up to 20 times. They showed that initial DOC removal of 30 to 60 % quickly decreased by up to 30 % during the first 9 re-uses and then stabilised at removal rates of 20 to 30 %. Whilst this multiple use reflects full and pilot-scale operation, the single bench-scale studies are useful as they show how different types of NOM exchanges on resin when it has a fully available exchange capacity.

When comparing NOM removal at bench-scale using a single resin dose, Fearing *et al*., (2004); Jefferson *et al*., (2004); Johnson and Singer, (2004); and Kim *et al*., (2005) were able to remove 66 to 93 % of DOC from high SUVA waters (>4 $L.m^{-1}.mg^{-1}$ DOC). Whilst for low SUVA waters (<4 $L.m^{-1}.mg^{-1}$ DOC) at bench-scale the removal roughly equaled to that of observed in the high SUVA waters, had however consistently lower rates ranging from 40 to 80 %.

Table 2.4 Overview of treatment parameters and removal percent from magnetic resin treatment in full-scale, pilot-scale and bench-scale
(*: Measured as TOC, NI: Not indicated)

Reference	Scale	Raw water values				Magnetic resin		Removal		UV_{254} additionally removed to DOC
		pH	DOC ($mg.L^{-1}$)	UV_{254} (m^{-1})	SUVA ($L.m^{-1}.mg^{-1}DOC$)	Dose ($mL.L^{-1}$)	Time (min.)	DOC (%)	UV_{254} (%)	(%)
Allpike *et al*., 2005	Full	7.1	5.7	32.6	5.7	NI	NI	57	46	-11
Nestlerode *et al*., 2006b	Full	7.3-8.1	2.0-7.0*	5.4-24.5	2.7-3.5	NI	NI	60	NI	NI
Drikas *et al*., 2003	Full	NI	3.2	4.3	1.3	8	20	58.5	76.7	18.2
Hamm and Bourke, 2001	Full	7.4	3.4*	12.2	3.6	6	30	44*	60	16
Boyer and Singer, 2006	Pilot	6.6-6.9	4.8	15.5	3.2	15	20	73	72	-1
Shorrock and Drage, 2006	Pilot	7.8	6.8	14.7	2.2	20	10	34	55	21
Wert *et al*., 2005	Pilot	7.9	3.2*	2.9	0.9	20	15	30*	60	30
Zhang *et al*., 2006	Pilot	6.8-7.5	6.5*	NI	NI	10	20	60*	NI	NI
Boyer and Singer, 2005	Bench	8.1	5.1	10.2	2	4	20	41	55	14
Boyer and Singer, 2005	Bench	7.5	5.1	19.3	3.8	5	20	72	83	11
Cook *et al*., 2002	Bench	NI	5.8	13.7	2.4	6	15	64	82	18
Cook *et al*., 2002	Bench	NI	10	34.6	3.5	8	15	74	84	10
Fearing *et al*., 2004	Bench	5.9-6.9	7.8-11.2	32.5-50.1	4.5-5.1	10	60	66.1-82.1	65.5-86.5	0.6-4.4
Humbert *et al*., 2005	Bench	7.0-7.9	6.3	15.6	2.5	8	30	80	85	5
Jefferson *et al*., 2004	Bench	NI	8.5	50.6	6.0	20	NI	76	77	1
Johnson and Singer, 2004	Bench	8.1	5.9	40.4	6.9	8	30	93	95	2
Kim *et al*., 2005	Bench	7.9	4	9.5	2.4	8	30	40	67	27
Kim *et al*., 2005	Bench	7.3	4.9	14.3	2.9	8	30	62	79	17
Kim *et al*., 2005	Bench	7.7	16	65.4	4	8	30	70	80	10

However no clear trend was observed between the SUVA and DOC removal (Figure 2.3). Low regression coefficients of 0.2 and 0.5 for full-scale/pilot scale and bench-scale respectively confirmed that DOC removal of a similar extent was possible in waters of different SUVA levels, while the removal could largely vary for waters of similar SUVA. This indicates that other parameters such as MW or charge density play an important role in the removal of NOM by magnetic resin. This is in agreement with Drikas *et al.*, (2003) who stated that the character of the organics in each individual source actually governed their removal by magnetic resin.

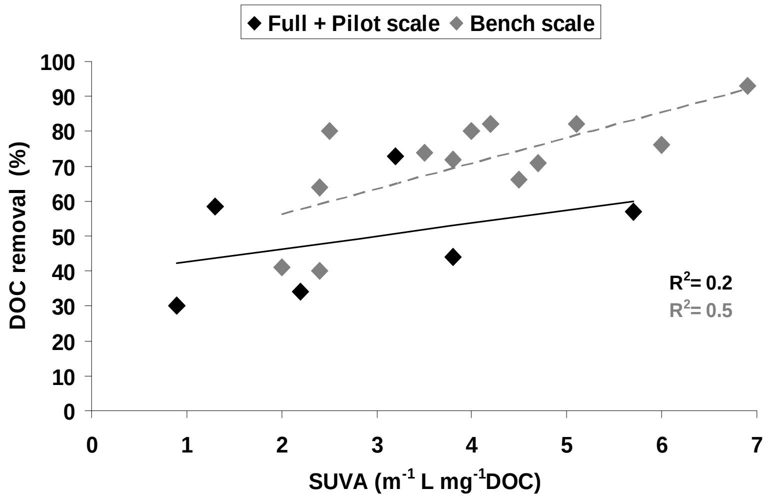


Figure 2.3 DOC removal vs. SUVA values (adapted from references in Table 2.4).

When comparing DOC and UV_{254} removal, UV_{254} absorbing material showed a trend for preferential removal by magnetic resin over DOC. For example, in both full and pilot-scale trials the treatment of waters with high SUVA values of 5.7 and 3.6 L.m^{-1}.mg^{-1} DOC removed 11 and 16 % more UV_{254} absorbing material than DOC respectively (Allpike *et al.*, 2005; Hamm and Bourke, 2001). Drikas *et al.*, (2003); Boyer and Singer (2006); Shorrock and Drage (2006) and Wert *et al.*, (2005) who treated waters with SUVA values of 0.9-3.2 L.m^{-1}.mg^{-1} DOC, removed up to 30 % more UV_{254} absorbing material than DOC (Figure 2.4). Similarly at bench-scale, there was 10-27 % more removal of UV_{254} than DOC in low-moderate SUVA waters and 0.6-10 % more removal of UV_{254} than DOC in high SUVA waters.

This trend for preferential removal of UV_{254} absorbing material has been previously reported for other anion exchange resins by Afcharian *et al.*, (1997). In their study the UV_{254} absorbance was removed by 90 % compared to 70 % for DOC by two styrenic macroporous resins. This selectivity of UV_{254} absorbing NOM increased with the number of aromatic rings in the resin. Thereby the styrenic resins, which contain aromatic structures making them hydrophobic, were described to be more selective to remove aromatic NOM than acrylic resins due to higher electrostatic interactions and hydrophobic bonding by their matrix (Gustafson and Lirio, 1968).

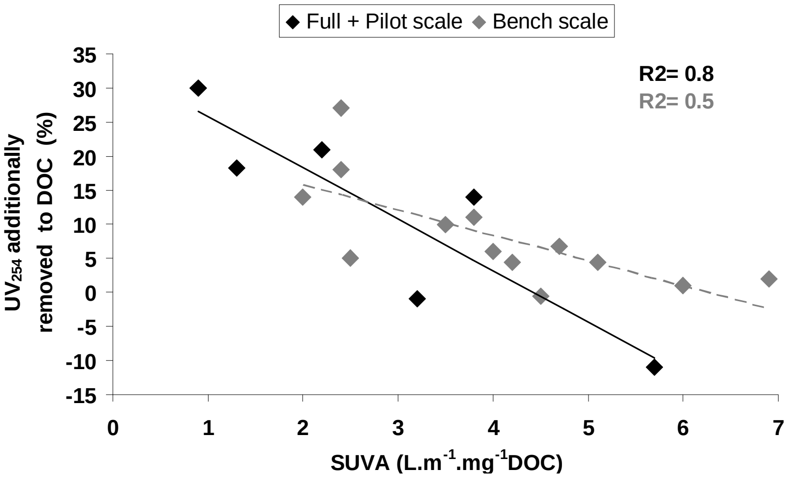


Figure 2.4 Additional UV_{254} removal percentage above DOC removal vs. increasing SUVA values (adapted from references in Table 2.4).

2.5.3 Removal of different NOM fractions by magnetic resin

A number of studies have focused on the change of the NOM fractionation before and after magnetic resin treatment (Boyer and Singer, 2006; Kim *et al.*, 2005 and Zhang *et al.*, 2006). The data generally shows that the hydrophobicity of NOM is not a criteria for removal by magnetic resin, as HPOA, HPIA and HPINA reduction ranged from 0-76 %, 41.8-89 % and 36-69.1 % respectively over five sources (Figure 2.5). Fearing *et al.*, (2004) treated NOM fractions isolated from water containing 75, 9 and 16 % of HPOA, HPIA and HPINA with 10 $mL.L^{-1}$ magnetic resin (60 min. c.t.) and reported similar removal of 60 and 43 % for HPOA and HPINA respectively. However Fearing *et al.*, (2004) was only able to remove 25 % of the HPIA fraction, which was related to a potential exclusion of some high MW compounds classified as HPIA from pore diffusion. Size exclusion as a limiting factor for the removal of a specific fraction was also suggested by Croué *et al.*, (1999), who was able to reduce HPOA, HPIA and HPINA by 40, 75 and 85 %, respectively, when using a macroporous styrenic resin. Size exclusion on anion exchange resins had been described to occur for high MW NOM that is able to block the resin surface or its pores (Gottlieb *et al.*, 1996; Lee *et al.*, 1997; Hebb *et al.*, 2003; Gönder *et al.*, 2006). Size exclusion as a reason for low removal of HPIA in the case of Fearing *et al.*, (2004) appeared more probable as this fraction had been described in different studies beside HPOA to dispose of ionised functional groups (Croué *et al.*, 1999, Sharp *et al.*, 2005b) and allowing them to be good candidates for anion exchange.

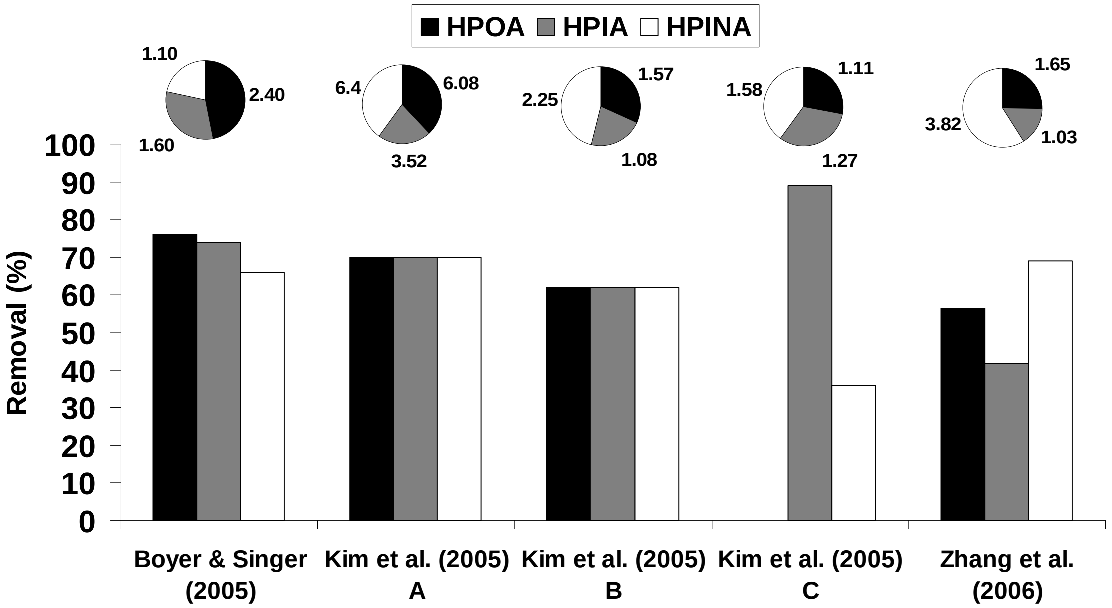


Figure 2.5 Removal percentage of different NOM fractions by magnetic resin (adapted from: Boyer and Singer, 2005; Kim *et al.*, 2005; Zhang *et al.*, 2006).

To date no study on magnetic resin or other anionic resins has related charge density to removal performance. This is surprising given that charge density has been reported above to vary considerably among the fractions and given that anion exchange resins are known to have an affinity for highly charged fractions (Anderson and Maier, 1979).

NOM removal by anion exchange resins does not have to only occur by an ion exchange mechanism but can be removed by other mechanisms. For example it was seen by Symons *et al.*, (1995) that no chlorine release could be measured when removing TOC fractions <1 kDa with anion exchange resin. Symons *et al*., (1995) related this to the TOC being removed by surface adsorption (Van der Waals forces); a mechanism which had already been suggested by Anderson and Maier (1979) and Kunnin and Suffet (1980). Bolto *et al*., (2004) reported 45 to 78 % removal of hydrophilic neutral compounds for a styrenic resin, described however surface adsorption to be more likely to happen on a hydrophobic resin rather than on a hydrophilic resin such as magnetic resin. Nonetheless such a secondary mechanism allowing the removal of HPINA by magnetic resin could not be excluded, as this fraction, with the exception of Croué *et al*., (1999), had been described to have a charge density below the level of detection (Edzwald, 1993; Sharp *et al*., 2006b).

2.5.4 Impact of molecular weight on magnetic resin and coagulation removal efficiency

Coagulation is widely known to preferentially remove high MW NOM (Huang *et al*., 1996; Sharp *et al*., 2006c) while anion exchange resins remove NOM of lower MW as was shown earlier in other studies (Anderson and Maier, 1979; Croué *et al*., 1999; Bolto *et al*., 2004). Fearing *et al*., (2004) and Jefferson *et al*., (2004) both used high performance size exclusion chromatography (HPSEC) to investigate the MW of NOM removed by magnetic resin (Figure 2.6). In their work three elution time ranges have been taken from the HPSEC profiles, using an UV_{254} detector, to compare the impact of treatment by 1) magnetic resin; 2) magnetic resin and coagulation (combined treatment) and 3) coagulation. The elution time ranges were 0-8.5, 8.6-10.4 and 10.5-11.5 minutes, which represented approximate MW ranges of >5 kDa, 5-2 kDa and <2 kDa respectively. The raw waters investigated in these two studies were both highly coloured waters with high SUVA values of between 4.5 and 6.0 $L.m^{-1}.mg^{-1}$ DOC.

Magnetic resin preferentially removed the material eluting between 8.6 and 10.4 minutes (90-98 %), while the removal of high MW NOM (0-8.5 min) was poor (15-40 %). Significant removal (60-75 %) of the low MW material eluted between 10.5 and 11.5 minutes was observed. Fearing *et al*., (2004) and Jefferson *et al*., (2004) removed this low MW material to 60 and 75 % respectively. Coagulation with 8 and 14 $mg.L^{-1}$ Fe was able to remove up to 100 % the NOM eluting between 0 to 10.5 minutes in both studies. For the low MW material, eluting at 10.4 to 11.5 minutes different results were seen for both studies when using coagulation only. While Fearing *et al.*, (2004) reported a 75 % reduction, Jefferson *et al.*, (2004) reported a 60 % reduction of that material.

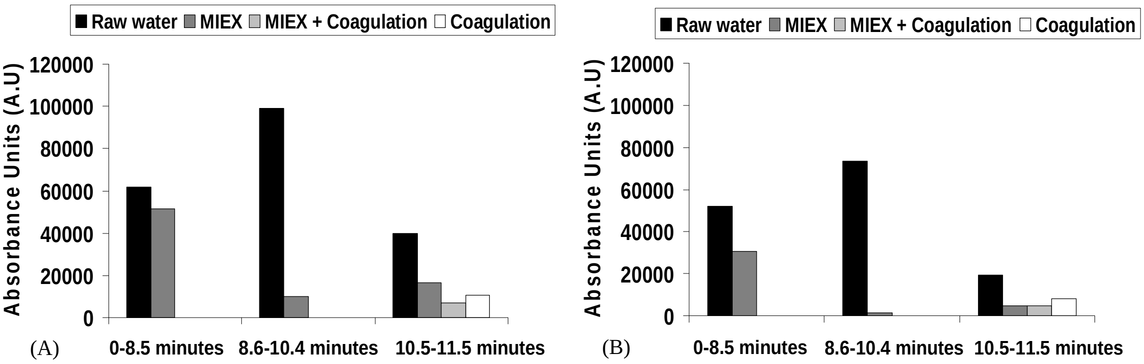


Figure 2.6 Reduction of different molecular weight fractions by magnetic resin, coagulation and combined treatment (Magnetic resin and coagulation): (A) Fearing *et al.*, 2004; (B) Jefferson *et al.*, 2004.

When comparing the DOC level it was observed that coagulation gave slightly higher removal than magnetic resin in both studies. 75-83 % were obtained after coagulation and 66-76 % for magnetic resin. SUVA was affected more by coagulation with a 60-80 % reduction observed when compared to magnetic resin treatment. While Jefferson *et al.*, (2004) reduced SUVA by 30 % with magnetic resin, Fearing *et al.*, (2004) reported no decrease after magnetic resin treatment, indicating that the poorly removed high MW NOM was responsible for most of the UV_{254} absorbance.

While combined treatment of magnetic resin and coagulation reduced coagulant dose from 14 to 5 $mg.L^{-1}$ Fe and removed all the NOM eluting between 0 to 10.4 minutes it has also increased the removal of low MW material from 75 to 85 % (Fearing *et al.*, 2004). Jefferson *et al.*, (2004) reported that the removal of low MW material did not increase with combined treatment above the 75 % achieved by magnetic resin only, which was better than the 60 % achieved by coagulation only. In summary, combining magnetic resin treatment and coagulation gave a broader range of removal in terms of MW, given the preferential removal of higher MW and lower MW material by coagulation and anion exchange respectively (Anderson and Maier, 1979; Croué *et al*., 1999; Bolto *et al*., 2004).

High removal by magnetic resin, up to 95 %, of low MW material (1-2 kDa) in full-scale treatment was also reported by Drikas *et al*., (2003) who showed that 95 %of NOM was in the size of 1-2 kDa in a low SUVA water (SUVA: 1.3 $L.m^{-1}.mg^{-1}$ DOC). Coagulation of that raw water removed only 65 % of this low MW material and combined treatment could not improve the removal efficiency of magnetic resin only. Following from this data the findings of Anderson and Maier (1979); Croué *et al*., (1999) and Bolto *et al*., (2004) that anion exchange resins preferentially remove low MW material and hence make it more advantageous for the treatment of sources dominated by that material can be supported. The presence of high MW NOM is more suitable for treatment by coagulation.

Combining magnetic resin with coagulation has been reported to produce larger and stronger flocs (1000 ± 200 μm) than coagulation alone (720 ± 84 μm) (Jefferson *et al*., 2004). The flocs from this combined treatment were also reported to be more resistant to high shear rates and shown to have greater settling rates than flocs from coagulation only. For example a standardised floc of 500 μm diameter had a settling rate of 3.5 $m.h^{-1}$ and 1.3 $m.h^{-1}$ after combined treatment and coagulation only respectively, which would be beneficial for solid-liquid separation processes such as sedimentation as less time would be required for flocs to settle in that process. Jefferson *et al*., (2004) suggested that the impact on floc properties after magnetic resin pre-treatment could be related to the removal of low MW material prior to coagulation. This would result in an incorporation of more high MW material in the flocs when compared to coagulation only where the full range of MW compounds is contained within the floc matrix. Nestlerode *et al*., (2006b) reported the same trend at the water treatment plant of Green Valley (California, USA), where a water of moderate SUVA level (2.7-3.5 $L.m^{-1}.mg^{-1}$ DOC) was treated by magnetic resin. They reported a 30 % coagulant reduction and that the installation of a magnetic resin treatment plant enhanced floc properties, evidenced by increased settling rates and reduced amounts of solids loading onto the filters.

2.5.5 Impact of magnetic resin dose variation in high and low SUVA waters

The discussion so far indicates that high MW NOM is poorly removed by anion exchange resins. Previous studies reported that this poor removal of high MW NOM, can result from a physical blockage of the resin surface by this material (Gottlieb *et al*., 1996; Lee *et al*., 1997; Hebb *et al*., 2003). Increasing the resin dose provides more easily accessible external exchange area and this can lead to higher NOM removal (Singer and Bilyk, 2002; Tan *et al*., 2005). Hence the impact of different magnetic resin doses in different sources was subsequently investigated. As no such tests had been undertaken using NOM with defined molecular weight, it was interesting to compare studies with high and low SUVA waters, which have been described to be dominated by higher and lower MW material respectively (Edzwald, 1993; Croué, 2004). Therefore only bench-scale studies were considered for comparison as the single use of the resin in these studies guaranteed that the presented removal rates had not been influenced by preliminary loadings.

A comparison of DOC removal between waters with similar DOC to magnetic resin ratios (mg.L^{-1} to mL.L^{-1}) in high and low SUVA waters which contained different levels of DOC and had been treated with different resin doses, providing different exchange surface areas, could not be made as there are too many parameters. However a comparison of the DOC removal in 4 low-moderate SUVA waters (1.3-2.9 L.m^{-1}.mg^{-1} DOC) and 4 high SUVA waters (3.4-6.9 L.m^{-1}.mg^{-1} DOC) using magnetic resin doses ranging depending of the study from 1 to 12 mL.L^{-1} showed that increasing the resin concentration had a higher impact in high SUVA waters. When increasing the resin dose from the lowest to the highest concentration, a DOC removal increase of between 26 to 47 % was seen for the high SUVA waters (Drikas *et al*., 2002; Johnson and Singer, 2004; Boyer and Singer 2005 and Kim *et al*., 2005 (A) (Figure 2.7 (A)). For the four studies on low-moderate SUVA waters (Drikas *et al*., 2003; Humbert *et al*., 2005; Kim *et al*., 2005 B; Kim *et al*., 2005 C) an increase in resin dose had less impact on DOC removal than for the high SUVA waters with a removal increase of 0 to 26 % (Figure 2.7 (C)).

To further investigate the relationship between removal and SUVA, the exponential functions obtained from Figure 2.7 (A) and (C) were extrapolated. The variable x in the functions was replaced by numbers ranging from 1 to 12, which represented the DOC to magnetic resin ratios (mg.L^{-1} to mL.L^{-1}) ranging from 1:1 to 12:1 and make up the x axis of Figure 2.7 (B) and (D).

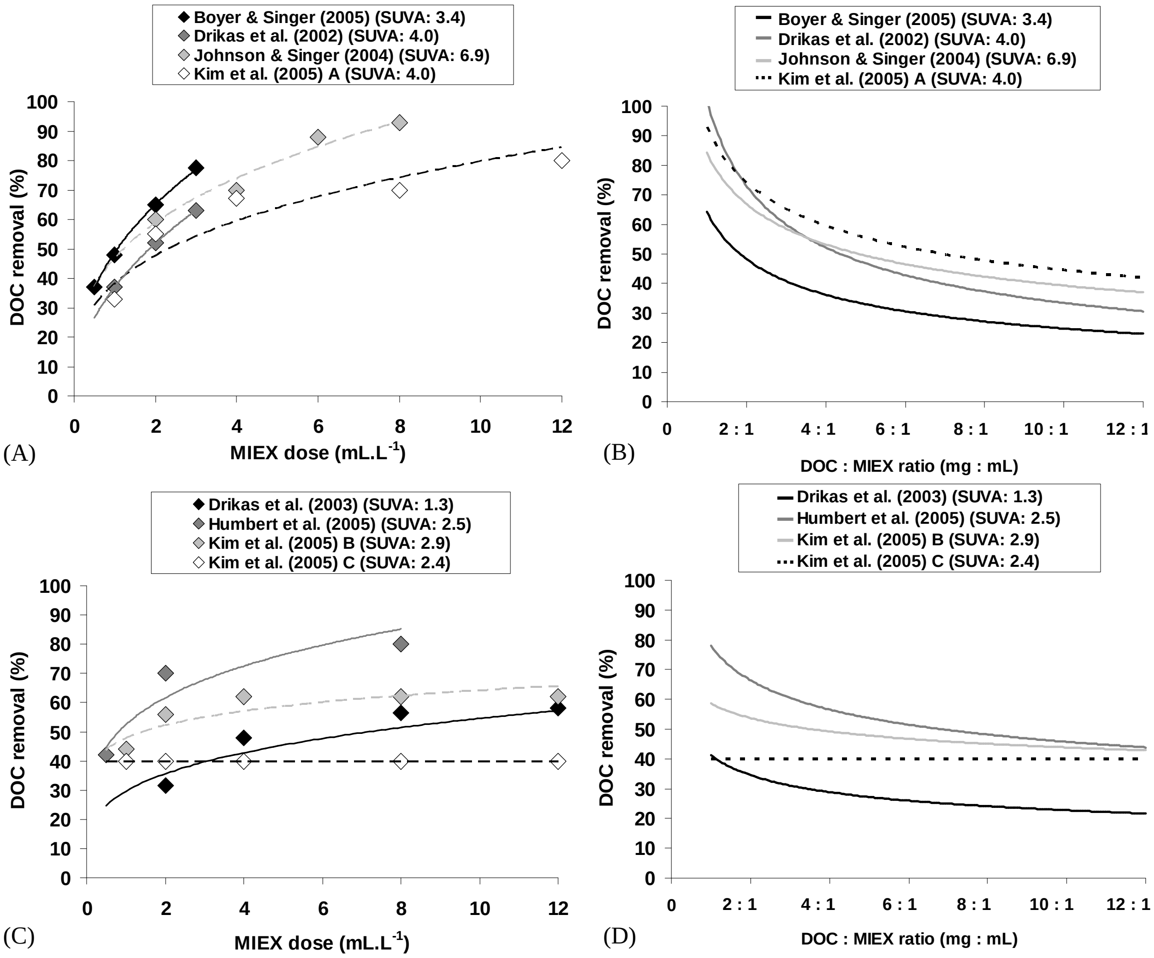


Figure 2.7 Effect of increasing magnetic resin doses (MIEX® doses) on the DOC removal in high ((A), (B)) and low ((C), (D)) SUVA waters (adapted from Boyer and Singer, 2005; Drikas *et al.*, 2002; Drikas *et al.*, 2003; Humbert *et al.*, 2005; Johnson and Singer, 2004; Kim *et al.*, 2005).

Changing the DOC to magnetic resin dose ratio from 1:1 to 12:1 reduced the DOC removal level by 41 to 69 % in high SUVA waters and by 0 to 37 % in low to moderate SUVA waters respectively. This shows that a loss in DOC removal capacity with increasing DOC to resin ratio was more important in high SUVA waters compared to that in low SUVA waters and had to be related to the NOM type present in the different waters. In this case the high MW of NOM was thought to be the crucial factor and that increased resin doses would allow more efficient removal, reducing the necessity of coagulant for their efficient removal.

2.5.6 Impact of magnetic resin, coagulation and combined treatment on the formation of disinfection by products (DBPs)

Chlorination of water containing NOM leads to the formation of disinfection by-products (DBPs) through oxidation, substitution and addition reactions of organic molecules by chlorine (Chang *et al*., 2006; Zhu *et al*., 2007). By reducing the concentration of NOM the formation of DBPs can be minimised.

Boyer and Singer (2005) and Drikas *et al*., (2003) both reported the impact of magnetic resin on THM formation in low SUVA waters. These raw waters had an overall THMFP of 150 (1.3 $L.m^{-1}.mg^{-1}$ DOC) and 123 $\mu g.L^{-1}$ (2 $L.m^{-1}.mg^{-1}$ DOC) as reported by Boyer and Singer (2005) and Drikas *et al*., (2003) respectively (Table 2.5). Magnetic resin reduced the overall THMFP down to 113.2 and 47 $\mu g.L^{-1}$ for Boyer and Singer (2005) and Drikas *et al*., (2003) respectively. These were lower values than those obtained after coagulation only, which were of 138.6 and 79 $\mu g.L^{-1}$ for Boyer and Singer (2005) and Drikas *et al*., (2003) respectively. The same trend of lower residual levels after magnetic resin was also seen by Boyer and Singer (2005) for the overall HAAFP. This parameter was reduced from an initial 90.5 $\mu g.L^{-1}$ in the raw water down to 45.2 and 75.1 $\mu g.L^{-1}$ by magnetic resin and coagulation.

Higher reduction by magnetic resin (90.8 $\mu g.L^{-1}$) than by coagulation (176.4 $\mu g.L^{-1}$) was observed in a third water with a higher SUVA level (3.8 $L.m^{-1}.mg^{-1}$ DOC) and with the overall raw water THMFP of 294 $\mu g.L^{-1}$ as reported by Boyer and Singer (2005). The overall HAAFP followed the same trend as the overall THMFP since the initial raw water level (224 $\mu g.L^{-1}$) was more efficiently removed by magnetic resin (67.2 $\mu g.L^{-1}$) than by coagulation (145.6 $\mu g.L^{-1}$).

Contrary to this, in a fourth source of high SUVA (4.5 $L.m^{-1}.mg^{-1}$ DOC) the reported overall raw water THMFP of 685 $\mu g.L^{-1}$ was less reduced by magnetic resin (225 $\mu g.L^{-1}$) than by coagulation (62.5 $\mu g.L^{-1}$) (Fearing *et al*., 2004). Fearing *et al*., (2004) also showed that coagulation removed more DOC (76 %) than magnetic resin alone (66 %) (Section 2.5.4), which would, after magnetic treatment alone leave more organic material available to react with chlorine. Furthermore, while SUVA had been reduced by 80 % by coagulation, indicating the removal of aromatic compounds, it was not reduced noticeably by magnetic resin, leaving a higher level of highly aromatic material in the water. These compounds are often reported to have a higher DBPFP than non-aromatic material (Kitis *et al*., 2001; Tan *et al*., 2005). Therefore the higher THMFP shown after magnetic resin treatment alone for Fearing *et al*., (2004) can be related not only to the higher level of residual DOC, but also to its character. This was confirmed by comparing the specific reactivity of DOC which was lower after coagulation (22.3 $\mu g.mg^{-1}$ C) than after magnetic resin treatment (59.2 $\mu g.mg^{-1}$ C).

The same trend of a higher specific reactivity in higher SUVA water was also observed for the source of moderate SUVA investigated by Boyer and Singer, (2005). In their work magnetic resin did not affect the SUVA level, while coagulation reduced it by 35 % and a specific THM reactivity of 64.9 and 51.9 $\mu g.mg^{-1}$ C was measured after magnetic resin treatment and coagulation respectively. For the HAAFP a higher specific reactivity was also seen after magnetic resin treatment (48 $\mu g.mg^{-1}$ C) than after coagulation (42.8 $\mu g.mg^{-1}$ C). The lower overall reactivity after magnetic resin (THMFP: 90.8 $\mu g.L^{-1}$, HAAFP: 67.2 $\mu g.L^{-1}$) compared to coagulation (THMFP: 176.4 $\mu g.L^{-1}$, HAAFP: 145.6 $\mu g.L^{-1}$) can only be attributed to the increased DOC removal after magnetic resin (70 %) when compared to coagulation (30 %). This statement stands in contrast to the results of Fearing *et al*., (2004) who reported the opposite trend.

A lower overall THMFP and HAAFP after magnetic resin due to an increased DOC reduction was also observed for the low SUVA waters. The specific THM reactivity was 33.6-37.7 and 34.6-37 $\mu g.mg^{-1}$ C and thus very similar after magnetic resin and coagulation respectively (15.1 and 18.8 $\mu g.mg^{-1}$ C for the HAAs) but the DOC level was reduced by 40 to 50 % by magnetic resin, while it was reduced by 30 to 35 % by coagulation alone. The better SUVA reduction of 25-45 % by magnetic resin in comparison with 5-25 % by coagulation did not seem to have influenced the reactivity of the residual DOC in this case.

Subsequent coagulation of the magnetic resin treated water did not have any significant impact on the measured parameters (DOC, SUVA, THMFP, HAAFP) in the low SUVA source investigated by Boyer and Singer (2005). For Drikas *et al*., (2003) the overall THMFP and the specific reactivity however raised to 59 µg.L^{-1} and 38.6 µg.mg^{-1} C respectively. Nonetheless those values were still observed to be lower than those obtained after coagulation only. This showed that magnetic resin was the more efficient method to reduce the overall DBPFP in the investigated low SUVA sources.

Subsequent coagulation was on the other hand beneficial in the moderate and high SUVA waters. Here, this combined treatment had the effect of giving the lowest overall THMFP, with values of 34 µg.L^{-1} for Fearing *et al*., (2004) and 74.8 µg.L^{-1} for Boyer and Singer (2005). The overall HAAFP nonetheless remained stable with 67.2 µg.L^{-1} (Boyer and Singer, 2005). For Boyer and Singer (2005) this reduction of the overall THMFP was related to a further DOC removal (3 %) as the specific reactivity of the THMs (62.3 µg.mg^{-1} C) and HAAs (67.2 µg.mg^{-1} C) remained close to those obtained after magnetic resin treatment. While for Fearing *et al*., (2004), beside a further DOC reduction (8%), the lowest levels were seen for the specific reactivity of the THMs (11.7 µg.mg^{-1} C) and the SUVA (0.5 L.m^{-1}.mg^{-1} DOC) which showed that coagulation was essential to efficiently reduce aromatic NOM that causes a high THMFP in high SUVA sources.

Table 2.5 Comparison of DOC and SUVA reduction by magnetic resin, coagulation and combined treatment (Magnetic resin and Coagulation) and its impact on the disinfection by-product formation potential (DBPFP) (Adapted from: Boyer and Singer (2005); Drikas *et al*., (2003); Fearing *et al*., (2004). NI= Not Indicated

Reference	Treatment	DOC (mg.L^{-1})	SUVA (L.m^{-1}.mg^{-1} DOC)	THMFP (µg.L^{-1})	THMFP (µg.mg^{-1} C)	HAAFP (µg.L^{-1})	HAAFP (µg.mg^{-1} C)
Boyer and Singer, 2005	Raw water	5.1	3.8	294	57.6	224	43.9
(Bench-scale)	60 mg.L^{-1} Alum	3.4	2.5	176.4	51.9	145.6	42.8
	5 mL.L^{-1} MIEX®	1.4	3.9	90.8	64.9	67.2	48.0
	5 mL.L^{-1} MIEX® + 16 mg.L^{-1} Alum	1.2	2.3	74.8	62.3	67.2	56.0
Fearing *et al*., 2004	Raw water	11.2	4.5	685	59.6	NI	NI
(Bench-scale)	14 mg.L^{-1} Fe	2.7	1.0	62.5	22.3	NI	NI
	20 mL.L^{-1} MIEX®	3.8	4.6	225	59.2	NI	NI
	20 mL.L^{-1} MIEX® + 5 mg.L^{-1} Fe	2.9	0.5	34	11.7	NI	NI
Boyer and Singer, 2005	Raw water	5.1	2	150	29.4	90.5	17.7
(Bench-scale)	10 mg.L^{-1} Alum	4	1.9	138.6	34.6	75.1	18.8
	2 mL.L^{-1} MIEX®	3	1.5	113.2	37.7	45.2	15.1
	2 mL.L^{-1} MIEX® + 5 mg.L^{-1} Alum	3.4	1.2	107.5	31.6	45.2	13.3
Drikas *et al*., 2003	Raw water	3.2	1.3	123	37.8	NI	NI
(Full-scale)	80 mg.L^{-1} Alum	2.1	1	79	37	NI	NI
	8 mL.L^{-1} MIEX®	1.4	0.7	47	33.6	NI	NI
	8 mL.L^{-1} MIEX® + 10 mg.L^{-1} Alum + 0.2 mg.L^{-1} cationic polymer	1.5	0.7	59	38.6	NI	NI

2.6 Conclusions

- Comparison of different anion exchange resins showed that a macroporous, polyacrylic structure with a reduced bead size providing an increased surface area such as magnetic resin was most advantageous for efficient NOM removal. However other anion exchange resins designed with pore diameters of up to 7000 nm that enable a rapid pore diffusion of NOM were seen to have similar efficiency as magnetic resin for water treatment.

- An affinity of magnetic resin for UV_{254} absorbing material was observed in all compared water sources.

- HPOA, HPIA and HPINA had been reduced to similar extents by magnetic resin and did not reveal a preference for a specific NOM fraction.

- Considering that magnetic resin was designed to remove NOM by anion exchange, the equal removal of HPOA, HPIA and HPINA, which all disposed of a certain UV_{254} absorbance, was expected to have occurred due to the reported functionality of all three fractions. However a secondary removal path of uncharged NOM by surface adsorption (eg. Van der Waals forces) could not be excluded.

- HPSEC chromatography has shown that NOM of a higher MW was less efficiently removed by magnetic resin when compared to material of a lower MW. An increase of the magnetic resin dose was however seen to give a better removal of NOM in high SUVA waters, reported to be more abundant in high MW organic molecules. This was explained by higher resin concentrations providing a larger easily accessible external exchange area that allows an increased removal of large molecules that can block the resin beads.

- The preferential removal of mid to low MW material and reduced DBPFP values has shown magnetic resin as an advantageous alternative treatment option to coagulation for DOC reduction in low SUVA waters. While in high SUVA waters, abundant in aromatic high MW material, coagulation was observed to remain essential to maximise DOC removal and subsequently reduce the DBPFP.

- Magnetic resin treatment followed by coagulation also resulted in stronger, larger and faster settling flocs, allowing an efficient solid-liquid separation by sedimentation. This was related to the incorporation of more high MW material, that was less efficiently removed by magnetic resin, into the floc matrix.

3. Materials and Methods

3.1 Summary of water treatment works

This section briefly describes the different water treatment works (WTW) from which the water samples, used to investigate the DOC removal efficiency of magnetic resin and coagulation in different sources, were taken. The raw water and magnetic resin waste brine sampling points at each treatment work are denoted by a "*" in the individual process schematic figures. Albert WTW, Penwhirn WTW and Wanneroo WTW were chosen as examples of highly coloured waters. Aireys WTW, Barcombe WTW, Kluizen WTW and Draycote WTW were chosen as examples of low coloured waters.

3.1.1 Albert WTW (Yorkshire Water)

Albert WTW is located on the western side of Halifax in Yorkshire (UK) treating moorland surface water (33000-55000 m^3 d^{-1}) which has drained through a peat catchment system, before reaching the reservoir of the plant. The treatment consists of coagulation with ferric sulphate, flocculation, dissolved air flotation (DAF), chlorination, rapid gravity sand filtration and manganese removal in pressure filters (Figure 3.1).

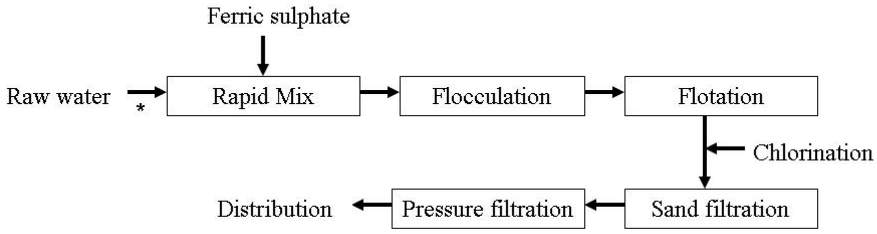


Figure 3.1 Process schematic of Albert WTW (Yorkshire Water).

3.1.2 Barcombe WTW (South East Water)

Barcombe WTW is located close to Brighton in East Sussex (UK) treating reservoir and river water (45000-60000 m^3 d^{-1}). Due to high levels of algae in the reservoir a sonificator was installed to destroy them. The plant is composed of two parallel treatment trains of which the first one (average of 10000 m^3 d^{-1}) was designed to treat only the water coming out of the river, while the second one (average of 35000 m^3 d^{-1})

was designed to treat river water, reservoir water or a blend of both. The treatment processes for both works follow the same stages. The treatment consists of coagulation with polyaluminiumchloride and a polymer, flocculation, DAF, sand filtration, ozonation, granulated activated carbon (GAC) filtration and chlorination (Figure 3.2).

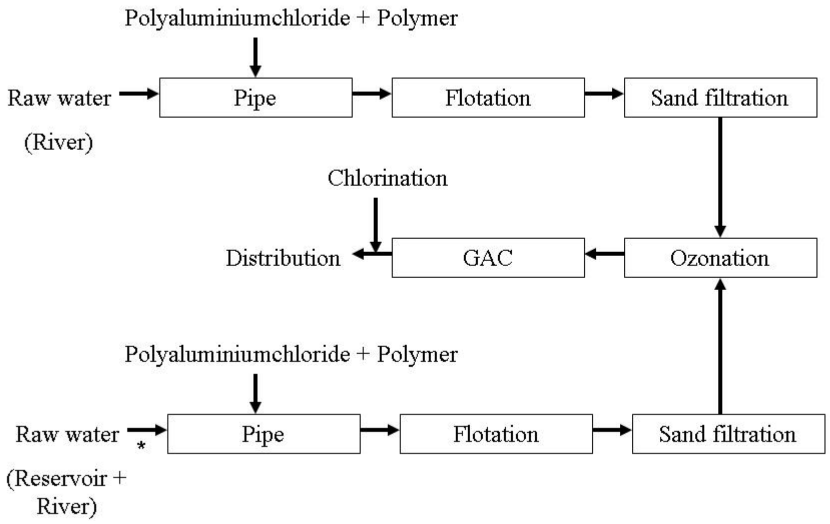


Figure 3.2 Process schematic of Barcombe WTW (South East Water).

3.1.3 Draycote WTW (Severn Trent Water)

Draycote WTW is located close to Dunchurch in Warwickshire (UK) treating low land river water coming from the rivers Avon and Leam and from the Brownsover Pond (22000-36000 m^3 d^{-1}). The treatment consists of coagulation with ferric sulphate, flocculation, DAF, rapid gravity sand filtration, GAC and chlorination (Figure 3.3).

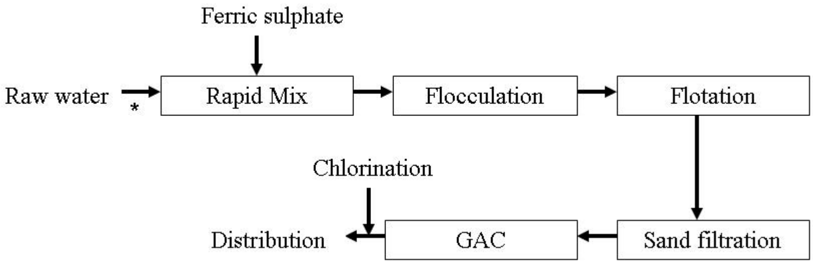


Figure 3.3 Process schematic of Draycote WTW (Severn Trent Water).

3.1.4 Penwhirn WTW (Scottish Water)

Penwhirn WTW is located close to Stranraer in Dumfries and Galloway (UK) treating moorland surface water (13000-14000 m^3 d^{-1}). The treatment consists of coagulation with aluminium sulphate, flocculation, DAF, GAC, rapid gravity sand filtration, and chlorination (Figure 3.4).

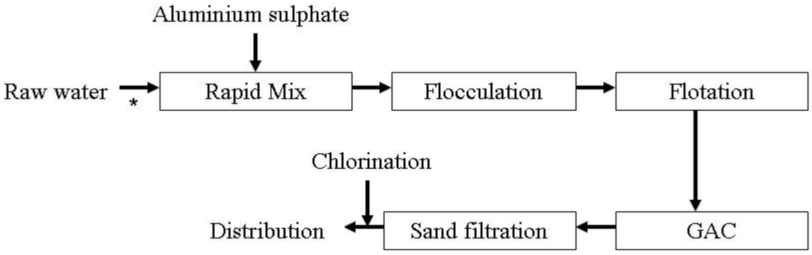


Figure 3.4 Process schematic of Penwhirn WTW (Scottish Water).

3.1.5 Wanneroo WTW (Western Australia Water Corporation)

Wanneroo WTW is located close to the city of Wanneroo in Western Australia (Australia) and treats water from different bore holes (160000-220000 m^3 d^{-1}) in two different treatment streams. The first treatment stream (80000-110000 m^3 d^{-1}) consists of Fe oxidation by spray aeration and pre-chlorination, coagulation with aluminium sulphate, flocculation, DAF, sand filtration, ozonation, chlorination and fluoridation (Figure 3.5). The second treatment stream (80000-110000 m^3 d^{-1}) consists of the same treatment steps like in the first stream with an additional magnetic resin treatment step between Fe oxidation and coagulation.

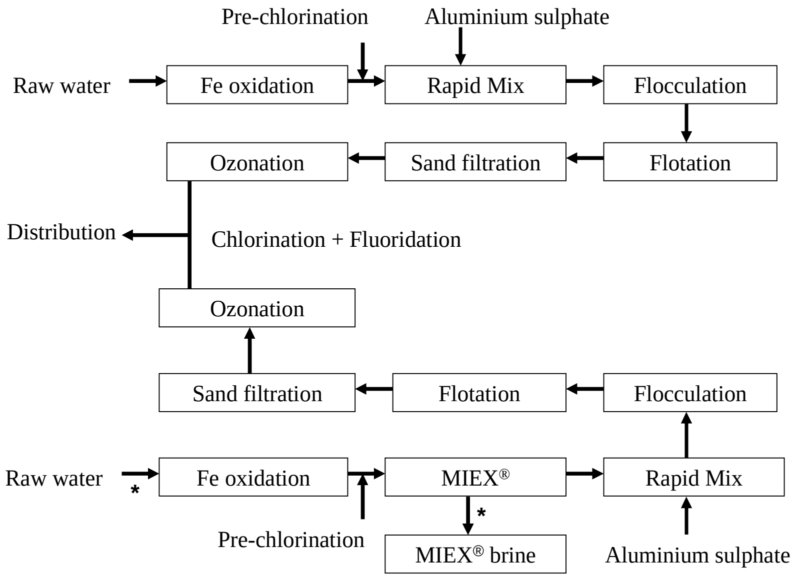


Figure 3.5 Process schematic for Wanneroo WTW (Western Australia Water Corporation).

3.1.6 Aireys Inlet WTW (Barwon Water)

Aireys Inlet WTW is located close to Geelong in Victoria (Australia) treating water from the 514,000 m^3 Painkalac Reservoir situated in the Angahook State Park (1000-2850 m^3 d^{-1}). The treatment consists of magnetic resin treatment, coagulation with aluminium sulphate, flocculation, DAF, ultrafiltration and chlorination (Figure 3.6).

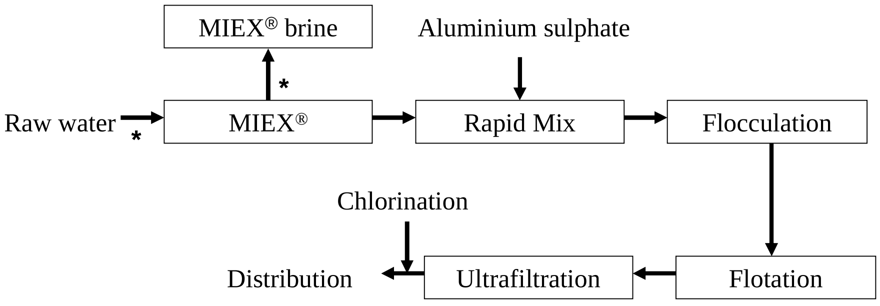


Figure 3.6 Process schematic for Aireys Inlet WTW.

3.1.7 Kluizen WTW (Vlaamse Maatschappij voor Watervoorziening)

Kluizen WTW is located close to Ghent (Belgium) treating water from two different reservoirs (≤ 1200 m^3 d^{-1}). The treatment consists of magnetic resin treatment, coagulation with aluminium sulphate, flocculation, DAF, sand filtration, ozonation, GAC and chlorination (Figure 3.7).

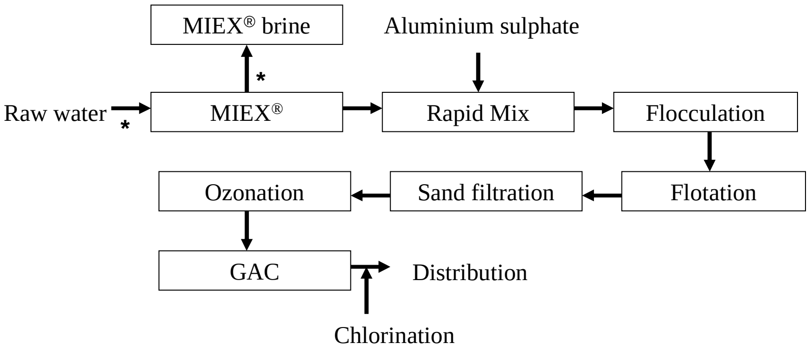


Figure 3.7 Process schematic for Kluizen WTW.

3.2 Bench scale testing

3.2.1 Coagulation–Sedimentation

For coagulation jar testing 1 L of test water was filled into a 1 L glass jar (Fisher Scientific, Loughborough, UK). The jar was placed on a variable speed jar-tester (PB-900, Phipps and Bird, Cambridge, UK).

The water was first mixed for 90 seconds at 200 rpm (revolutions per minute) after the addition of coagulant. The used coagulant was ferric sulphate ($Fe_2(SO_4)_3$/Mistral 600 Ea West). The desired coagulation pH was reached by addition of 0.1 M sodium hydroxide (NaOH) and 0.1 M hydrochloric acid (HCl) solution (Fisher Scientific, Loughborough, UK). The pH was monitored with a Jenway 3310 pH meter (Jenway Ltd, Essex, UK). The coagulated water was then flocculated for 15 minutes at 30 rpm to allow the flocs to grow. The jar was then removed from the jar tester and the flocs were allowed to settle for 15 minutes.

3.2.2 Magnetic Resin

3.2.2.1 Novel magnetic resin continuous bench-scale testing method

Magnetic resin MIEX® was provided by Orica Advanced Water Technologies Pty. Ltd., Australia. It was prepared by measuring equal doses of 10-30 ml resin into 50 mL measuring cylinders (Fisher Scientific, Loughborough, UK) and allowed to settle overnight. Before using the magnetic resin additional adjustments of the required doses were made using a plastic pipette (Fisher Scientific, Loughborough, UK) and the resin was allowed to settle for another hour.

1 L of the tested water was filled into a 1 L glass jar (Fisher Scientific, Loughborough, UK) and placed on a variable speed jar-tester. The jar tester was set to 150 rpm for time periods of between 10 to 30 minutes. The measuring cylinders containing resin were shaken and the resin was added to the water sample. Residual resin in the measuring cylinders was rinsed with small amounts of deionised water (DI) into the jar.

After the mixing period had finished the resin was allowed to settle for exactly 5 minutes by placing the jar on a large magnet to improve the settling rate of the resin beads. The supernatant was then poured into a 25 L plastic container (Fisher Scientific, Loughborough, UK) and the jar containing the settled resin, was put back in the jar tester after having been refilled with fresh raw water.

This procedure was repeated 15 to 30 times to simulate conditions similar to those in a large-scale resin treatment plant, where the resin is used several times before being regenerated.

Samples were taken after every re-use of the resin before decanting the supernatant and from the 25 L plastic container after every second addition of supernatant followed by a thorough mixture of the blended water. The first sampling method was defined as giving “separated samples” while the second one was defined to provide “combined samples”. The resin service in bed volumes (BV) during the continuous bench scale tests was calculated according to equation 3.1:

$$BV = \frac{V_{water}}{C_{\mathrm{Resin}}} \qquad \text{Equation 3.1}$$

Where V_{water} = Volume of treated water in mL

And C_{Resin} = Resin concentration used for continuous water treatment in mL

3.2.2.2 Magnetic resin doses applied on raw and synthetic waters

For the four natural sources of Draycote, Barcombe, Penwhirn and Albert, which had similar DOC levels of 9.4 to 11.8 $mg.L^{-1}$, as well as the model compounds (10 ± 0.5 $mg.L^{-1}$ as DOC) a first magnetic resin dose of 10 $mL.L^{-1}$ at 10 minutes contact time was applied for 15 repetitive uses. The purpose of this was to establish a similar magnetic resin to DOC ratio of 1:1 for all waters in order to make comparisons. For Draycote, Barcombe and Albert a second continuous treatment series using a magnetic resin of 20 $mL.L^{-1}$ at 30 minutes contact time was applied at 15 repetitive uses to investigate the impact of changing resin doses and contact times on NOM removal. For Penwhirn a second continuous treatment series using a magnetic resin dose of 10 $mL.L^{-1}$ at 20 minutes contact time for 15 repetitive uses was undertaken, to investigate only the impact of increased contact times on NOM removal.

In a final step humic acid and a second catchment of Albert water were treated for 15 and 30 repetitive uses respectively with 10 and 30 $mL.L^{-1}$ magnetic resin at 10 minutes contact time. This step was undertaken to investigate the impact of increased resin doses as well as the performance of the resin under extended use.

3.2.2.3 Combined magnetic resin and coagulation treatment

For combined treatment, magnetic resin pre-treated water was coagulated as described in Section 3.2.1.

3.2.2.4 Dialysis of magnetic resin brine solution

Before coagulation the magnetic resin brine solution which contained ±120 $g.L^{-1}$ NaCl was desalinated by dialysis to avoid damage on the used TOC 5000-A Analyser and HPLC (High performance liquid chromatography device). 500 mL of brine solution was filled into a 67 mm diameter Spectra/Por®7 Membrane (BIO-259-0206, Spectrum Laboratories Inc., Rancho Dominguez, California, USA). Both ends of the membranes were closed watertight with Universal Closures (BIO-284-030 M, Spectrum Laboratories Inc., Rancho Dominguez, CA, USA). The closed membrane was submerged for 21 days in 4.5 L of reverse osmosis (RO) water (0.1802 $m\Omega.m^{-1}$) contained in a 5 L Stack-N-Store tray (NB 7482, NES Arnold, Leicestershire, UK), and put on a Bibby Stuart magnetic stirrer plate (Bibby Stuart Ltd., Staffordshire, UK) for continuous water movement around the membrane. The RO water which was processed in the laboratory by a reverse osmosis membrane filtration unit (USF Elga, High Wycombe, UK) was changed every two days.

For comparative analysis the dialysed brine solutions which contained DOC levels of 500 to 1000 mg.L^{-1} were diluted down with RO water to concentrations similar to those of their respective raw waters. Thereby a deviation of 0.5 mg.L^{-1} DOC from the raw water value was allowed. Before investigation and treatment of the different brine solutions the pH was however regulated to the value of the respective waters. This step was necessary to avoid a peak shifting due to changes in the molecular weight (MW) distribution by formation or breakage of intra and intermolecular hydrogen bonds by differing pH values (Piccolo *et al*., 2003).

3.2.2.5 Continuous flow interruption test on magnetic resin

The continuous flow interruption test method was adapted from Kressmann and Kitchener (1947). Two magnetic resin tests were carried out at equal doses up to 1000 BV. While one test was carried out in a continuous manner, the second test was interrupted for 24 hours at 500 BV. The supernatant was decanted and replaced with RO water which was analysed for DOC at the beginning and at the end of the interruption period, to discover organic material leaching of the resin.

3.3. Elemental and physical analysis of magnetic resin beads

3.3.1. Sample preparation

1 mL of virgin magnetic resin was shock frozen for 2 minutes in a liquid nitrogen bath (BOC, Manchester, Greater Manchester, UK) and broken with a hammer to expose the inner surfaces of the beads for analysis. The magnetic resin beads were fixed with a cyanoacrylate resin (RS Components Ltd., Northamptonshire, UK) on a sample holder and introduced into the SEM.

3.3.2 High-resolution cross-sectional scanning electron microscope (SEM)

The investigation of the external and internal pore size as well as the elemental composition of magnetic resin was carried out using a high-resolution cross-sectional scanning electron microscope (SEM) Phillips XL30 SFEG (Philips Analytical, Munich, Germany) with energy dispersive x-ray analysis detection system (EDX). A focused electron beam was scanned over a specimen such that the interaction between the beam and the specimen excites various forms of radiation including secondary electrons and x-rays. The radiation is detected and analysed to reveal information regarding the composition and topography of the specimen. The contrast and resolution in SEM are functions of incident beam energy and intensity and specimen properties. Two types of detectors were used to obtain information from the specimen, a secondary electron detector (SE) and EDX detector. The secondary electrons have low energy and their detection is ideal for the examination of sample surface profiles. Such topographic imaging allowed the evaluation of the pore size. The INCA™ software (Oxford Instruments, Buckinghamshire, UK) for EDX analysis was used in combination with the SEM and EDX detector to determine the elemental composition of magnetic resin.

3.3.3 Magnetic resin water content

The measurement of the water content of magnetic resin was carried out using an adaptation of procedure 2540 D in “Standard Methods for the Examination of Water and Wastewater” (American Public Health Association, 1992). The description of the method is as follows:

20 mL of magnetic resin were prepared as described in section 3.2.2.1. The magnetic resin was vacuum-filtered using a 1 µm glass fibre filter (GF 52, Schleicher and Schuell Microscience GmbH, Dassel, Germany) and a KNF VP4 vacuum-filtration pump (Neuberger UK, Ltd, Oxfordshire, UK) until all traces of water were removed.

The filter containing the magnetic resin was removed and weighed on a Precisa 125A Scale (Precisa Technical Services, Radlett House, Buckinghamshire, UK). Then the filter was transferred to a 109-0 ceramic weighing dish (Haldenwanger, Berlin, Germany) and dried for 24 hours at 105 °C in a hotbox oven with fan (Sanyo Gallenkamp PLC, Loughborough, UK). A blank glass-fiber filter was also dried under the same conditions. The dried filter containing magnetic resin and the blank filter were weighed as already described. The wet and dry weight of magnetic resin expressed in gram of total suspended solids (g_{TSS}) is determined by equation 3.2:

$$g_{TSS} = \frac{(M_{F+R} - M_F)}{V_S} \qquad \text{Equation 3.2}$$

Where M_{F+R} = weight of filter and residue

And M_F = weight of filter in g

And V_S = Sample volume in mL

The water content in percent (%) of magnetic resin (MIEX® resin $_{W\%}$) was determined by equation 3.3:

$$MIEX_{W\%} = \frac{100*(g_{TSSW} - g_{TSSD})}{g_{TSSW}} \qquad \text{Equation 3.3}$$

Where g_{TSSW} = Wet weight of magnetic resin in g.mL^{-1}

And g_{TSSD} = Dry weight of magnetic resin in g.mL^{-1}

3.3.4 Magnetic resin mean particle size distribution under operating conditions

The magnetic resin mean particle size distribution under operating conditions was measured with the equipment that will be described in more detail in Section 3.7.1. Three doses of settled 10 mL magnetic resin were mixed for 10 minutes at 150 rpm and 10 individual measurements were taken from each sample. The speed of the peristaltic pump, needed to introduce the slurry into the measurement cell, was set to the same speed of 150 rpm to avoid any further resin bead agglomeration than potentially happening in the mixing jar. The mean particle size distribution under operating conditions was obtained from an average of the 30 individual measurements.

3.3.5 Magnetic resin rate constant

The rate constant K in terms of UV$_{254}$ absorbance for magnetic resin was calculated by equation 3.4 (Mortimer, 1996):

$$K = \left(\frac{1}{C_{(A)}} - \frac{1}{C_{0(A)}}\right) * \frac{1}{t} \qquad \text{Equation 3.4}$$

Where $C_{(A)}$ = Concentration of NOM at n minutes contact time in mg.L^{-1}

And $C_{0(A)}$ = Concentration of NOM at 0 minutes contact time in mg.L^{-1}

And t = contact time in minutes

3.3.6 Magnetic resin bead settling velocity by Stoke's law

The settling velocity values of magnetic resin obtained by direct image capture (Section 3.7.3) were compared for confirmation of the method to the settling velocity values (S) ($m.s^{-1}$) obtained by Stoke's law (Schwoerbel, 1999) which was as follows (equation 3.5):

$$S = \frac{2}{9} * g * r^2 * \frac{\rho_p - \rho_f}{\mu * F} \qquad \text{Equation 3.5}$$

Where g = Gravity in $m.s^{-2}$
And r = Particle radius in m
And ρ_p = Density of particle in $kg.m^{-3}$
And ρ_f = Density of water in $kg.m^{-3}$
And μ = Viscosity of water at 20 °C in $Pa.s^{-1}$
And F = Form resistance factor of sphere (F=1 in this case as particles assumed to be perfect spheres).

3.4. Pilot plant testing

3.4.1 Magnetic resin pilot plant

The magnetic resin pilot plant trials were conducted by Albert WTW (Yorkshire, UK) using a 1 $m^3.h^{-1}$ pilot rig provided by Orica Watercare UK (Figure 3.8). The optimum resin dose and contact time of 30 $mL.L^{-1}$ and 13 minutes respectively were established in preliminary continuous jar testing studies.

Magnetic resin was mixed in a contact tank using the optimised dose conditions with raw water and then led to a gravity settling tank for solid-liquid separation. 96.7 % of the settled resin was recycled back to the contact tank for immediate re-use, while 3.3 % were diverted to a regeneration tank containing a 12 w% NaCl regenerant solution, which gave a resin service of 1000 bed volume (BV). The diverted resin was replaced with the same amount of fresh regenerated resin flowing towards the contact tank. After regeneration the diverted resin was led to a storage tank and stored until re-use.

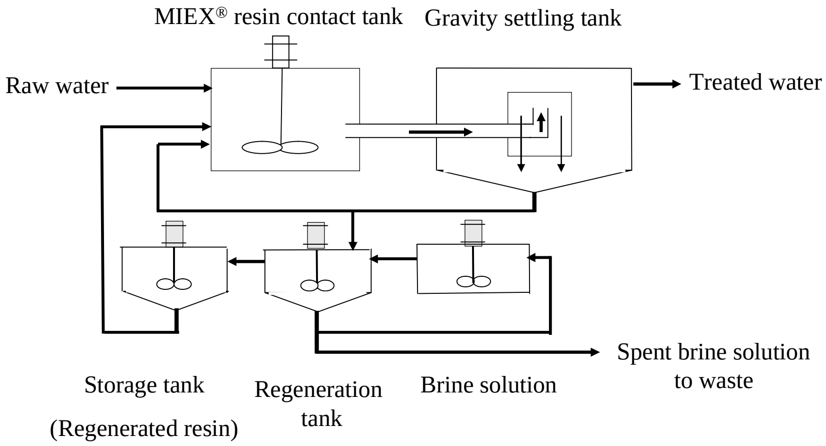


Figure 3.8 Schematic of the Albert WTW magnetic resin pilot plant.

These optimised operating conditions resulted in a resin service of 1010 bed volumes (BV) which was calculated according to equation 3.6:

$$BV = \frac{1}{\mathrm{Re}\,g_{\%} * C_{\mathrm{Resin}}} \qquad \text{Equation 3.6}$$

Where $Reg_{\%}$ = Resin regeneration rate in %
And C_{Resin} = Resin concentration in $mL.L^{-1}$

3.4.2 Coagulation pilot plant

Raw water and magnetic resin treated water was tankered from Albert WTW, (Yorkshire, UK) to a pilot plant at Cranfield University (Bedfordshire, UK), operated at a flow rate of 0.27 $m^3.h^{-1}$ (Figure 3.9). The pilot plant was operated for three hours for each coagulation condition. Each three hour run was repeated to ensure good quality control.

Ferric sulphate and 0.01 M NaOH solution at a pH of 4.2 were added to the raw or magnetic resin treated water and was rapidly mixed for three minutes. The water was then fed into two flocculation tanks, where floc growth was allowed for 33 minutes using picket fence stirrers. The water then passed to a dissolved air flotation unit (Model products, Bedfordshire, UK) operating at a flow rate of 7 $m^3.m^{-2}\,h^{-1}$ at a 22 % recycle ratio and an air concentration of 88 $mg.L^{-1}$, which resulted in an overall final product water volume of 0.33 $m^3.h^{-1}$. DI water was used for the production of the saturated air. The water was then passed through a 0.3 m diameter filter column (Model products, Bedfordshire, UK) operating at a flow rate of 9 m^3 m^2 h^{-1} and containing 16/30 grade sand (1-0.5 mm diameter) at a depth of 1 m. After passing through the filter, the treated water passed through an on-line turbidity meter. Samples for analysis were taken after the flotation unit and after sand filtration.

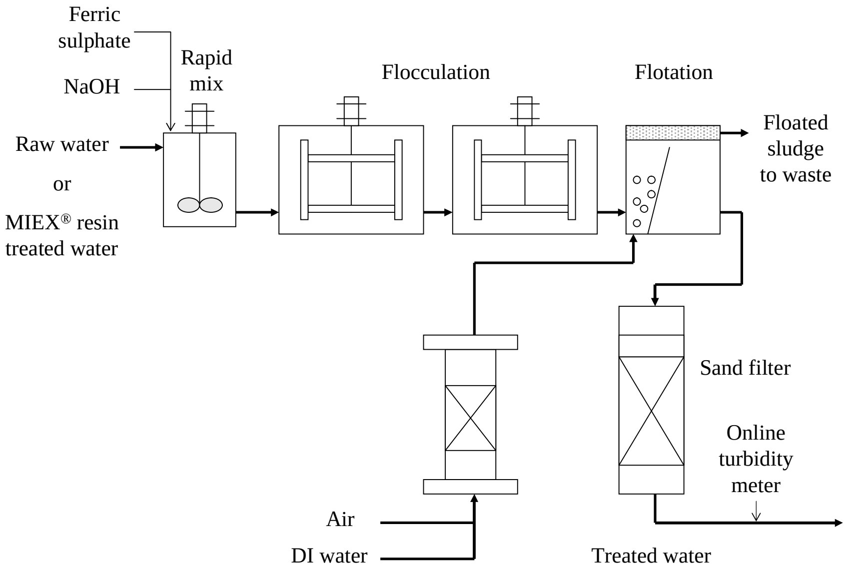


Figure 3.9 Schematic of the Cranfield University coagulation, dissolved air flotation (DAF) and sand filter pilot plant.

3.4.3 Coagulation pilot plant-Sampling and analysis

Samples for analysis of DOC, UV_{254} absorbance, turbidity and zeta potential were taken every 15 minutes during each experimental run after DAF and after sand filtration.

For the measurement of the total trihalomethane formation potential (THMFP) samples were taken every hour after filtration and analysed after a method adapted from procedure 5710 in “Standard Methods for the Examination of Water and Wastewater” (American Public Health Association, 1992) described in Section 3.8.9**.**

The size, strength and settling rate was investigated for flocs formed during coagulation only and for flocs formed during subsequent coagulation of magnetic resin pre-treated water with a coagulant dose reduced by 60 % after the methods described in sections 3.7.1 and 3.7.2.

3.5 Fractionation

Bulk waters were fractionated into their hydrophobic acid (HPOA), hydrophilic acid (HPIA) and hydrophilic non-acid (HPINA) fractions by XAD resin adsorption techniques using a method adapted from Malcolm and McCarthy (1992). The used resins were Amberlite XAD-8 and Amberlite XAD-4 (Rohm and Haas, PA, USA), with specific surfaces of 750 $m^2.g^{-1}$ and 140 $m^2.g^{-1}$ respectively. Amberlite XAD-8 is an acrylic ester polymer showing a slight polarity. The average particle size of XAD-8 is of 25 to 50 mesh with a pore diameter of 25 nm.

XAD-4 is a styrene divinylbenzene polymer of non-polar character, with an average particle size of 60 to 80 mesh and a pore diameter of 5 nm. (Martin-Mousset *et al.*, 1996).

3.5.1 Resin preparation

3.5.1.1 Amberlite XAD-8 resin

Amberlite XAD-8 resin (60 mL) was mixed with 300 mL of 0.1 M NaOH solution and the fines were decanted. This procedure was then repeated. The resin was stored for 24 hours in 300 mL of methanol. The resin was sequentially Soxhlet extracted for 24 hours each with methanol, diethyl ether, acetonitrile and methanol again (300 ml). The extracted resin was packed into a glass column and rinsed with RO water until the column effluent DOC was < 0.5 $mg.L^{-1}$.

To remove all impurities the columns were rinsed with 300 mL of 0.1 M NaOH solution followed by 300 mL of 0.1 M HCl solution to remove impurities. Finally 300 mL RO water were passed through the columns to remove remaining HCl. The water passed through the resins was tested with colour-fixed pH-Fix 0-14 indicator sticks (Fisher Scientific, Loughborough, UK) to make sure a neutral pH of 7 had been reached.

3.5.1.2 Amberlite XAD-4 resin

The Amberlite XAD-4 resin was prepared as seen for the Amberlite XAD-8 resin.

3.5.2 Fractionation methodology

2 L of raw inlet water, model compound solutions (described in detail in Section 3.6), diluted magnetic resin brine solution or magnetic resin treated water and 20 L of coagulated water samples were passed through a 1 µm glass fibre filter (GF 52, Schleicher and Schuell Microscience GmbH, Dassel, Germany) and acidified to pH 2 with 1 M HCl solution. The acidified water was first passed through the XAD-8 resin column and hereafter through the XAD-4 column using a persistaltic pump (505 S, Watson-Marlow Bredel Pumps Limited, UK).

The volume of both resin types was set to 30 $mL.L^{-1}$ of acidified water. For the fractionation of a 2 L sample the volume of either resin was 60 mL. For a 20 L sample 600 mL of either resin were used.

The HPOA fractions were removed by the XAD-8 resin and the HPIA fraction was removed by the XAD-4 resin. The effluent from both columns contained the HPINA fraction. The fractions were removed from the columns by back-eluting them with 0.1 M NaOH solution until the out-coming liquid was clear.

The HPOA fraction was placed into a plastic container and reduced to pH 1 with a 1 M HCl solution to precipitate out the humic acid fraction (HAF) that is insoluble at that pH range. The plastic bottle was stored for over 24 hours and put the next day into a centrifuge (Rotanta 96 R, Hettich Zentrifugen, Tuttlingen, Germany) for 20 min at 7500 rpm. The HAF fraction settled down as a brown mass at the bottom of the bottle and the liquid containing the fulvic acid fraction (FAF), which remained in solution and was decanted into another bottle. The HAF fraction was re-dissolved by adding 50 mL of 0.1 M NaOH solution with a plastic pipette.

The recovery of the DOC in the different fractions was quantified by measuring the influent DOC of the water and the DOC and volume of the fractions produced. The un-extracted material characterised as HPINA fraction was not quantified. A basic schematic of the fractionation is shown in Figure 3.10.

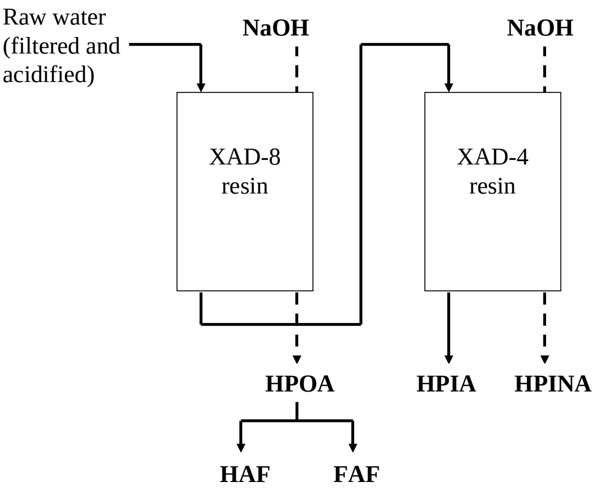


Figure 3.10 Schematic of resin fractionation process

3.5.3 Calculation of required XAD resin dose

The hydrophobic-hydrophilic separation of the DOC fractionation is determined by the adsorption or elution of organic solutes on XAD-8 resin. This arbitrary hydrophobic-hydrophilic designation is controlled by the polarity of the solute and by the ratio of the resin quantity to the volume passing through the resin bed. Most organic solutes (including hydrophilic solutes) show some affinity for XAD-8. Therefore the hydrophobic-hydrophilic split is not clear but is an operationally defined separation in which the crossover of hydrophilic solutes into the hydrophobic fraction can be mathematically defined. For the DOC fractionation, hydrophobic solutes are defined as those solutes that are retained by more than 50 % on XAD-8 at a given ratio of resin to water passed through the column. Hydrophilic solutes are defined as those solutes that are eluted by more than 50 % at the same ratio of resin to water eluent (Leenheer, 1981).

To design a DOC fractionation, it is referred to the column distribution coefficient, $k'_{0.5r}$, of a hypothetical solute that is 50% retained and 50% eluted at the hydrophobic-hydrophilic break.

The breakthrough volume or elution volume V_E of a solute from an XAD-8 resin column is defined as (equation 3.7):

$$V_E = V_0 * (1 + k') \qquad \text{Equation 3.7}$$

Where V_0 = void volume

And k' = (mass of solute sorbed on XAD-8) ÷ (mass of solute dissolved in water)

Since the breakthrough volume V_E, where effluent concentration is 50% of influent concentration, does not correspond to the effluent volume of 50% retention, $V_{0.5r}$ is defined as (equation 3.8):

$$V_{0.5r} = 2 * V_E \qquad \text{Equation 3.8}$$

and can also be expressed as (equation 3.9):

$$V_{0.5r} = 2V_0 * (1 + k'_{0.5r}) \qquad \text{Equation 3.9}$$

It is assumed that the column distribution coefficient, $k'_{0.5r}$, is 50.

Example of calculation of required XAD-8 resin dose V_0:

Sample volume: 1 L ($V_{0.5r}$ = 1000 mL)

$k'_{0.5r} = 50$

Void volume of XAD-8 resin: ~65 %.

Calculation:

Conversion of $V_{0.5r} = 2V_0(1 + k'_{0.5r})$

to: $$V_0 = \frac{((V_{0.5r} /(1 + k'_{0.5r}))}{2}$$

$$V_0 = \frac{((1000 /(1 + 50))}{2}$$

$V_0 = 9.8$ mL

As the void volume of XAD-8 resin is ~65% of its bulk column volume, a 9.8 mL ÷ 0.65 = 15 mL volume of XAD-8 resin is required to fractionate 1 L of water.

3.6 Model compounds

3.6.1 Sample preparation

The model compounds were obtained in analytical grade powder and pellet form from Sigma-Aldrich (Dorset, UK). The only exception was humic acid which was purchased in technical grade as no analytical grade was commercially available. The model compounds were weighed using a Precisa 125A Scale (Precisa Technical Services, Radlett House, Buckinghamshire, UK). The weighed powders were added to a 1L volumetric flask (Fisher Scientific, Loughborough, UK) and topped up with RO water to obtain stock solutions of 250 mg.L^{-1} DOC. These stock solutions were added into 25 L plastic containers and topped up with 24 L of RO water to obtain 10 mg.L^{-1} DOC solutions. A variation of 0.5 mg.L^{-1} DOC was thereby allowed. The prepared solutions were stored at 4 ºC for no longer than 2 weeks before use.

3.6.2 Removal isotherms

The removal isotherms were established by measuring the removal efficiency of the different model compounds by metal-hydroxide precipitate. In a first step 10 mg Fe ($Fe_2(SO_4)_3$/Mistral 600 Ea West) were added to 1 L of RO water in a glass jar under 2 minutes of rapid mix at 200 rpm, standing in variable speed jar-tester. The pH was regulated to a value of 4.5 using 0.1 M NaOH and 0.1 M HCl solution. In a second step different doses of the model compounds of 1, 3, 7, 10 and 15 mg.L^{-1} as DOC were added to the water during a 3 minutes rapid mix period at 200 rpm. Finally a 15 minutes flocculation period at 30 rpm was allowed and the DOC level was measured. The classical Freundlich isotherm equation, which has been used in many adsorption studies and accurately describes much adsorption data, was selected to model the obtained results (Vernon and Snoeyink, 1990). This equation has the form (equation 3.10):

$$q_e = K * C_e^{1/n}$$ Equation 3.10

and can be linearised as follows (equation 3.11):

$$\log q_e = \log K + \frac{1}{n} \log C_e$$ Equation 3.11

Where q_e = Equilibrium solid-phase concentration in mg.mg^{-1}

And K = Freundlich constant related to the capacity of the adsorbent for adsorbate

And 1/n = Function of strength of adsorption

And C_e = Equilibrium liquid-phase concentration in mg.L^{-1}

3.7 Floc characteristics

3.7.1 Floc strength and re-growth

The floc strength was measured during the coagulation and flocculation process using a method adapted from Farrow and Warren (1993). Thereby a dynamic laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK) was coupled with a variable speed jar-tester (PB-900, Phipps and Bird, Cambridge, UK). In this work the rpm of the stirrer was used as descriptor for the shear rate, instead of the traditionally used mean velocity gradient (G) which is unlikely to accurately describe the complexity of the turbulent flow inside stirred vessels (Boller and Blaser, 1998). The G values have been described to be able to largely vary within a stirred medium with the maximum G value to be found close to the impeller (Francois, 1987; Bouyer *et al.*, 2001). Considering that the calculable G values were therefore not representative, a simpler indicator of shear rate such as the rpm was used in this thesis.

The water was first mixed for 90 seconds at 200 rpm and the desired coagulant dose ($Fe_2(SO_4)_3$/Mistral 600 Ea West) was added and the pH adjusted. This short mixing period was followed by 15 minutes of mixing at 30 rpm to allow the flocs to grow as described in section 3.2.1. This was followed by a period of increased shear rate to monitor potential floc breakage. Different periods of increased shear rate were undertaken separately at rpm levels of 30, 40, 50, 75, 100, 150 and 200.

The floc strength factor (%) calculation was hereby adapted from Francois (1987) and defined as following (equation 3.12):

$$\text{Floc strength factor} = \left(\frac{FI_2}{FI_1}\right) * 100 \qquad \text{Equation 3.12}$$

Where FI_1 = Floc size at end of floc growth period in μm

And FI_2 = Floc size at end of the period of increased shear rate in μm

For floc re-growth analyses, a period of slow stir at 30 rpm was allowed after the period of increased shear rate. The particle size was hereby monitored before and after exposure to the different levels of shear rate.

The floc re-growth factor (%) calculation was hereby adapted from Francois (1987) and defined as following (equation 3.13):

$$\text{Floc re-growth factor} = \left[\frac{(FI_3 - FI_2)}{(FI_1 - FI_2)}\right] * 100 \qquad \text{Equation 3.13}$$

Where FI_1 = Floc size at end of floc growth period in μm

And FI_2 = Floc size at end of increased shear rate period in μm

And FI_3 = Floc size at end of re-growth period in μm

The size to which tannic acid flocs were able to grow at 30 rpm, could however not be measured by the method described above. This was because tannic acid flocs grew to sizes too large to allow them entering the measurement cell of the dynamic laser diffraction instrument. Therefore the size to which these flocs could grow was determined by a manual measurement following the method described under Section 3.7.3.

3.7.2 Calculation of the mean velocity gradient

The root-mean-square velocity gradient (G, s^{-1}) occurring during the periods of increased shear was calculated from Camp and Stein (1943) and calculated according to equation 3.14:

$$G = \sqrt{\frac{P}{\mu V}} \qquad \text{Equation 3.14}$$

Where P = Power requirement in W

And μ = Dynamic viscosity in $Ns.m^{-2}$ (Schwoerbel, 1999)

And V = Flocculator volume in m^{-3}

The power requirement P was calculated according to Crail *et al.*, (2004) (equation 3.15):

$$P = k * \rho * n^3 * D^5$$ Equation 3.15

Where k = Coefficient of friction of stainless steel impeller (Kanechira, 1995)
And ρ = Mass density of water at 20 ºC in kg.m^{-3} (Schwoerbel, 1999)
And n = Impeller revolutions in s^{-1}
And D = Diameter of impeller in m

3.7.3 Floc settling

The settling velocity of flocs was measured by direct image capture of individual flocs settling in a constant temperature settling column (Model products, Bedfordshire, UK). The floc aggregates were introduced into the settling column with a wide mouthed pipette (5 mm diameter) via a tapered entry port to ensure the flocs settled into the centre of the column. The settling column was enclosed by a water bath to avoid thermal currents disrupting the settlement of the flocs. A CV M90 colour close-coupled device (CCD) camera (JAI UK Ltd., Middlesex, UK) was used to take the images of the flocs. Image analysis software (Image Pro Plus from Media Cybernetics, Maryland, USA) was used to determine the floc settling velocity. The image analysis software was calibrated against a graticule (Pyser-SGI Ltd., Kent, UK) which was introduced into the settling tank. The graticule displayed one centimetre scale bar which was subdivided into 100 µm units. The falling flocs were captured as image sequences. As a focused floc passed in front of the camera, the image grabber was manually triggered to take a series of 5 images. The time between the frames was set to 0.5 second. This meant that the distance travelled by the floc could be calculated per frame and therefore per time period, thus giving a settling velocity. The projected area of the floc presented in front of the camera was determined using the analysis software and converted to an equivalent diameter. This standardised diameter was recorded along with its settling velocity for 100 aggregates for each set of coagulation conditions.

3.7.4 95 % confidence zone of the regression line and 95 % confidence limits of individual estimates

The 95 % confidence zone of the regression line obtained from the different floc settling tests as well as the 95 % confidence limits of the data points were calculated as described by Fowler *et al.*, (1992). Thereby the 95 % confidence zone of the regression line was obtained by calculating the standard error (S.E.) of estimated particle sizes by equation 3.16:

$$S.E. = \pm\sqrt{s_r^2 * \left[\frac{1}{n} + \frac{\left(x' - \bar{x}\right)^2}{SS_x}\right]}$$ Equation 3.16

And the 95 % confidence limits of the data points (95 % C.L) by equation 3.17

$$95\% C.L. = y' \pm t * \sqrt{s_r^2 * \left[1 + \left(\frac{1}{n}\right) + \frac{\left(x' - \bar{x}\right)^2}{SS_x}\right]}$$ Equation 3.17

Where y’ = individual estimate of settling velocity (y) in µm.s^{-1}

And t = degrees of freedom (Appendix 2 (Fowler *et al.*, 1992))

And s_r^2 = residual variance in µm

And n = population number

And x’ = individual estimate of bead size (x) in µm

And $\bar{x}$ = mean value of x in µm

And SS$_x$ = Sum of squares of x in µm

3.7.5 Floc microscopy

Qualitative floc structural characteristics were investigated using an Olympus BHB light microscope (Olympus European, Hamburg, Germany) and the image analyse software described in section 3.7.2. Flocs were placed in an adapted microscope slide consisting of a glass slide base with a raised glass border of 3 mm depth to provide space to contain whole flocs and which was covered with another microscope slide on top.

3.7.6 Floc fractal dimensions

The fractal dimension of flocs can be applied to the understanding of floc aggregation mechanisms that affect their properties and can be deduced from their settling velocity.

A modified expression of Stoke's law was seen by Jefferson and Jarvis (2006) to help determine the fractal dimension (D_f) and is defined as following (equation 3.18):

$$V_S = \frac{d_{floc}^{\,Df-1} * 4 * k * g}{3 * A(\beta) * \mu}$$ Equation 3.18

Where Vs = Floc settling velocity in $m.s^{-1}$
And d_{floc} = floc diameter in m
And k = Proportionality constant in $kg.s^{-D}$
And g = Acceleration due to gravity in $m.s^{-2}$
And A(β) = Correction for advection through the floc
And μ = Viscosity of medium in $m.s^{-1}$

Thus the slope of a log-log graph of the floc settling velocity against the floc size corresponds to D_f -1 and the fractal dimension was calculated by the following equation (3.19):

$$D_f = slope + 1$$ Equation 3.19

3.8 Analytical techniques

All samples were passed through a 1 µm glass fibre filter (GF 52, Schleicher and Schuell Microscience GmbH, Dassel, Germany) before DOC, UV_{254} absorbance, colour and HPSEC measurements.

3.8.1 Dissolved organic carbon (DOC)

The dissolved organic carbon was measured using a Shimadzu TOC 5000-A Analyser (Shimadzu, Milton Keynes, UK). As some of the analysed waters contained increased levels of $CaCO_3$ (inorganic carbon (IC)), which can damage the catalyst, the DOC level of the samples was measured using a Non-Purgeable Organic carbon method (NPOC). The samples were pre-treated by adding 2 M HCl solution (10 $\mu L.mL^{-1}$ sample). Before the DOC content of the samples was measured, zero-graded air (80 % N_2, 20 % O_2, 0 % CO_2) was injected into the sample and the carbonate (IC fraction) purged out. A drawback of the NPOC method is that any volatile organic compounds will also be purged away with the IC. The machine was calibrated using a total carbon (TC) standard, which was prepared by dissolving potassium hydrogen phthalate (2.125 g) in RO water (1 L). The standards produced had a concentration of 1000 mg L^{-1} DOC and working standards were diluted with RO water to concentrations of 0, 2.5, 5, 10, 25 and 50 mg L^{-1} DOC.

3.8.2 Ultraviolet absorbance (UV_{254})

Ultraviolet absorbance at 254 nm (UV_{254}) (m^{-1}) which results from aromatic structures and hydrogenated double bonds in organic compounds (Edzwald and Tobiason, 1999) was measured with a Jenway UV/Visible spectrophotometer (Jenway 6505, Patterson Scientific Ltd., Luton, UK). RO water was used as a blank to calibrate the spectrophotometer and obtain a zero reading.

3.8.3 Specific ultraviolet absorbance

Specific UV absorbance (SUVA) (m^{-1} .L mg^{-1}) was calculated as the UV absorbance at 254 nm (m^{-1}) divided by the DOC (mg L^{-1}) as described by Edzwald (1993).

3.8.4 Colour

The colour of the water, which is the absorbance measured at 400 nm and converted to Hazen units (Mitchell and McDonald, 1992), was determined using a Jenway UV/Vis Spectrophotometer (Jenway 6505, Patterson Scientific Ltd., Luton, UK). Thereby a conversion factor of 12 adapted from Murray (2005) was used. One Hazen unit was defined as the colour produced by a standard solution of platinum in the presence of cobalt (Mitchell and McDonald, 1992).

3.8.5 Turbidity

The turbidity (NTU) caused by suspended matter such as clay, silk, microscopic organisms, soluble coloured organic compounds and finely divided organic and inorganic matter (Parsons and Jefferson, 2006) was carried out using an adaptation of procedure 2130 B in “Standard Methods for the Examination of Water and Wastewater” (American Public Health Association, 1992). The used apparatus was a Hach 2100 turbidimeter (Camlab, Swindon, UK).

3.8.6 Zeta Potential

The zeta Potential (mV) or electrophoretic mobility, which results from the charge difference between an ion cloud around a charged particle and the surrounding bulk solution (Amirtharajah and O'Melia, 1990; Ratnaweera *et al.*, 1999) was measured with a Zetasizer 2000 HSA (Malvern Instruments, Worcestshire, UK).

3.8.7 Charge load and charge density

3.8.7.1 Charge load and charge density measurement by colloid titration

The charge load or total surface charge, arising from the functional groups on a molecule (Sharp *et al.*, 2006b) was determined by an adjusted method used by Kam and Gregory (2001) based on colloid titration, which was as follows:

The cationic polymer polydiallyl dimethylammoniumchloride (polyDADMAC) was obtained from Sigma-Aldrich (Dorset, UK) as a 20 wt.% aqueous solution. This was then diluted to a 0.1 % solution with the charge density calculated to be 6.2 meq.g^{-1} from the manufacturer's information. A beaker containing raw water or treated water samples and a magnetic stirrer were placed on a magnetic stirrer plate (IKAMAG ReO, IKAMAG Labortechnik, Staufen, Germany). The pH of the sample was adjusted to 7 with 0.1 M NaOH and 0.1 M HCl solution. Then varying amounts of 0.05 to 1 mL.L^{-1} polyDADMAC were added to the beaker until the point of zero charge or isoelectric point (i.e.p.) had been established. This was repeated twice and the volume of polyDADMAC solution was used to calculate the charge load of the water sample.

The charge load (C_L) was obtained by equation 3.20:

$$C_L = V_{pD0.1\%} * C_{D\,pD0.1\%} \qquad \text{Equation 3.20}$$

Where $V_{pD0.1\,\%}$ = Volume used of 0.1 % polyDADMAC solution

And $CD_{pD0.1\,\%}$ = Charge density of 0.1 % polyDADMAC solution

The charge density which standardises the charge per g of DOC is calculated by dividing the charge load (meq.mL^{-1}) by the amount of DOC in the sample (mg.L^{-1}). The charge density (C_D) is obtained by equation 3.21:

$$C_D = \frac{C_L}{A_{DOC}}$$ Equation 3.21

Where C_L = Charge load in meq.L^{-1} of sample
And A_{DOC} = Amount of DOC in mg.L^{-1} of sample.
The charge density is normally expressed in meq.g^{-1}. The result obtained by equation 3.21 is therefore multiplied by a factor of 1000.

3.8.7.2 Charge load and charge density calculation

Due to the small size of resorcinol and L-glutamic acid and the inability to detect them by colloid titration the charge load and charge density had to be calculated by a re-arrangement of the acid dissociation equation (Stephenson and Judd, 2002), which was as follows (equation 3.22):

$$A^{-} = \frac{K_a * HA}{H^{+}}$$ Equation 3.22

Where A^{-} = Conjugated base
And K$_a$ = Acid dissociation constant (10^{-pKa})
And HA = Used acid in g.Mol^{-1}
And H^{+} = Concentration of hydrogen ions in Mol.L^{-1} ($10^{\text{-pH of solution}}$).

Example of calculation of charge density of resorcinol:

$K_a = 10^{-9.3} = 5.01*10^{-10}$
HA = 110.1 g.Mol^{-1}
$H^{+} = 10^{-10} = 1*10^{-10}$ Mol.L^{-1}

$$A^{-} = \frac{\left(5.01*10^{-10}\right)*110.1}{1*10^{-10}}$$

A^{-} = 551.6 Mol.L^{-1}

Considering that at the used pH of 10 one hydrogen ion was dissociated, the charge was quoted as 1 eq for 106.7 g of resorcinol. The charge density of 1 g resorcinol was therefore calculated to be: 1/551.6 = 0.0018 eq.g^{-1}. The charge density is normally expressed in meq.g^{-1}. The result was therefore multiplied by a factor of 1000, which gave a charge density of 1.8 meq.g^{-1} resorcinol.

3.8.8 High Performance Size Exclusion Chromatography (HPSEC)

3.8.8.1 Apparatus

High performance size exclusion chromatography (HPSEC) analyses were carried out using a high performance liquid chromatography device (HPLC) (Shimadzu VP Series, Shimadzu, Milton Keynes, UK) with a UV detector set to 254 nm. The mobile phase was 0.01 M sodium acetate at a flow rate of 1 mL min^{-1}. The used column was a BIOSEP-SEC-S3000 7.8 mm (ID) × 30 cm and the guard column was a 'Security Guard' fitted with a GFC-3000 disc 4.0 mm (ID) × 3.0 mm (Phenomenex UK, Cheshire, UK). The samples were introduced in the machine in Shimadzu LC Silicone/PTFE wider screw cap 2 mL vials. (Fisher Scientific UK Ltd, Loughborough, UK). For each sample a chromatogram of UV_{254} (absorbance units) against time (minutes) was detected.

3.8.8.2 HPSEC calibration

The HPSEC calibration shown here was developed at Cranfield University using a raw water sample taken in April 2002 from the Albert WTW (Goslan, 2003). The calibration procedure was as follows:

Ultrafiltration was performed under nitrogen pressure (30-60 psi) in a stirred cell reactor (Model 8200, Millipore, Massachusetts, USA). Membranes with molecular weight cut-offs (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). The YM membranes were made of regenerated cellulose and the YC membrane was made out of cellulose acetate. The YM membranes were rinsed with NaOH (0.1 mol), NaCl (0.1 mol) solution and DI water to remove the wetting agents before use. The YC05 membrane was rinsed with NaCl (1.0 mol) and DI water. Raw water samples of 110 mL were filtered through each membrane at room temperature and five 20 mL samples of permeate were collected (approximately 90 % of the original sample). Each sample was analysed for DOC and UV_{254} absorbance. Then the samples were run on the HPSEC for analysis. Each chromatogram exhibited five distinct peaks. These peaks corresponded to peaks observed in a raw water sample analysed by HPSEC. As the membrane pore size decreased, the height of the peaks decreased. The remainder of NOM measured as the reduction of the heights of the peaks was plotted against the log

MWCO value of the membranes as given by the manufactures. The MW assigned to the different retention times and measured in Dalton (Da), are presented in Table 3.1. Thereby the MW of a compound is the mass of one molecule of that substance, relative to the unified atomic mass unit u, which is equal to 1/12 the mass of one atom of carbon-12. From that definition one hydrogen atom has a mass of 1 Da (Housecroft and Constable, 2006; Judd, 2006).

Table 3.1 Molecular weight (MW) assigned to different retention times.

Retention time (minutes)	MW (kDa)
0-8.5	>5
8.6-9.0	5-3.5
9.1-9.7	3.5-2
9.8-10.4	2-1
10.5-10.8	1-0.5

3.8.9 Trihalomethane formation potential

The measurement of the trihalomethane formation potential (THMFP) was carried out using an adaptation of procedure 5710 in “Standard Methods for the treatment and Examination of Water and Wastewater” (American Public Health Association, 1992). The description of the method is as follows.

3.8.9.1 Reagents

a) Hypochlorite (HOCl) solution: Sodium hypochlorite (13 %. 0.4 mL) was diluted to 25 mL with RO water in a volumetric flask (Fisher Scientific, Loughborough, UK) and mixed well. The diluted solution was placed in a conical flask containing 5 mL acetic acid and ~1 g potassium iodide estimated on a spatula. The contents of the flask were mixed well and titrated with 0.1 M aqueous sodium thiosulphate prepared with RO water until the yellow colour of the liberated iodine was almost discharged. 1 g of iodine indicator powder was added and the titration continued until the blue/black colour had been discharged and the volume of the solution was recorded. The chlorine concentration (C_{Cl2}) of the sodium hypochlorite solution was calculated according to equation 3.23:

$$C_{Cl2} = \frac{(M * 35.45 * V_{Tr})}{V_{HypoCl}} \qquad \text{Equation 3.23}$$

Where M = Molarity of titrant
And 35.45 = Molecular weight of chlorine in $g.Mol^{-1}$
And V_{Tr} = Volume of titrant in mL
And V_{HypoCl} = Volume of hypochlorite added in mL

The required titrant volume had to be at least of 10 mL. If this was not the case, then an amount of hypochlorite solution of 0.8 mL had to be used. The hypochlorite concentration should be measured each time a dosing solution is made and discarded if the chlorine concentration falls below 20 mg $Cl_2.mL^{-1}$.

b) Chlorine dosing solution (1000 mg $Cl_2.L^{-1}$): The required volume of hypochlorite solution (V_{HypoCl}) was calculated according to Equation 3.24:

$$V_{HypoCl} = \frac{1250}{C_{HypoCl}} \qquad \text{Equation 3.24}$$

Where *1250* = Dilution factor
And C_{HypoCl} = Hypochlorite concentration in mg $Cl_2.mL^{-1}$

The calculated volume was diluted to 250 mL in a volumetric flask with RO water. It was mixed and transferred to an amber bottle with a PTFE-lined screw cap and refrigerated. The free chlorine concentration was measured by DPD powder pillow photometric method using a HACH DR/2010 spectrophotometer (Camlab. Ltd., Cambridgeshire, UK). This solution was discarded after 1 week.

c) Phosphate buffer: 68.1 g potassium dihydrogen phosphate (KH_2PO_4) and 11.7 g sodium hydroxide (NaOH) were dissolved in 1 L RO water. The buffer was refrigerated and discarded after 1 week.

d) Sodium sulphite solution: 10 g sodium sulphite was dissolved in 100 mL RO water. It was used for dechlorination. 0.1 mL destroyed about 5 mg residual chlorine. The solution was discarded after 2 weeks.

e) DHBA solution: Anhydrous 3,5-dihydroxybenzoic acid, (0.078 g) was dissolved in

2 L RO water. This solution needed to be made fresh before each use.

f) Hydrochloric acid (concentrated, 1 M and 0.1 M).

g) Sodium hydroxide (1 M and 0.1 M).

3.8.9.2 Method

Sample chlorination

The appropriate volume of chlorine dosing solution was calculated using the formula:

$$5\ \text{mg}\ CL_2.\ L^{-1}\ \text{per mg DOC}.L^{-1}$$

This volume was put in a 250 mL bottle with 5 mL phosphate buffer to stabilise the pH at 7 and was filled up completely with sample water. This bottle was stored for seven days in an incubator at 25 °C ± 2 °C.

Reagent blank

1 mL chlorine dosing solution was placed in a 50 mL volumetric and made up to the mark with phosphate buffer. A 22 mL PTFE-lined screw cap vial was completely filled with the mixture and stored at 25 °C ± 2 °C for seven days.

Quality control samples

1 mL chlorine dosing solution was diluted to 1 L with RO water. 5 mL phosphate buffer was added to each of two 250 mL bottles. 1 mL DHBA solution was added to one bottle and each bottle completely filled with the diluted chlorine dosing solution and capped with PTFE-lined screw caps. These were also stored with the sample at 25 °C ± 2 °C for seven days.

Sample analysis

After seven days of storage, 0.088 mL sodium sulphite solution was placed in a 22 mL vial and gently and completely filled with sample. If the sample was not being analysed immediately, the pH was reduced to < 2 by adding 5 drops of concentrated acid. The vial was sealed with a PTFE-lined screw cap. The sample was refrigerated, but brought to room temperature before analysis by gas chromatography (GC) (Perkin/Elmer

Turbomass Gold, Connecticut, USA). The THMFP can be reported as a single value according to equations 3.25 and 3.26:

$$THMFP,\ \mu g.L^{-1} = A + B + C + D$$ Equation 3.25

$$THMFP,\ \mu g.L^{-1}\ as\ CHCl_3 = A + 0.728\ B + 0.574\ C + 0.472\ D$$ Equation 3.26

Where A = µg $CHCl_3.L^{-1}$

B = µg $CHBrCl_2.L^{-1}$

C= µg $CHBr_2Cl.L^{-1}$

D = µg $CHBr_3.L^{-1}$

Blank analysis

After seven days of storage, 1 mL of sulphite reducing solution was added to 5 mL of the reagent mixture in a 250 mL bottle without mixing. The bottle was immediately completely filled with RO water and capped with a PTFE-lined screw-cap. A portion was analysed for THMs using the same method as for the sample. The sum of all THMs should be < 5 µg.L^{-1} $CHCl_3$.

Quality control sample analysis

After holding the sample for seven days in the dark 1 mL of sulphite reducing solution was added to each of two 250 mL bottles and 5 mL of the reagent mixture added without mixing. The bottles were immediately completely filled with RO water and capped with PTFE-lined screw-caps. A portion of each was analysed for THMs using the same method as for the sample. The THM concentration of the solution containing the added DHBA minus the concentration of the solution without the DHBA (the true blank) should equal 119 µg.L^{-1} THM as $CHCl_3$. If the THM concentration of the true blank exceeds 20 µg.L^{-1}, purer reagent water is required.

3.8.10 Determination of alkalinity by titration

The measurement of the raw water alkalinity was carried out using an adaptation of procedure 2320 B in “Standard Methods for the treatment and Examination of Water and Wastewater" (American Public Health Association, 1992). The description of the method is as follows:

100 mL of raw water were filled in a conical flask (Fisher Scientific, Loughborough, UK) and 3 drops of bromocresol green/methyl red indicator (Fisher Scientific, Loughborough, UK) were added, which turned the colour of the sample to a pale blue.

The conical flask was then placed under a titration burette (Fisher Scientific, Loughborough, UK), containing 0.02 M HCl solution (Fisher Scientific, Loughborough, UK), which was added until the sample colour turned from pale blue to pale yellow.

The alkalinity (mg.L^{-1} as $CaCO_3$) of the raw water sample was then calculated according to Equation 3.27:

$$Alkalinity = \frac{A * N * 50{,}000}{samplevolume(mL)}$$ Equation 3.27

Where A = Volume of standard acid titrant added to raw water sample in mL

And N = Normality of standard acid used (in this case 0.02 M HCl)

And 50,000 = Conversion factor for standard acid to calcium carbonate equivalent

4. Results and Discussion

4.1 Physico-chemical properties of magnetic resin

4.1.1 Aim

The aim of the research presented in this section was to investigate the general physico-chemical properties of magnetic resin. Various research studies have described magnetic resin as a macroporous polyacrylic resin with a good ability to swell (Slunjski *et al*., 1999; Fearing *et al*., 2004; Allpike *et al*., 2005; Wert *et al*., 2005). However none of these studies have been able to provide data regarding the pore size, water content or exact particle size distribution of the resin. All these parameters are important factors when using the magnetic resin process including the removal of large NOM molecules and also the impact on the downstream treatment of the water.

4.1.2 Pore size and water content (%)

Initial attempts to measure the mean pore size distribution of magnetic resin using a high-resolution cross-sectional scanning electron microscope (SEM) were unsuccessful. However the increase in magnification necessary to be able to discern structures below 1 μm, required an increase of the electron beam voltage (5-30 kV), which unfortunately resulted in melting and vaporisation of the scanned surface, making any measurement impossible. The median pore size of 9.7 nm as provided by the manufacturer (Dahlke, 2002) was therefore used for further discussion.

The International Union of Pure and Applied Chemistry (IUPAC) described macropores to be ≥ 50 nm in diameter (Sing *et al*., 1985). The median pore size of the magnetic resin was therefore significantly less than that considered to be in the macroporous range and categorised the resin as mesoporous, which comprises pores of 2 to 50 nm diameter (Sing *et al*., 1985). However the resin was thought to have a distribution of pore sizes, the larger of which may lie in the macroporous range (Nguyen, 2007). The pore diameter given for the magnetic resin placed it at the lower end of the range of commercially available resins for NOM removal with diameters ranging from 5 to 7000 nm as indicated for VPOC-1064® and IRA-938® (Symons *et al*., 1995).

Although the pore size reported by Dahlke (2002) could not be confirmed by SEM, the method was able to identify sporadic large cavities with a median diameter of 2.5 µm on the beads outer surfaces (Figure 4.1. (A)). These were thought to form during the resin production process when the cross-linking agent for pore formation is added (Ahmed *et al.*, 2004). Figure 4.1 (B) shows a partial connection between the outer bead surface and the sponge-like inner-bead structure, containing voids with a mean diameter > 5 µm. Due to its highly porous inner structure, which is connected with the outside, it was likely that water would be able to penetrate into the resin providing a high moisture content necessary for efficient NOM diffusion during water treatment as well as during regeneration (Meyers, 1995; Gottlieb, 1996; Bolto *et al.*, 2002). However caution must be applied when interpreting the diameters of the outer-bead cavities and the inner-bead voids, due to the previously mentioned potential expansion of these openings by freeze drying.

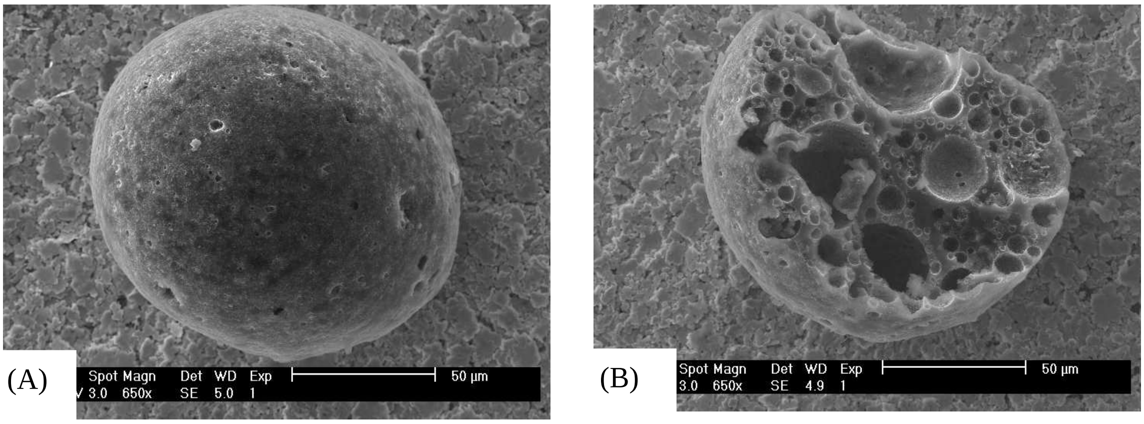


Figure 4.1 SEM pictures of magnetic resin beads imbedded in cyanoacrylate resin: (A) External bead structure, (B) Internal bead structure.

Investigation of the total suspended solids of 10 mL magnetic resin using an adaptation of procedure 2540 D in “Standard Methods for the Examination of Water and Wastewater” (American Public Health Association, 1992), revealed a weight of 1.28 kg L^{-1} and 0.22 kg L^{-1} for wet and dry resin respectively (Section 3.3.3). The difference in weight confirmed that the resin had a very high water content of nearly 83 %. This places the resin at the top end of the range of moisture contents of 40 to 80 % reported for other resins (Meyers, 1995; Afcharian *et al*., 1997; Lee *et al*., 1997; Bolto *et al*., 2004; Humbert *et al*., 2005).

4.1.3 Particle size distribution and surface area

SEM images of individual magnetic resin beads indicated that the average bead diameter was 165 ± 55 µm, which compared to the 150 to 200 µm, reported in the literature for the resin (Cadee *et al*., 2000; Budd *et al*., 2003; Boyer and Singer, 2005; Humbert *et al*., 2005). The magnetic resin beads are at least 2 to 5 times smaller than other available anion exchange resins such as IRA 400® and S3628A® with bead sizes of 300 to 1250 µm (Afcharian *et al*., 1997; Bolto *et al*., 2004).

When monitoring the particle size by dynamic laser diffraction at a mixing speed of 150 rpm, which is the same level as applied during the bench-scale DOC removal tests, a particle size distribution ranging from 10 up to 700 µm with a median size of 235 µm was measured (Figure 4.2). This shows that the resin has the ability to rapidly agglomerate due to its magnetic properties either under the rapid mixing conditions or when entering the measurement cell of the dynamic laser diffraction instrument. However due to the small difference between an individual bead size and the average agglomerate size, an impact on the total available resin surface by bead agglomeration was not expected.

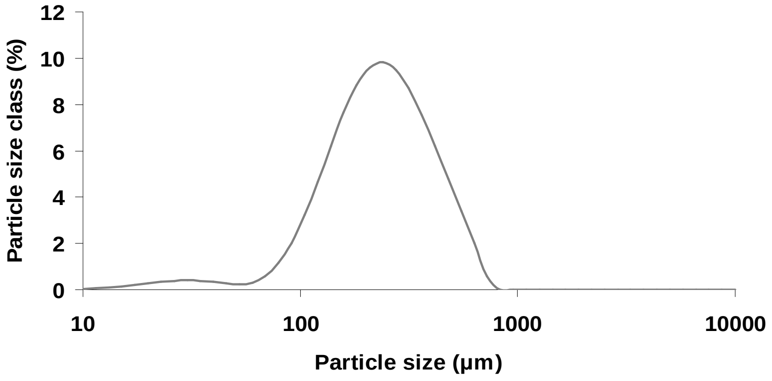


Figure 4.2 Particle size distribution of magnetic resin.

The total surface area of the resin, which includes the external as well as the pore internal surface, could not be investigated here due to patent protection on the resin.

However the manufacturers of magnetic resin report a total surface area value of 27.9 to 36.7 $m^2.g^{-1}$ (Dahlke, 2002). Considering that total surface area values of 23 to 409 $m^2.g^{-1}$ have been reported for other commercially available macroporous anion exchange resins such as DOWEX-MSA1® and XE-510®, magnetic resin lied at the lower end of the range (Brattebo *et al.*, 1987; Symons *et al.*, 1995). The reduced bead size of magnetic resin was reported to increase the external surface area up to 4 times per unit weight when compared to other resins (Slunjski *et al.*, 1999; Wert *et al.*, 2006). A result of this increased external surface area was described to be an increase in exchange between DOC and exchangeable chloride on the easily accessible external surface and a reduction of the reliance on slow intraparticle diffusion associated with active sites inside the bead pores (Singer and Bilyk, 2002). Indeed a small but accessible surface was proven to be more effective for NOM removal than a large but hardly accessible surface inside small pores as reported by Symons *et al.*, (1995) who treated a TOC solution with a MW > 10 kDa with different resins. In that study a styrenic resin with a mean pore diameter of 20 nm and a total surface area of 409 $m^2.g^{-1}$ (XE-510®) removed 50 % of the TOC, while a styrenic resin with a much larger and more accessible mean pore diameter of 7000 nm but with a small surface area of only 7 $m^2.g^{-1}$ (IRA-938®) removed 88 % TOC.

It follows from this comparative data that magnetic resin appear to be a good resin for NOM removal due to the increased external surface with easily accessible exchange sites and a high moisture content theoretically enabling increased NOM diffusion inside the pores. Considering the DOC removal of up to 93 % in highly coloured waters the latter statement seems well supported (Johnson and Singer, 2004).

4.1.4 Settling rate of magnetic resin

An investigation of the settling characteristics of magnetic resin by direct image capture demonstrated a characteristic log-log relationship between bead sizes and settling velocity (Figure 4.3). When calculating settling velocities from the power equation of $y = 0.3632\ x^{1.8653}$, displayed by plotting the individual data points, a value of 4970 $\mu m.s^{-1}$ (17 $m.h^{-1}$) was obtained for the measured bead size (x) of 165 μm. This value could be confirmed when applying Stokes law (Section 3.3.6), which provided a similar settling velocity value of 14.9 m.h^{-1}. This is comparable to the average settling velocity of 25 m.h^{-1} reported by Smith e*t al*., (2002) for magnetic resin in a large scale settler.

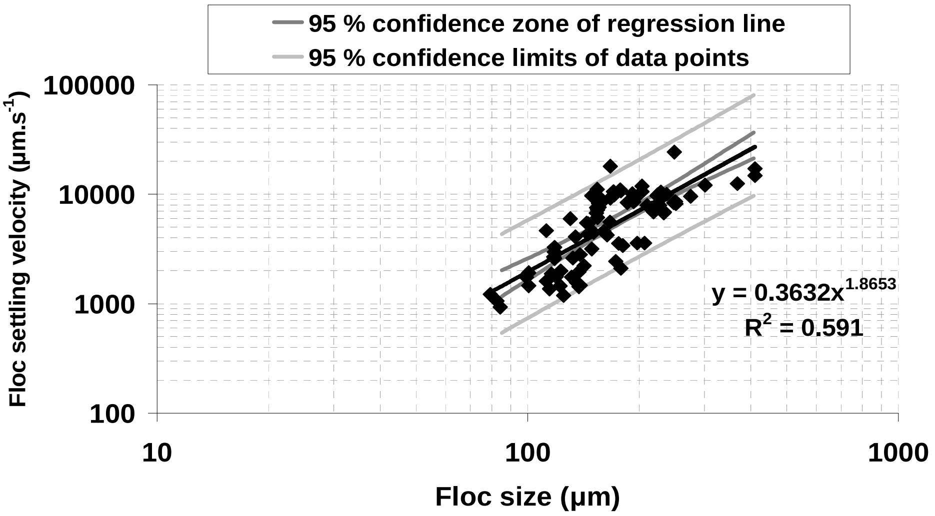


Figure 4.3 Settling rate of magnetic resin beads with calculated 95 % confidence zone of the regression line and 95 % confidence limits of the data points.

Nonetheless the individual data points showed a large degree of scattering around the regression line, which resulted in a relatively low regression coefficient (R^2) of 0.591. A closer inspection of the data showed that 95 % confidence limits on individual values estimated from the regression line had wide intervals. For 165 µm particles the confidence limits ranged from 1900 to 14000 µm.s^{-1} (6.8 to 50 m.h^{-1}). This wide variance of settling velocity for a specific particle size was because it proved impossible to isolate single magnetic resins beads before introduction in the settling column apparatus. Several beads were therefore introduced into the column at one time for each measurement. In doing so, the beads were observed to rapidly interact with each other and form aggregates within seconds, which increased the settling velocity (Figure 4.4). This observation was presumed to be caused by the magnetic properties of the resin, allowing individual beads to attract each other while settling and thereby increasing their settling velocity.

When comparing the settling rate of magnetic resin beads and agglomerates with the settling rate of flocs formed during the coagulation of NOM by Fe-salts a large difference was observed. For instance, a standardised Fe-NOM floc of 500 μm diameter has been shown to have a settling rate of 415 $\mu m.s^{-1}$ (1.5 $m.h^{-1}$) (Jefferson *et al*., 2004), which was more than 10 times slower than the settling rate of an average 165 μm resin particle. Considering that the resin process normally requires a subsequent coagulation stage to remove residual NOM and resin carry-over (Slunjski *et al*., 2000b), enclosure of the resin into the floc matrix could have significant impact on the resulting floc physical characteristics (such as size, strength and settling or rise velocities).

To be able to define the potential impact of these fast settling resin beads on the solid-liquid separation processes required after coagulation, the investigation of the floc characteristics in terms of size, settling and strength, with and without magnetic resin pre-treatment, was carried out as part of this thesis (Section 4.4)

Figure 4.4 Magnetic resin bead agglomerate of 400 μm equivalent diameter.

4.2 Continuous magnetic resin bench-scale tests on different raw waters and model compounds

4.2.1 Aim

The aim of the work reported in this section was to investigate relationships between DOC removal by magnetic resin in different natural raw waters with differing character in terms of hydrophobicity, molecular weight and charge density. This work used the bench-scale method to simulate the resin loading with NOM experienced during continuous use. Variation of contact time and resin dose was undertaken as they have been reported to have a significant effect on NOM removal. In addition to the natural water sources investigated, the removal of several well defined organic model compounds by magnetic resin was investigated. The model compounds were treated both separately and in mixtures to investigate the impact of potential interactions between different NOM types on removal by the magnetic resin.

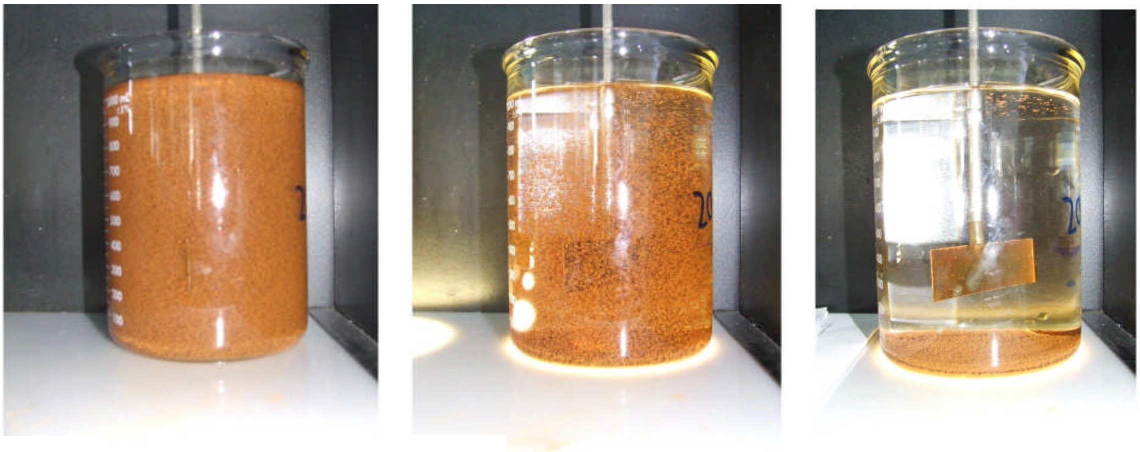
4.2.2 Bench-scale test method

The magnetic resin process has been developed as a continuous process, based on the direct re-use of 90 to 95 % of the resin. As described in Chapter 2, most of the bench-scale research reported the impact of magnetic resin on water quality (Johnson and Singer, 2004; Humbert *et al*., 2005) in a single use which means that the total anion exchange capacity is available for DOC exchange. During continuous use of the resin, however, the resin is used repeatedly before being regenerated. Such continuous use was observed to reduce the exchange capacity of the resin. For example, a reduction of 20 % UV_{254} absorbance removal was reported for a loaded magnetic resin used in pilot-scale when compared to freshly regenerated or virgin resin (Hamm and Bourke, 2001). This decrease in ion exchange capacity has not been considered in any of the reported single use studies in bench-scale tests.

One bench-scale method with re-use of the resin for several treatment cycles has been previously reported (Slunjski, 2004). Each cycle consisted of contacting magnetic resin with raw water for a set length of time in a 1 L beaker followed by a settling period for solid-liquid separation (Figure 4.5). The treated supernatant is then decanted into a collecting tank before re-using the resin with fresh raw water (Section 3.2.2.1).

For this work, the continuous magnetic resin bench-scale tests consisted of 15 repetitive uses of the resin. This was chosen to simulate the number of recycling cycles every magnetic resin bead encounters before regeneration. This resulted from the calculation that at a 10 % and 5 % regeneration rate, every bead is used 10 to 20 times before being withdrawn from the process.

In the following experiments the magnetic resin doses from 10 to 30 mL.L^{-1} were evaluated which resulted in resin services of 1500 to 495 BV at the chosen 15 repetitive re-uses (Section 3.2.2.1). The contact times were varied from 10 to 30 minutes to investigate the impact of prolonged exposure time and increased exchange surfaces on DOC removal. A settling period of five minutes followed after each re-use.



(A) (B) (C)

Figure 4.5 Continuous mixing of magnetic resin in a bench-scale jar tester: (A) Resin during mixing at 150 rpm, (B) Resin at 0 rpm and 0 minutes settling period, (C) Resin after 5 minutes settling period.

4.2.3 Characteristics of analysed raw waters and organic model compounds

4.2.3.1 Raw waters

The investigated lowland river water and algae laden reservoir water were collected from Draycote WTW and Barcombe WTW respectively. These waters were characterised by high DOC values of 11.8-9.4 mg.L^{-1}, low UV$_{254}$ absorbance of 13.9-

16.5 m^{-1} and low specific UV_{254} absorbance (SUVA) of 1.3 to 1.7 $L.m^{-1}.mg^{-1}$ DOC (Table 4.1).

Table 4.1 Raw water characteristics of the investigated UK sources of Draycote, Barcombe, Penwhirn and Albert.

Water sources and sampling date	Draycote (23.11.04)	Barcombe (23.08.05)	Penwhirn (21.03.05)	Albert (10.01.06)	Albert (09.10.06)
DOC ($mg.L^{-1}$)	10.7	9.6	11.8	9.4	10.2
UV_{254} (m^{-1})	13.9	16.5	66.0	60.1	47.8
SUVA ($L.m^{-1}.mg^{-1}$ DOC)	1.3	1.7	5.6	6.4	4.7
Zeta Potential (mV)	-10.8±0.3	-12.7±3.3	-16.7±1.0	-12.4±3.2	-15.0±4.6
Charge density ($meq.g^{-1}$ DOC)	0.3	1.9	5.5	6.5	5.0
Charge load ($meq.L^{-1}$)	0.003	0.019	0.065	0.061	0.051
Turbidity(NTU)	1.4	13.1	1.0	1.8	3.9
pH	8.1	7.7	5.2	5.9	6.7
Alkalinity ($mg.L^{-1}$ $CaCO_3$)	157	112	3	4	8

The two moorland surface waters were collected from Penwhirn WTW and Albert WTW. The source of Albert was sampled at two different times of the year as more water was required to investigate the effect of different magnetic resin doses on NOM removal. Albert and Penwhirn had similarly high DOC values as typical for the low SUVA waters (10.7 to 9.6 $mg.L^{-1}$), but had an increased UV_{254} absorbance of 47.8 to 66.0 m^{-1}. This resulted in high SUVA values of 5.0 to 6.5 $L.m^{-1}.mg^{-1}$ DOC.

The zeta potential of the waters investigated was between -10.8 to -16.7 mV. The charge density was shown to be much lower in the low SUVA waters (0.3 to 1.9 $meq.g^{-1}$

DOC) than in the high SUVA waters (5.0 to 6.5 meq.g^{-1} DOC). For context, charge density values up to 12.2 meq.g^{-1} DOC have been reported by Collins *et al.*, (1986) for other high SUVA sources. The same trend was observed for the charge load with values from 0.003 to 0.019 meq.L^{-1} and from 0.051 to 0.065 meq.L^{-1} for the low and high SUVA waters respectively.

The turbidity of the raw waters was low for Draycote, Penwhirn and Albert with values of 1.0 to 3.9 NTU. Barcombe, on the other hand had higher turbidity (13.1 NTU) due to a high concentration of green algae (*Chlorella vulgaris*. and *Scenedesmus* sp.) (Hayes, 2007).

The alkalinity of the raw waters was of a much higher level for the low SUVA sources of Draycote and Barcombe (112 to 157 mg.L^{-1} $CaCO_3$), than for the high SUVA sources of Penwhirn and Albert (3 to 8 mg.L^{-1} $CaCO_3$). However a correlation between decreasing alkalinity and increasing SUVA levels could not be seen in previous studies. Johnson and Singer (2004) and Humbert *et al.*, (2005) who investigated raw waters with SUVA values of 6.9 and 2.5 L.m^{-1}.mg^{-1}DOC respectively, measured alkalinity levels of 176 and 20 mg.L^{-1} $CaCO_3$ respectively.

Fractionation of the raw waters using XAD resins showed that Draycote was clearly dominated by hydrophilic material, with 60 and 20 % of its NOM characterised as HPIA and HPINA respectively (Figure 4.6). This predominance of hydrophilic material described to be of a low UV_{254} absorbance, due to a low content of intramolecular aromatic structures (Edzwald and Tobiason, 1999; Kitis *et al.*, 2001) agrees with the low SUVA indication of Draycote (1.3 L.m^{-1}.mg^{-1} DOC). The other low SUVA water of Barcombe was found to contain 50 % hydrophobic and 50 % hydrophilic NOM which is similar to the 50-59 % hydrophobic NOM reported by Martin-Mousset *et al.*, (2004) for typical river waters.

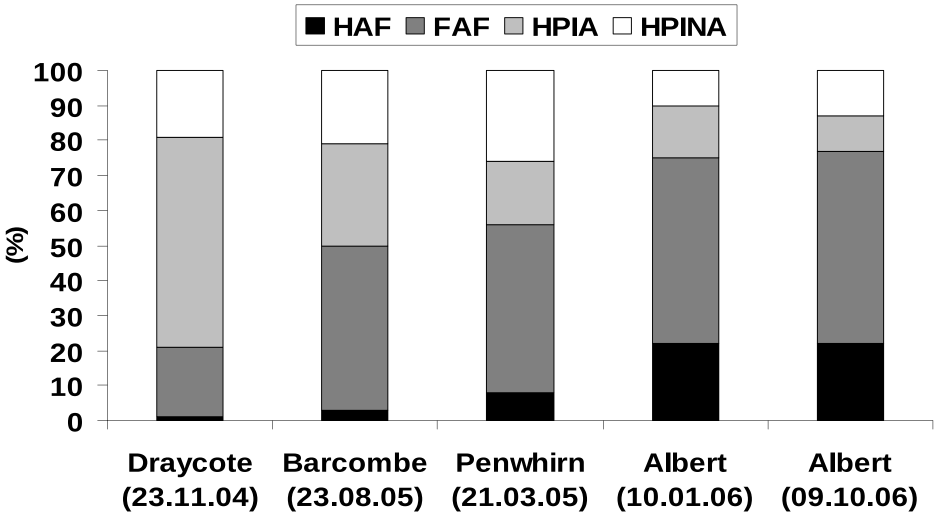


Figure 4.6 Raw water fractionation for Draycote, Barcombe, Penwhirn and Albert water.

Penwhirn contained 56 % and 44 % of hydrophobic and hydrophilic material respectively, a similar distribution of hydrophobic and hydrophilic NOM as Barcombe. However, Barcombe (SUVA: 1.7 $L.m^{-1}.mg^{-1}$ DOC) contained higher concentration of non-UV_{254} absorbing hydrophobic material than Penwhirn (SUVA: 5.6 $L.m^{-1}.mg^{-1}$ DOC).

The Albert water sample had pre-dominance of hydrophobic NOM (80 %) and is in agreement with previous work on this source by Fearing *et al*., (2004), who reported 71-75 % of hydrophobic NOM.

The molecular weight (MW) distribution of the four studied waters was investigated using high pressure size exclusion chromatography (HPSEC). The results were interpreted according to Pikkarainen *et al*., (2004) and Goslan (2003) with MW decreasing with increasing retention time (Section 3.8.8). The results are depicted in Fig. 4.7.

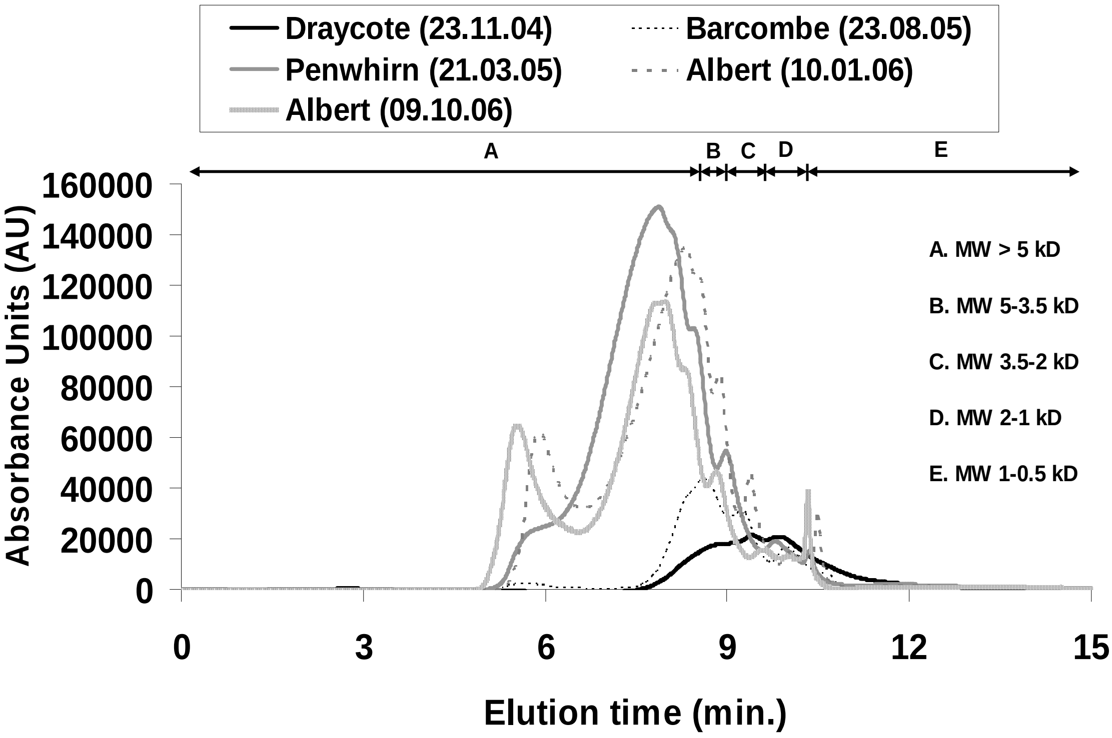


Figure 4.7 Raw water HPSEC profiles for Draycote, Barcombe, Penwhirn and Albert water.

For Draycote, a peak starting at 8 minutes elution time, representing NOM of a MW approximately >5 kDa was registered. After reaching its maximum between 9 to 10 minutes elution time, representing MW of approximately 5 to 2 kDa, the peak declined and disappeared at 13 minutes elution time, indicating an approximate MW of 1 to 0.5 kDa (Figure 4.7). For Barcombe a first shoulder eluting at 5.2 to 6.2 minutes was observed, representing NOM of a MW higher than 5 kDa, as well as a major peak at 8.7 minutes elution time which corresponds to NOM between 5 and 3.5 kDa. Two minor peaks were detected at 9.3 and 10 minutes elution time representing a MW of approximately 3.5-2 and 2-1 kDa respectively.

For Penwhirn and Albert water a first shoulder and an important peak respectively were detected at 5.6 to 6 minutes elution time representing NOM of MW higher than 5 kDa. Both sources had their highest peaks after 8 minutes (Penwhirn) and 8-8.5 (Albert) minutes elution time, representing NOM of MW approximately 5 kDa. This could be classified due to its longer retention time of a lower MW than the NOM eluting at 5.6 to 6 minutes. Several smaller peaks between 8.6 to 10.5 minutes elution time representing a MW of approximate 5-0.5 kDa, were seen for both sources.

In summary, the investigated low SUVA waters of Draycote and Barcombe contained NOM characterised by a low to medium hydrophobicty, medium to low MW and low charge density. The high SUVA waters of Albert and Penwhirn were characterised by NOM of a medium to high hydrophobicity, medium to high MW and a high charge density.

4.2.3.2 Organic model compounds

Seven organic model compounds have been selected to allow indication of any preferential removal by magnetic resin on the basis of hydrophobicty or size of any of the four NOM groups which can be isolated by fractionation of natural waters. These NOM groups are HAF, FAF, HPIA and HPINA. The investigated model compounds were selected on the premise that they are present in living organisms and can therefore appear in the NOM mixture in source waters (Naylor and Tolbert, 1956; Piccolo, 2002; Seiboth *et al.*, 2003; Barata-Soares *et al.*, 2004; Sütfeld *et al.*, 2005; Labieniec and Gabryelak, 2006). Based on this the following molecules were chosen since a relationship between them and the fractions can be expected (Table 4.2):

- Hydrophobic compounds (HAF and FAF)
    - Humic acid
    - Tannic acid
    - Resorcinol
- Hydrophilic acid compound (HPIA)
    - L-glutamic acid
- Hydrophilic neutral compounds (HPINA)
    - D-mannose
    - D-xylose

Molecular structures of the model compounds are depicted in Figures 4.8 and 4.9. The molecular structure of a single humic acid molecule was adapted from Kubicki and Apitz (1999) to present its potential structure in comparison to the other model compounds.

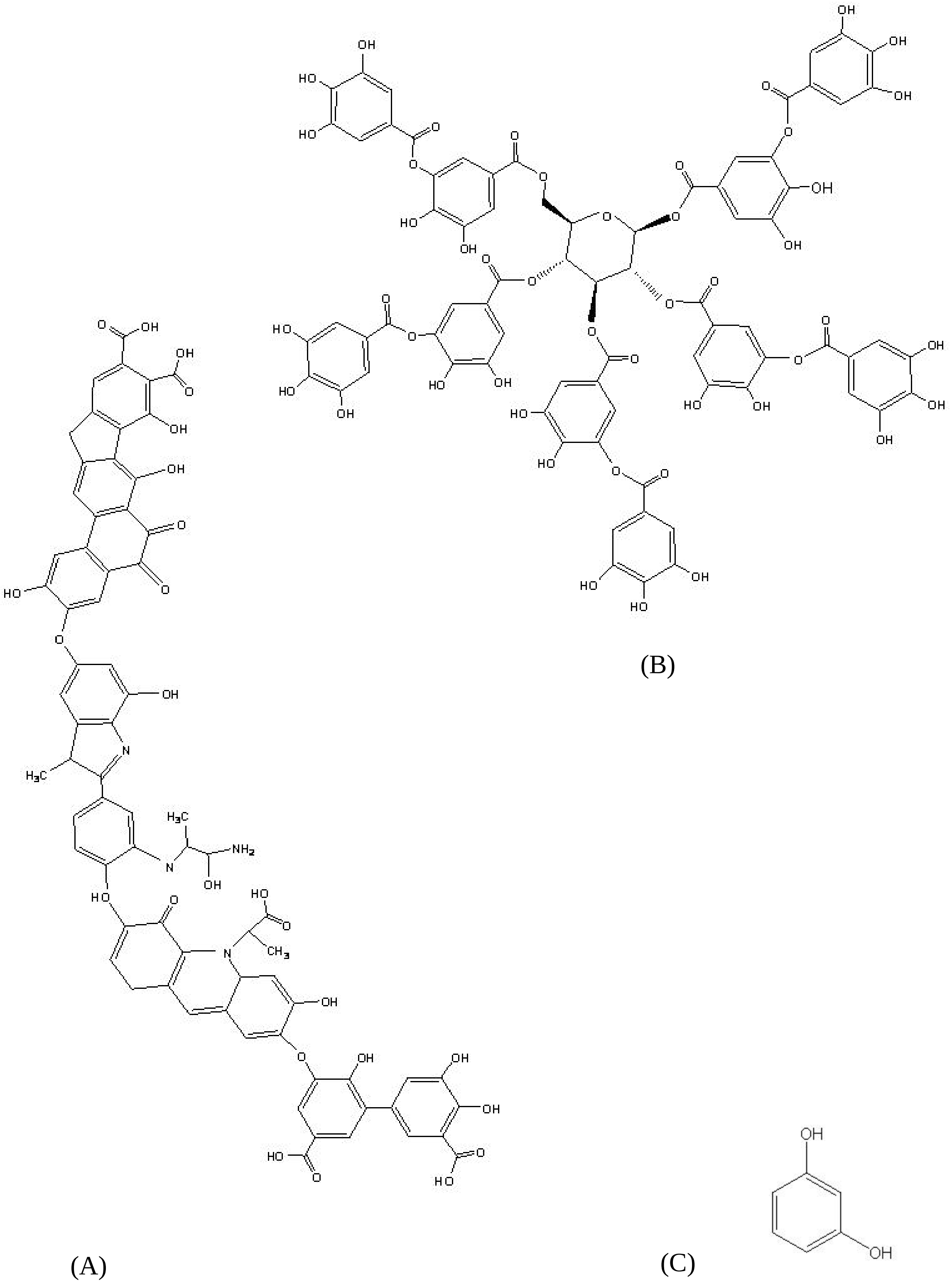
Poly(ethylene glycol) (PEG) was chosen as the only synthetic organic model compound to investigate a potential impact of the MW of hydrophilic neutral organic compounds on the removal efficiency of magnetic resin in comparison with D-mannose and D-xylose (Mortensen *et al*., 2007).

The MW distribution of the model compounds as indicated by Sigma-Aldrich (Sigma-Aldrich Company Ltd., 2006) ranged from 110.1 Da for resorcinol to 1701.2 Da for tannic acid. For humic acid, a specific MW could not be determined. This is because humic acid was the only model compound bought in technical grade, rather than in analytical grade which is of a higher purity. The single humic acid molecules had been described to form macromolecules by weak forces such as dispersive interaction, charge transfer complexes, hydrogen bonds, multivalent ion bridging or hydrophobic interactions (Piccolo *et al*., 2003; Porquet *et al*., 2003; Pena-Mendez *et al*., 2005). Hence it can be expected that the humic acid is the model compound with the highest MW.

Table 4.2 Physico-chemical characteristics of organic model compounds solutions.

	Model compounds						
Parameters	Humic acid	Tannic acid	Resorcinol	L-glutamic acid	D-mannose	D-xylose	Poly(ethylene glycol)
pH	5.1	5.2	5.6	4.4	5.5	5.4	5.5
DOC (mg.L^{-1})	9.5	9.9	9.7	10.3	10.2	9.9	10.0
UV$_{254}$ (m^{-1})	64.1	52.7	5.1	N.m.	N.m.	N.m.	3.0
SUVA (L.m^{-1}.mg^{-1} DOC)	6.8	5.3	0.5	N.m.	N.m.	N.m.	0.3
Zeta Potential (mV)	-44.8±1.4	/	N.m.	N.m.	N.m.	N.m.	N.m.
Charge density (meq.g^{-1} DOC)	6.2	3.8	N.m.	5.5****	N.m.	N.m.	N.m.
Charge load (meq.L^{-1})	0.059	0.038	N.m.	0.056	N.m.	N.m.	N.m.
Turbidity(NTU)	6.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
MolecularWeight (Da)*	N.i.	1701.2	110.1	147.1	180.2	150.1	1470
Formula*	N.i.	$C_{76}H_{52}O_{46}$	$C_6H_6O_2$	$C_5H_9NO_4$	$C_6H_{12}O_6$	$C_5H_{10}O_5$	$C_{66}H_{134}O_{34}$
pKa**	N.m.	N.m.	9.3	2.1	12.1	12.1	N.m.
Molecule type	Polyphenol	Polyphenol	Phenol	Amino acid	Sugar	Sugar	Polymer
Role***	Secondary metabolite in plants	Product of organic tissue decay	Alelo-Chemical in plants	Central role in nitrogen metabolism	Part of Hemi-cellulose	Precursor to Ascorbic acid	Impregnator for wood conservation (Artificial)

* Adapted from Sigma-Aldrich Company Ltd (2006); ** Adapted from Lide, (2006-2007); *** Adapted from Naylor and Tolbert, 1956; Piccolo, 2002; Seiboth *et al*., 2003; Barata-Soares *et al*., 2004; Sütfeld *et al*., 2005; Labieniec and Gabryelak, 2006; N.i.= Not indicated; N.m.= Not measurable, **** Calculation based on pK$_b$ value.



(B)

(A)

(C)

Figure 4.8 Hydrophobic model compounds (A) Humic acid (adapted from Kubicki and Apitz 1999) (B) Tannic acid (adapted from Sigma-Aldrich Company Ltd., 2006), (C) Resorcinol (adapted from Sigma-Aldrich Company Ltd., 2006).

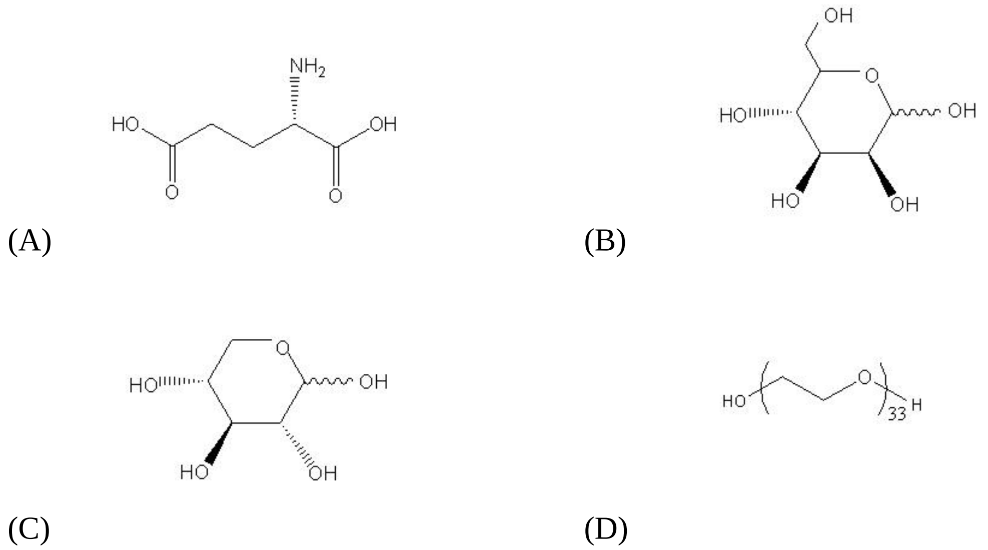


Figure 4.9 Hydrophilic model compounds (A) L-glutamic acid, (B) D-mannose, (C) D-xylose, (D) Poly(ethylene glycol) (adapted from Sigma-Aldrich Company Ltd., 2006).

Humic acid, tannic acid, resorcinol and PEG absorbed UV_{254} with values of 64.1, 52.7, 5.1 and 3.0 m^{-1} respectively. This was attributed to the aromatic structures and hydrogenated double bonds in those molecules.

Among the investigated model compounds the zeta potential could only be measured for humic acid (-44.8 ± 1.4 mV) as the particle size below 5 nm is below the measurement range of the zetasizer (Malvern Instruments, 1996). Humic acid had been described as consisting of small molecules that are able to form supra-molecular conformations. Such large supra-molecules are able to reach sizes between 2 and 50 nm (Cornel *et al*., 1986; Thurman and Malcolm, 1986) and are within the accuracy of the measurement of the zetasizer.

The humic acid and tannic acid showed charge density values of 6.2 and 3.8 $meq.g^{-1}$ DOC respectively. The charge density measurement for other model compounds did not show any sensible data, most likely due to the lack of the carboxylic groups on their molecules. The carboxylic functional groups can be found in an unbounded state on humid acid. Gustavson (1956) proposed that for tannic acid, the strongly acidic groups arise from some of the digallic acid residues that are bonded to the sugar molecule through phenolic groups rather than through the usual carboxyl linkages, thus leaving available titrable carboxyl groups. The carboxylic groups dissociate at a pH above 6 (Collins *et al*., 1986). Considering that addition of polyDADMAC to the tannic acid solution led to the formation of small particles, an interaction between the cationic polymer and the negative titrable carboxylic functional can be expected, making the charge detectable by the zetasizer.

This mechanism of particle formation has not been observed previously for resorcinol or any of the hydrophilic molecules. Different mechanisms were suggested for this phenomenon. Firstly, hydrophilic molecules have been described to adsorb or chemically bond water on their surfaces, which leads to particle stability, making them less removable by mechanisms such as charge neutralisation (Edzwald, 1993). Secondly it was shown that the performance of polyDADMAC decreases with decreasing MW of NOM (Eldridge *et al*., 2001). This could explain why no charge density was detectable for resorcinol. Thirdly, resorcinol, D-xylose, D-mannose and PEG contained only phenolic functional groups that dissociate only at pH values above 8 (Collins *et al*. 1986). This could be confirmed by the pKa values of 9.3, 12.1 and 12.1 reported for resorcinol, D-xylose and D-mannose respectively. L-glutamic acid has a low pKa of 2.1. This indicates that at the pH of treatment by magnetic resin (pH 4.4) a theoretical charge density of 5.5 meq.g^{-1} DOC based on the re-arrangement of the acid dissociation constant can be calculated (Section 3.8.7.2).

In terms of turbidity a value of 6.7 NTU could only be measured for humic acid while values <0.1 NTU were measured for the other model compounds. This was related to humic acid being the only model compound which contained filterable solids, such as ashes (Chiou *et al*., 1987). Furthermore humic acid was the only model compound causing a colouration of the water (160.4 Hazen Units) which would also contribute to turbidity.

XAD resin fractionation was used to verify the hydrophobicity of the different model compounds. The humic acid consisted to 70 % of DOC as HAF, while tannic acid and resorcinol consisted to 90 and 91 % of the as FAF. L-glutamic acid was classified as 78

% HPIA, while D-mannose, D-xylose and PEG was classified as 91, 93 and 90 % respectively as HPINA (Figure 4.10). However, it was observed that 7 to 30 % of the NOM from the different model compounds could be classified as ‘other fractions’. This could have been a result of impurities in the model compounds but this was unlikely given the high grade of each of the chemicals used. It can be therefore assumed that the overlap between fractions is responsible for this observation.

In the DOC fractionation, the hydrophobic solutes were defined as solutes retained by more than 50% on XAD-8 resin at a given ratio of resin to water (Leenheer, 1981) passed through the column. Therefore an exact fractionation cannot be expected from the method and retention of hydrophilic DOC on the XAD-8 resin as well as leakage of hydrophobic DOC from this resin cannot be excluded (Section 3.5.3).

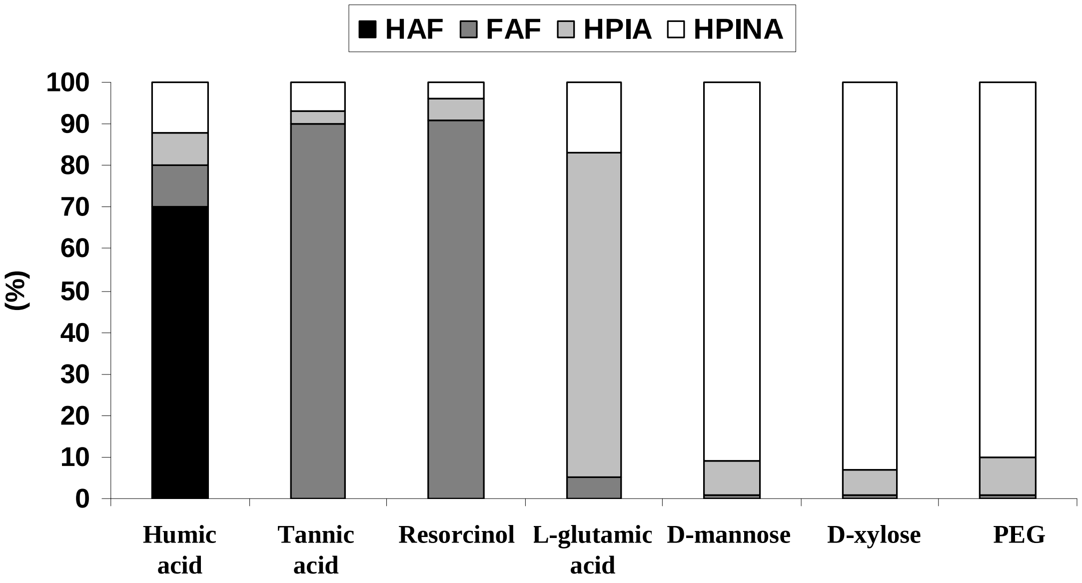


Figure 4.10 Fractionation of model compounds.

An investigation of the MW distribution using HPSEC showed that only tannic acid and humic acid were detectable by this method which is expected as these two compounds have measurable UV_{254} absorbance levels (Figure 4.11). A broad MW distribution of humic acid was observed, similar to that of Penwhirn and Albert water (shown in Figure 4.7). A first shoulder and a major peak were detected at 6 and 7.8 elution time and represent NOM of MW >5 kDa. The final peak was observed at 10.7 minutes elution time and represents NOM of MW <1 kDa. This variation was attributed to the heterogeneous distribution of different MW molecules that can be found in humic acids.

Furthermore, the ability of humic acid molecules to form supra-molecular conformations of varying size must be noted, as previously described (Piccolo *et al*., 2003; Porquet *et al*., 2003; Pena-Mendez *et al*., 2005) (Figure 4.11).

Tannic acid on the other hand showed one major peak at 10 minutes elution time, representing NOM of approximately 2-1 kDa. This was a very similar MW to that of 1701.2 Da indicated by the manufacturer (Sigma-Aldrich Company Ltd., 2006) and showed that this compound had a very uniform molecular composition.

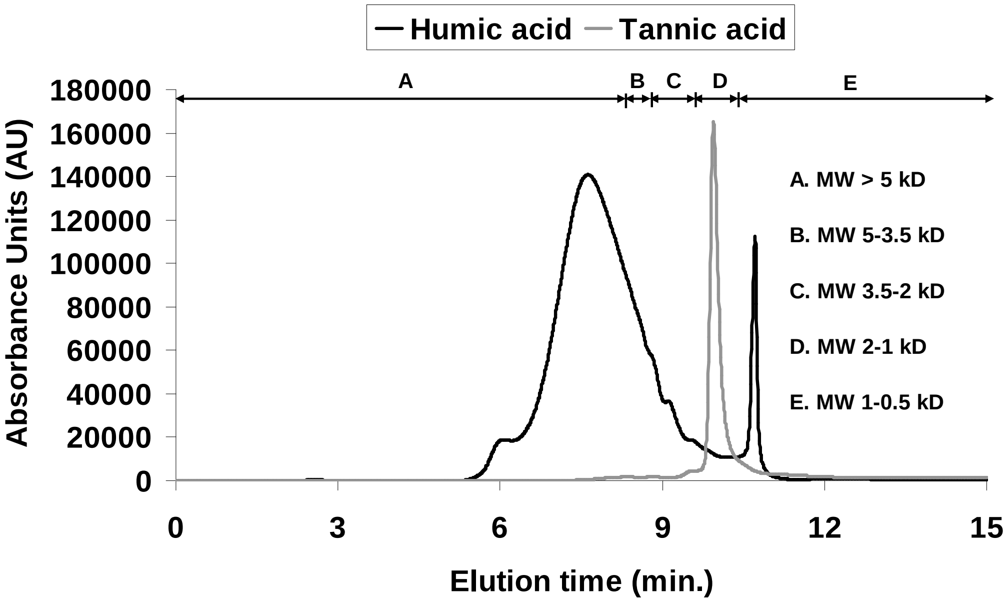


Figure 4.11 Raw water HPSEC profiles for humic acid and tannic acid.

4.2.4 NOM removal kinetics of magnetic resin in a high SUVA water

The impact of magnetic resin contact time, resin doses and repetitive use of the resin on NOM removal were investigated in a series of removal kinetics experiments. In a first step the impact of the re-use of resin pre-loaded with NOM, expected to block a part of its functional groups, was investigated as reported by Hamm and Bourke (2001). Secondly the impact of a prolonged contact time was investigated to see if this led to higher NOM removal for the same resin dose by allowing a diffusion of organic material attached to the bead surface towards the functional groups inside the pores (Gönder *et al*., 2006). Thirdly the impact of an increased resin dose was studied as this should provide a higher, easily accessible external exchange surface and thereby allow a higher NOM removal while eliminating a reliance on slow pore diffusion.

The Penwhirn raw water was used in the tests due to its high MW NOM content. It was expected that diffusion rate of NOM towards the pores of anion exchange resins becomes slower with increasing MW as reported by Gottlieb (1996); and Hebb *et al*., (2003) which should be noticeable for a high MW NOM. The results follow as UV_{254} absorbance.

The results of the treatment variation describe above are displayed in Figure 4.12.
The first treatment with 10 $mL.L^{-1}$ magnetic resin (100 BV) reduced the UV_{254} absorbance by 51 to 73 % after 2 to 10 minutes contact time respectively.

Re-usage of the same magnetic resin (200 BV) resulted in the reduction of the UV_{254} absorbance by 40 to 56 % after 2 to 10 minutes contact time respectively. The removal capacity of the resin was thereby reduced by 17 %. This was attributed to the partially loaded bead surfaces after the first resin use, as described by Hamm and Bourke (2001) and Kitis *et al*., (2007).

Doubling the contact time (10 $mL.L^{-1}$ (20 min.c.t.) 100 BV) resulted in the reduction of UV_{254} absorbance by 40 to 76 % after 2 to 20 minutes contact time respectively. The removal during the first 10 minutes was seen to be very similar to that measured at a contact time of 10 minutes only. Prolonging the contact time by 10 minutes increased the removal, however only slightly (1-6 %) when compared to removal during the initial 10 minutes.

When doubling the applied resin dose (20 $mL.L^{-1}$ (10 min.c.t.) 50 BV), the UV_{254} absorbance was reduced by 70 to 90 % after 2 to 10 minutes contact time respectively. This improved the final removal level by 17 % compared to a 10 mL magnetic resin dose after 10 minutes contact time. Increasing the resin dose was thereby shown to be more efficient to enhance NOM removal than increasing the contact time, which relies on the diffusion rate of NOM.

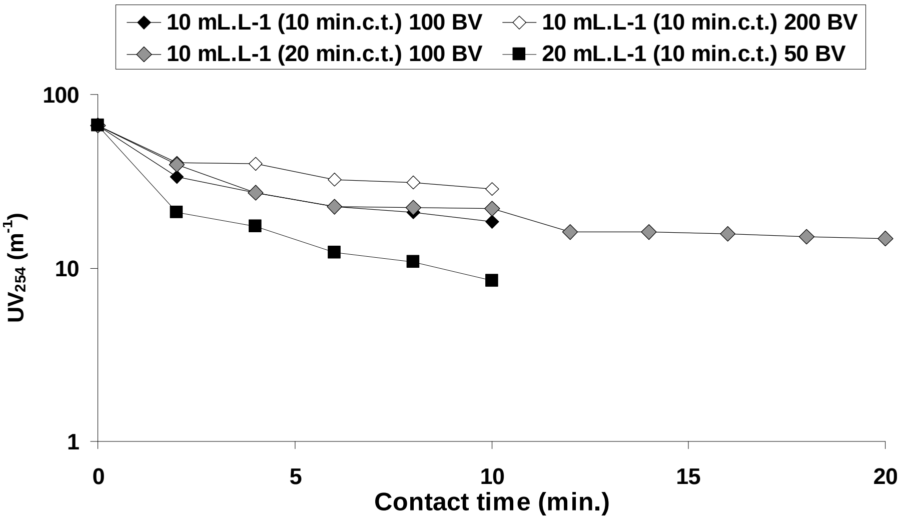


Figure 4.12 Comparison of NOM removal kinetics in terms of magnetic resin re-use, contact time and resin in Penwhirn raw water.

In general, a significant fraction of NOM was removed within 2 minutes contact time, while contact times exceeding 10 minutes were seen to be of little benefit (1-6 %). Humbert *et al.*, (2005) who compared, in a similar test, the magnetic resin to other resins with larger bead diameters and with a reduced external exchange area, related this to the increased external surface of magnetic resin which facilitates NOM removal and leads to pseudo-equilibrium shortly after ten minutes. Pseudo-equilibrium is described as a state when the kinetic reactions become so slow, that they look similar in removal rate to those of the final state of equilibrium (Dorfner, 1972; Talwalkar and Mahajani, 2006). Equilibrium is reached when the concentration of exchange ions in the liquid phase equals the concentration in the Nernst-film around the beads and no more NOM is being removed by the resin. The Nernst-film describes a symbolic layer of water around every bead of resin in a stirred medium through which NOM has to diffuse during the exchange process and was developed to model actual mass transfers from the liquid onto the bead surface (Dorfner, 1972; Choy *et al.*, 2004).

In order to identify the kinetic order of the removal of NOM by magnetic resin different linear relationships were plotted. However, no linear relationship of the level of residual UV_{254} absorbance (C(A)) or its natural logarithm (lnC(A)) against the contact time (t) could be observed. Therefore NOM removal by magnetic resin cannot be of 0 or 1st order. When plotting the inverse value of the concentration (1/C(A)) against time, a linear relationship was obtained (Figure 4.13) indicating that NOM removal by magnetic resin follows a reaction of 2nd order. The second order reactions indicate a dependence of the process on concentration of the reactants. In this case those are the concentration of magnetic resin in comparison to the concentration of NOM and the reaction (or contact) time (0 to10 minutes).

When calculating the rate constant (K) which quantifies the speed of a reaction (in this case the UV_{254} absorbance reduction) after equation 3.4 (Section 3.3.5), differences between virgin, loaded and increased resin doses were seen. The reactivity constant which indicates how fast a reaction is, normally increases with increasing levels of reactants, as an increased level of collisions between the different substances is expected. The decrease of K from 0.0014 to 0.0009 min^{-1} when re-using the resin (10 $mL.L^{-1}$ (10 min.c.t.)) was attributed to the reduced accessibility of the exchange surface on the resin, making it less evident for NOM to rapidly interact with available exchange sites (Figure 4.13). Increasing the resin dose to 20 $mL.L^{-1}$ resulted in the increase of K from 0.0014 min^{-1} to 0.0032 min^{-1}, and thus in a steeper slope of the linear trend line, which was influenced by higher, available external surface area. Finally, the reduction of K from 0.0014 min^{-1} to 0.0010 min^{-1} when increasing the contact time from 10 to 20 minutes was attributed to the reduced reaction speed after 10 minutes.

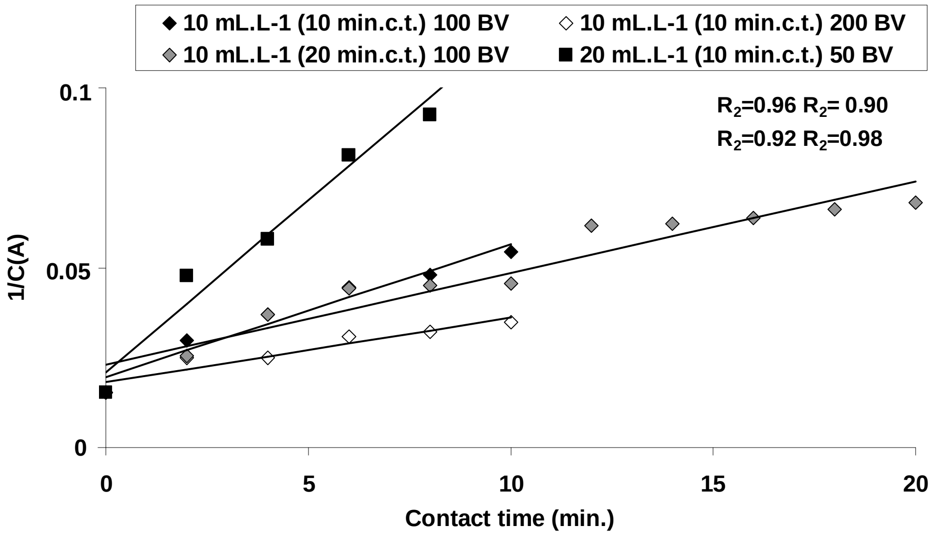


Figure 4.13 Kinetic reaction order of 2nd degree for magnetic resin.

4.2.5 DOC removal in different raw waters

Following from the previous section (Section 4.2.4) NOM removal by magnetic resin can be strongly influenced by resin dose and re-use of the same loaded resin, and also to a certain extent by contact time. Here all four water sources were evaluated to investigate the impact of NOM character on the treatment.

4.2.5.1 Draycote

When using the same 10 mL.L^{-1} magnetic resin dose for 15 times in Draycote water, NOM removal measured in terms of DOC was shown to remain relatively stable with increasing BV. 65 and 55 % DOC removal was found after 100 and 1500 BV respectively which resulted in a 55 % DOC reduction in the final combined product water (Figure 4.14). This is comparable to an overall 58.5 % DOC reduction reported by Drikas *et al.*, (2003) in a pilot-scale evaluation of a low SUVA water (1.3 L.m^{-1}.mg^{-1} DOC). At 100 and 1500 BV the UV$_{254}$ absorbance has been reduced by 75 and 55 %, which resulted in a 60 % reduction in the combined water, indicating a slight preference for UV$_{254}$ absorbing material as seen in the literature review. Changing the resin dose and contact time to 20 mL.L^{-1} and 30 minutes respectively, gave similar levels of DOC removal (70 and 60 % after 50 and 750 BV) of 60 % in the combined product water (Figure 4.15). The UV$_{254}$ absorbance was reduced by 80 and 65 % after 50 and 750 BV respectively which resulted in 70 % reduction in the combined product water, again showing a preference for UV$_{254}$ absorbing material.

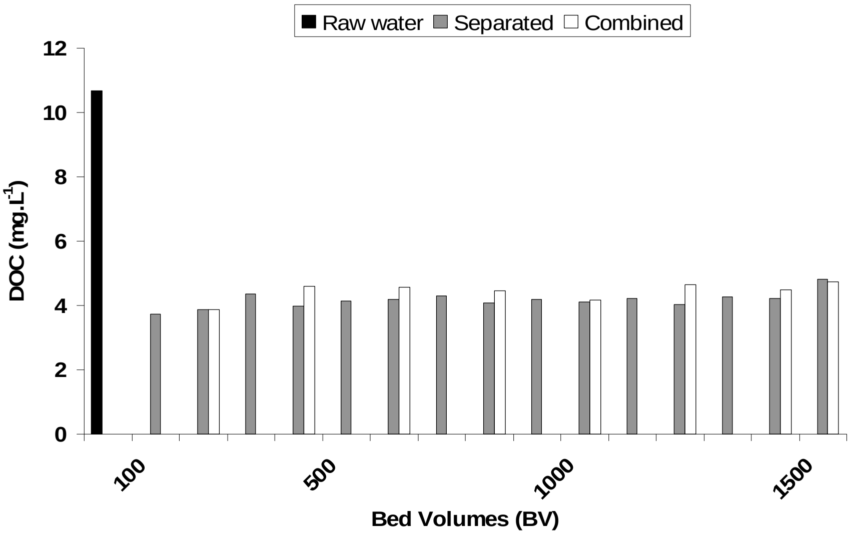


Figure 4.14 DOC residual after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) in Draycote water.

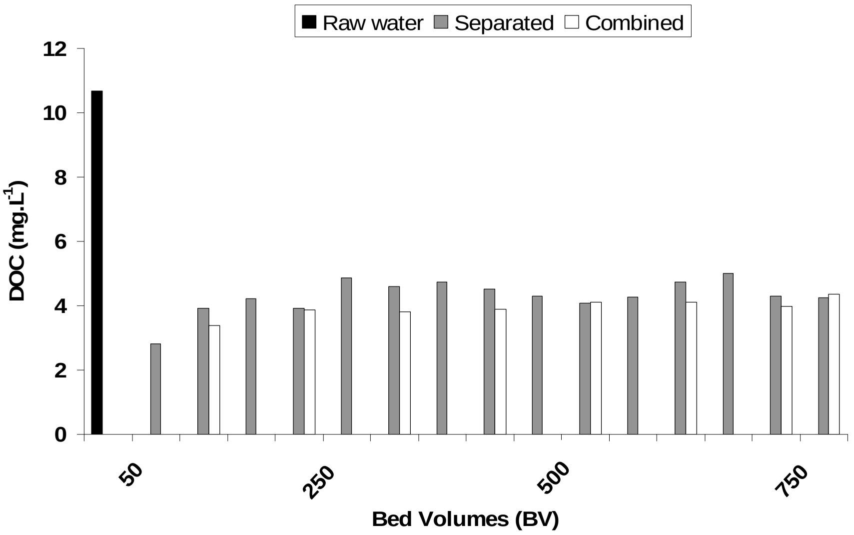


Figure 4.15 DOC residual after continuous magnetic resin treatment at bench-scale (20 mL.L^{-1}, 30 minutes contact time, 750 BV) in Draycote water.

HPSEC showed a similar removal trend to that of the DOC for both treatment options. When using a 10 mL.L^{-1} magnetic resin dose, the peak representing material of >5 to 1 kDa was reduced after 100 and 1500 BV by 70 and 50 % respectively which resulted in a 50 % reduction in the combined product water (Figure 4.16). When using a 20 mL.L^{-1} magnetic resin dose, the peak was reduced after 50 and 750 BV by 80 and 60 % respectively. With a 60 % reduction in the combined product water, a removal level similar to that of the 10 mL.L^{-1} magnetic resin dose was observed (Figure 4.17).

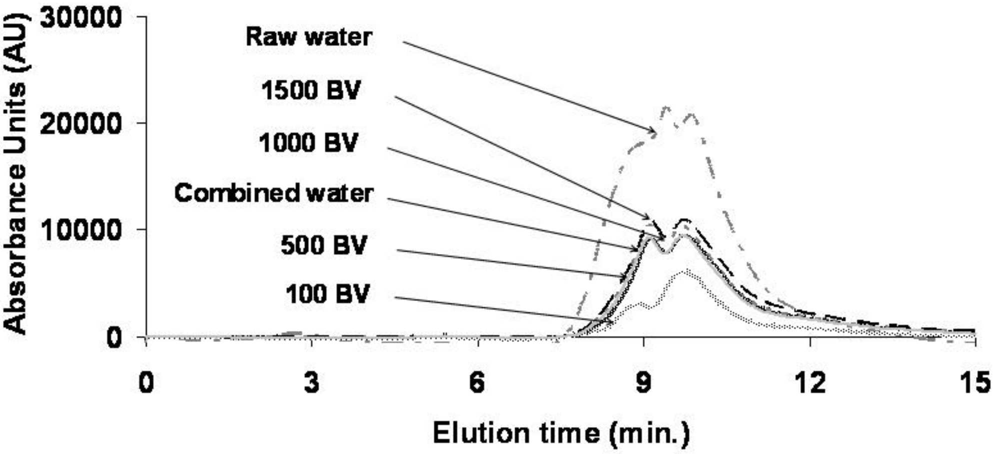


Figure 4.16 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) in Draycote water.

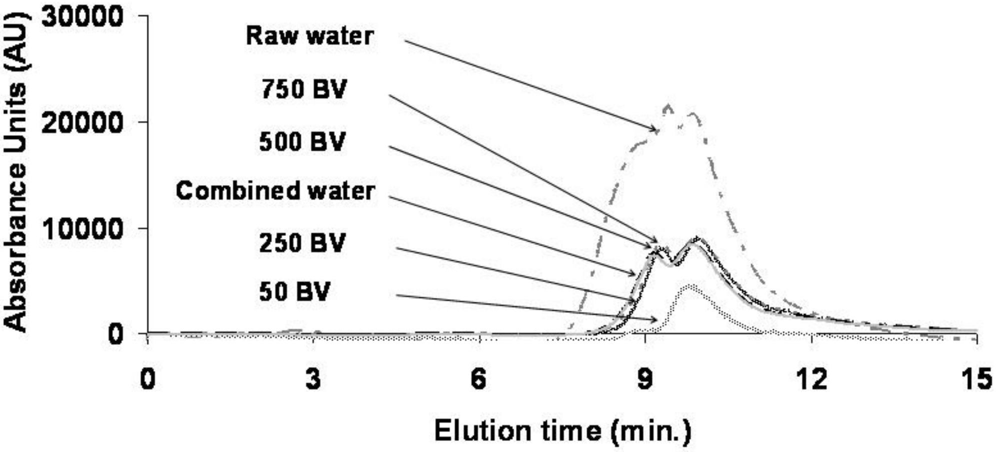


Figure 4.17 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (20 mL.L^{-1}, 30 minutes contact time, 750 BV) in Draycote water.

The investigation of the charge load showed that magnetic resin had reduced the initial level of 0.003 meq.L^{-1} to 50 % only. Bourke (2006) stated that 10 mL magnetic resin (1500 BV) had a total chloride capacity of 5 meq whereas in this study a total 0.045 meq of charge was removed after 15 re-uses and thus the saturation of the exchange capacity was not possible.

Considering however that both treatment options with 10 and 20 mL.L^{-1} magnetic resin removed NOM to a similar degree and at a constant level throughout the trials, two main conclusions were drawn. Firstly, all the magnetic resin removable NOM was effectively removed at the lower dose rate and therefore it was expected that equilibrium was reached. Secondly magnetic resin was able to effectively treat water that contained NOM of mainly hydrophilic character and thereby confirmed the good treatability of that type of organic material by anion exchange proposed by Anderson and Maier (1979); Croué *et al*., (1999) and Bolto *et al*., (2004).

4.2.5.2 Barcombe

For Barcombe a 10 mL.L^{-1} magnetic resin dose re-used 15 times, resulted in a relatively constant DOC reduction of 35 to 28 % over the whole trial. This gave a 33 % reduction in the combined product water (Figure 4.18), significantly lower than shown for Draycote. The UV$_{254}$ absorbance was reduced by 65 to 55 % between 100 and 1500 BV and gave a 65 % reduction in the combined product water, indicating a strong preference of magnetic resin for the UV_{254} absorbing material. Increasing the magnetic resin dose and contact time to 20 $mL.L^{-1}$ and 30 minutes respectively gave an initial 65 % DOC reduction, which decreased to 30 % and resulted in 45 % reduction in the combined product water (Figure 4.19). Again UV_{254} absorbance was preferentially removed with a 74 % reduction in the combined product water achieved at this higher dose. This trend of quickly decreasing DOC removal levels during continuous magnetic resin use was in accordance with Kitis *et al.*, (2007). In that bench-scale study continuous re-use of magnetic resin on five different source waters with SUVA values ranging from 2.7 to 5.1 $L.m^{-1}.mg^{-1}$ DOC, quickly decreased the initial DOC removal (30 to 60 %) by up to 30 % during the first 9 re-uses. The novel continuous bench-scale method was thereby seen to be advantageous in comparison to the widely used single resin use method. This is because the latter one would not have been able to predict the observed removal decrease and given false expectations towards the process efficiency.

As the initial DOC levels were similar for Draycote and Barcombe, the different removal performance can be related, to the character of NOM in both sources. The Barcombe water had higher charge density and higher hydrophobicity than Draycote (Section 4.2.3.1).

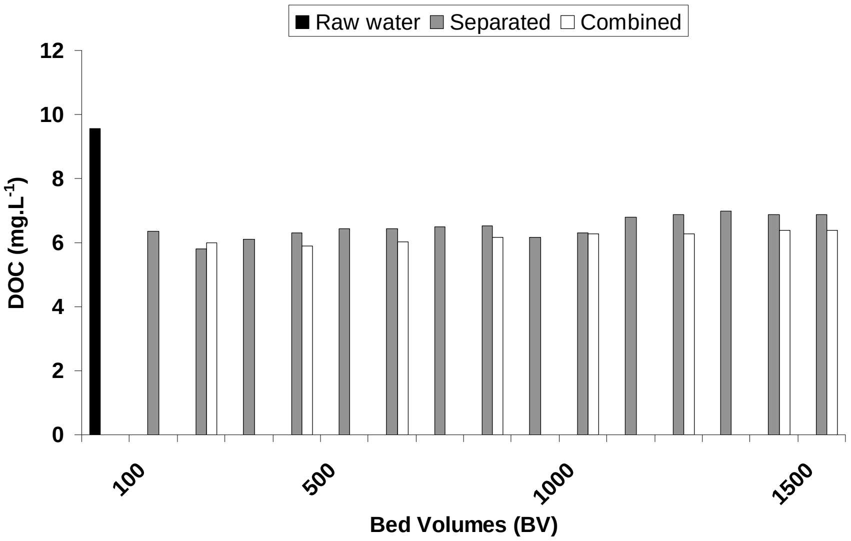


Figure 4.18 DOC residual after continuous magnetic resin treatment at bench-scale (10 $mL.L^{-1}$, 10 minutes contact time, 1500 BV) in Barcombe water.

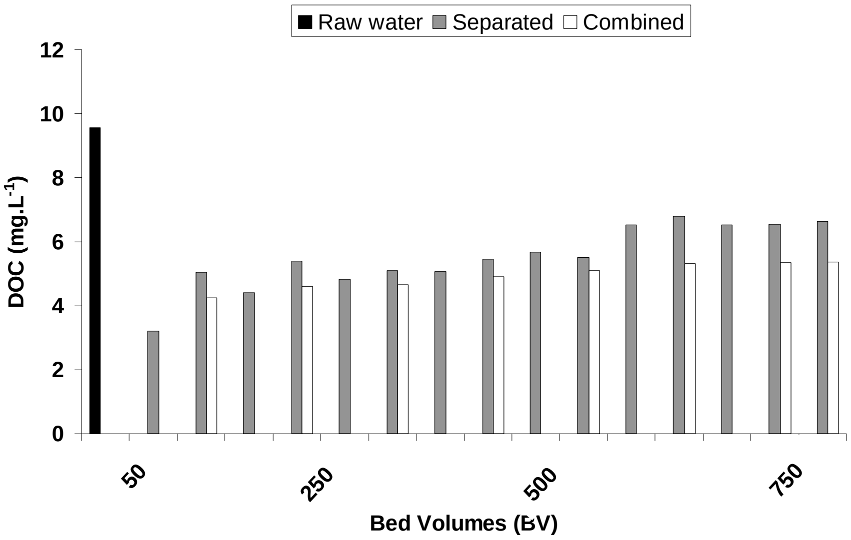


Figure 4.19 DOC residual after continuous magnetic resin treatment at bench-scale (20 mL.L^{-1}, 30 minutes contact time, 750 BV) in Barcombe water.

HPSEC showed that at both magnetic resin doses NOM eluting at 8.7 minutes (5 to 3.5 kDa) and at 9.3 to 10 minutes (3.5 to 1 kDa) were reduced by 90 to 50 % and 50 to 20 % respectively (Figure 4.20 and 4.21). This resulted in a 60 and 25 % reduction of the material eluting at 8.7 and 9.3 to 10 minutes respectively in the combined waters. The initial peak eluting at 5.2 to 6.2 minutes was reduced by 40 to 15 % and by 85 to 45 % for the 10 and 20 mL.L^{-1} resin doses respectively. This resulted in a 25 and 50 % reduction in the combined water and indicated that the increased resin dose which provided a larger exchange surface was able to enhance the removal of high MW NOM. However increased removal of the high MW NOM eluting between 5.2 and 6.2 minutes was observed only at the beginning of the experiment. The removal of that high MW NOM peak quickly decreased (85 to 45 %) in a similar way to the removal pattern of DOC in this water (65 to 30 %). A correlation between high MW material, able to physically block the resin, and a rapid reduction of the exchange capacity of magnetic resin was concluded from this.

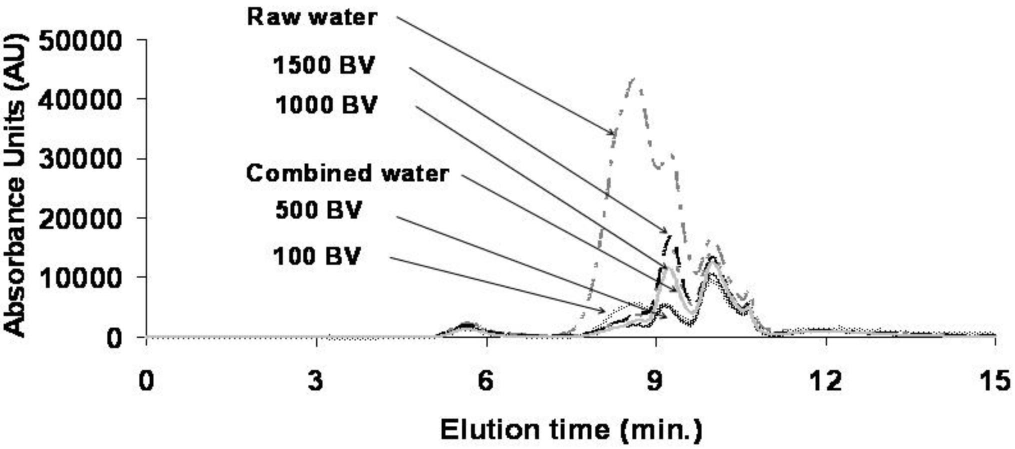


Figure 4.20 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) in Barcombe water.

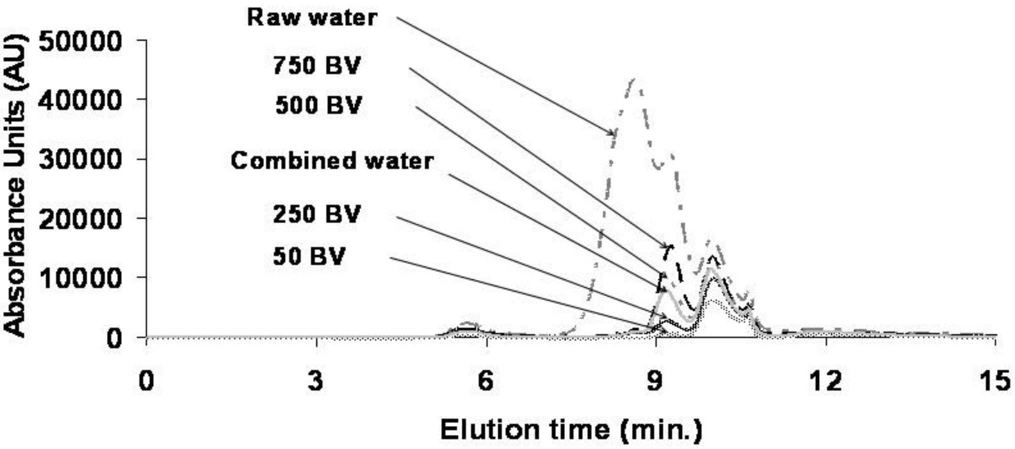


Figure 4.21 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (20 mL.L^{-1}, 30 minutes contact time, 750 BV) in Barcombe water.

However, considering the low SUVA and the small amplitude of the shoulder representing high MW material >5 kDa, a large fraction of non-UV$_{254}$ absorbing material was expected as already described for the fractionation of NOM in Barcombe water (Section 4.2.3.1).

Given that Barcombe was dominated by green algae (Hayes, 2007), it was probable that this water contained high concentrations of soluble algogenic material. Extracellular organic material (EOM) of the pre-dominant species Chlorella vulgaris and Scenedesmus sp. had been described to be of variable hydrophobicity (11 to 35 %

respectively) and of low SUVA, 0.5 to 1.5 $L.m^{-1}.mg^{-1}$ DOC, making them difficult to detect by HPSEC (Nguyen *et al*., 2005; Henderson *et al*., 2007). Furthermore EOM of Chlorella vulgaris and Scenedesmus sp. had been described to be of a MW of 16 to 100 kDa and to have a charge density of 3.2 $meq.g^{-1}$ (Henderson *et al*., 2006; Pivokonsky *et al*., 2006). While the charge density made them a candidate for anion exchange, their high MW could lead to a rapid blockage of the resin surface as described by other studies on anion exchange resins (Gottlieb *et al*., 1996; Lee *et al*., 1997; Hebb *et al*., 2003; Gönder *et al*., 2006) and thereby reduce the removal capacity.

Considering the charge removal in Barcombe water it was found that the 10 $mL.L^{-1}$ and 20 $mL.L^{-1}$ magnetic resin doses reduced the initial raw water charge load from 0.019 $meq.L^{-1}$ to 0.0014 and 0.009 $meq.L^{-1}$, which is equivalent to 35 and 50 % removal respectively. This is significantly lower that the total chloride exchange capacity of 5 and 10 meq for 10 and 20 mL of magnetic resin. Therefore for Barcombe, as observed for Draycote water, there is no evidence for a saturation of the exchange capacity by high functionality of NOM. This indicates that the loss of removal performance in Barcombe water was due to a mechanism of surface and pore blockage by high MW material, whereby an increase in resin dose provided a larger exchange surface and hence increased the overall removal.

4.2.5.3 Penwhirn

Penwhirn water complements the above assessment of resin surface blockage by high MW NOM since it is high a SUVA water and contains a higher percentage of high MW NOM detectable by HPSEC (physico-chemical properties described in 4.2.3.1).

Treatment of Penwhirn water with 10 $mL.L^{-1}$ magnetic resin at 10 minutes contact time gave DOC removals of 50 and 15 % after 100 and 1500 BV (Figure 4.22). This resulted in a combined product water DOC level reduction of 30 %, similar to the removal obtained with 10 $mL.L^{-1}$ magnetic resin for Barcombe (33 %). However, for Penwhirn water there was a 35 % reduction in the DOC removal over the trial length at 10 $mL.L^{-1}$ resin dose whilst for Barcombe the removal was constant. Monitoring of the UV_{254} absorbance showed a reduction of 65 and 25 % after 100 and 1500 BV respectively which resulted in a 35 % reduction in the combined product water. The SUVA was reduced by 10 % from 5.6 to 4.9 L.m^{-1}.mg^{-1} DOC. The UV_{254} absorbance removal was 5 to 15 % higher than DOC, showing that magnetic resin preferentially removed UV_{254} absorbing NOM species. The smaller difference between the UV_{254} absorbance and DOC removal in high SUVA sources should however not be interpreted as a preferential removal of material of low UV_{254} absorbance. It was explained in the literature review that the higher percentage of UV_{254} absorbing material in that water type makes a partial removal of it less noticeable.

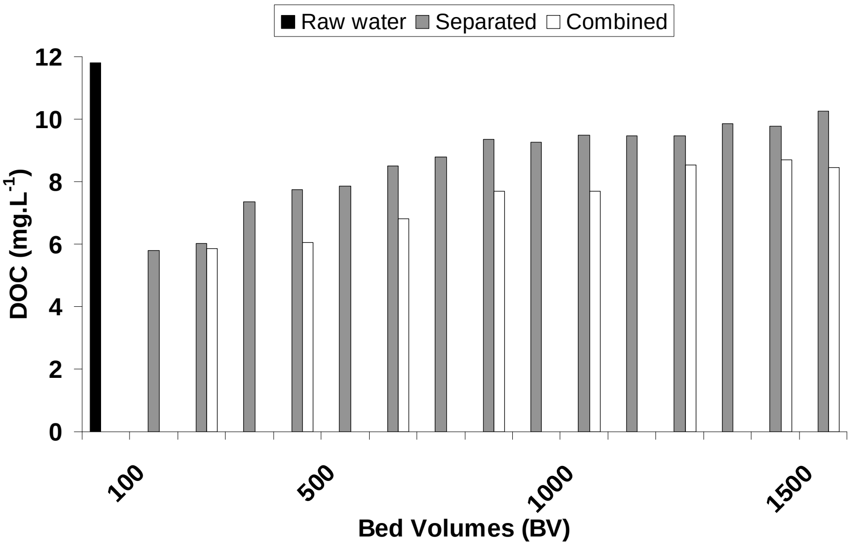


Figure 4.22 DOC residual after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) in Penwhirn water.

The investigation of the HPSEC profiles showed a first detectable shoulder at 6 minutes elution time indicating that material of a MW >5 kDa was not removed throughout the trial (Figure 4.23). The increased shoulder height after resin treatment relative to the raw water profile was related to the use of a new HPSEC column that was used during the investigation of the treated water. This was because the previous column had to be replaced due to its long service time. Used columns have been described to lose their retention capacity of different MW and can thereby slightly shift the peaks (Shimadzu, 2006).

The second and major peak that was detected at 8 minutes elution time indicating that NOM MW >5 kDa was removed after 100 and 1500 BV by 80 and 25 % respectively, which resulted in a 50 % reduction in the combined product water. The last peak detectable at 9.8 minutes elution time was removed by 95 and 30 % after 100 and 1500 BV which resulted in a combined overall 40 % peak reduction.

Penwhirn water was dominated by high MW organic compounds (>5 kDa) that showed a decreasing trend for removal with increasing use of the magnetic resin. This followed the same trend as for Barcombe water indicating that high MW organics quickly saturated the resin.

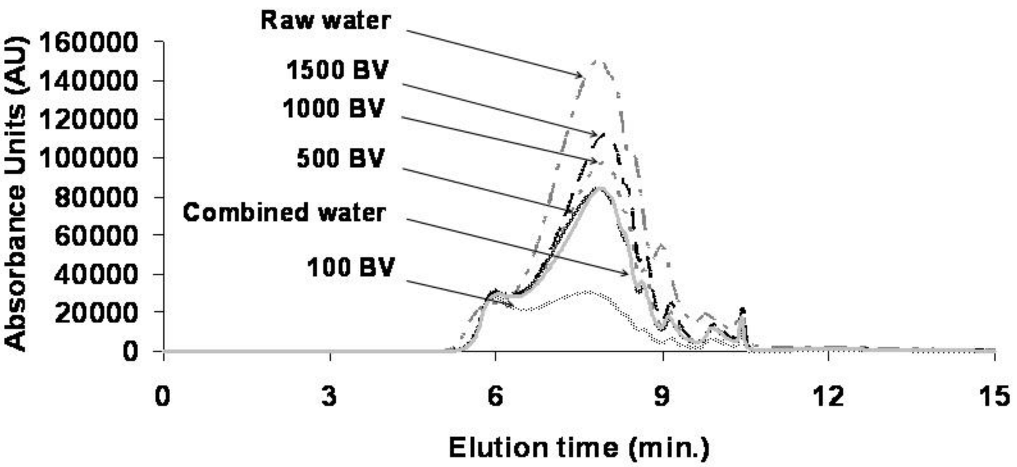


Figure 4.23 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) in Penwhirn water.

The charge load was reduced from an initial value of 0.065 meq.L^{-1} by 50 % to 0.034 meq.L^{-1} in the combined product water (0.465 meq in total). During the whole trial, the magnetic resin dose encountered a total charge of 0.975 meq, this was still 5 times less than the total chloride exchange capacity of the applied resin dose. Most functional groups on macroporous ion exchange resins have been shown to be situated inside the pores of the resin (>95 %) and therefore only accessible by diffusion (Symons *et al.*, 1995; Bolto *et al.*, 2002). Therefore it was questionable whether the total exchange capacity of magnetic resin was high enough to theoretically remove all charged NOM in the treated waters as NOM could not access these sites.

Two mechanisms were proposed to explain why NOM was unable to access all available exchange sites. Firstly the applied contact times were not sufficient to allow

NOM attached on the resin surface to be able to diffuse inside the pores due to slow diffusion rates (Gönder *et al.*, 2006). Secondly, the physical size of NOM molecules have been reported to reach sizes around 2 to 50 nm (Cornel *et al.*, 1986; Thurman and Malcolm, 1986). It was therefore probable that not all organic molecules would be able to access the pores of the resin which have a median diameter of 9.7 nm (Dahlke, 2002). This explanation may be particularly important given that pore sizes of between 30 to 50 nm had been recommended for good NOM removal (Oehme and Martinola, 1973).
A repetition of the continuous magnetic resin test on Penwhirn water with contact times of 20 minutes did not result in any increased removal of DOC, UV_{254} absorbance or the peaks detectable by HPSEC. This trend confirmed the statement made previously (Section 4.2.4), which agreed with Humbert *et al.*, (2005), that contact times exceeding 10 minutes were of little benefit during magnetic resin treatment.

A so-called flow interruption test adapted from Kressman and Kitchener (1947) however was able to show that NOM from Penwhirn water was at least partially able to enter the pores of magnetic resin, but that extended contact time was necessary. This test was carried out with a 10 $mL.L^{-1}$ magnetic resin dose at 20 minutes contact time for 1000 BV. During the first 500 BV the DOC removal rate was seen to be similar for both tests. At 100, 300 and 500 BV, DOC had been removed by 65, 50 and 45 % respectively for the continuous series and to 72, 55 and 45 % for the interrupted test (Figure 4.24).

For the continuous test a DOC removal decrease was observed with increasing BV. At 600, 800 and 100 BV the DOC was removed by 35, 30 and 25 % DOC respectively while 60, 45 and 40 % DOC reduction respectively were measured during the interrupted test. Considering that the analysis of the RO water supernatant did not show an increase in DOC after the 24 hour break period it was concluded that a large part of NOM had diffused towards the pores and thereby restored the removal level to 85 % of that achieved during the first use of magnetic resin (100 BV). However it appeared from this 24 h interruption test that increased time periods were necessary to allow increased levels of pore diffusion that at least exceeded the investigated 20 minutes contact time. Therefore an increase in dose to provide more exchange surface for high MW was expected to be more efficient for process optimisation.

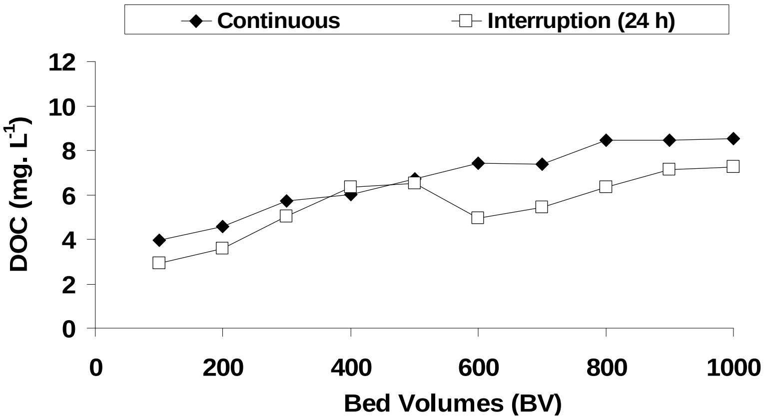


Figure 4.24 Impact of 24 h interruption on DOC reduction efficiency in Penwhirn water treated with 10 $mL.L^{-1}$ magnetic resin (20 min. c.t.).

4.2.5.4 Albert

The use of 10 $mL.L^{-1}$ magnetic resin for 15 repetitive loadings on Albert water, dominated by hydrophobic, high MW material, showed the same decreasing removal trend as observed for Barcombe and Penwhirn. After 100 and 1500 BV, the DOC was reduced by 65 and 5 % respectively which gave a 25 % reduction in the combined product water (Figure 4.25). The UV_{254} absorbance was reduced by 65 and 20 % at 100 and 1500 BV respectively, which resulted in 30 % reduction in the combined water.
When applying a 20 $mL.L^{-1}$ magnetic resin dose at 30 minutes contact time the DOC was removed by 71, and 25 % after 50 and 750 BV respectively which resulted in a 45 % reduction in the combined product water (Figure 4.26). While following the same trend of rapid removal decrease seen when applying a 10 $mL.L^{-1}$ resin dose, the higher dose of 20 $mL.L^{-1}$ was able to remove 20 % more DOC. The UV_{254} absorbance was reduced by 80 and 40 % after 50 and 750 BV respectively which resulted in a 45 % reduction in the combined product water. Thereby for both treatment options a SUVA reduction of only 10 % from 6.4 to 5.7 m^{-1} L mg^{-1} DOC was determined. This can be related to the higher amount of UV_{254} absorbing material in that water type making a partial removal of it less noticeable as was described for Penwhirn.

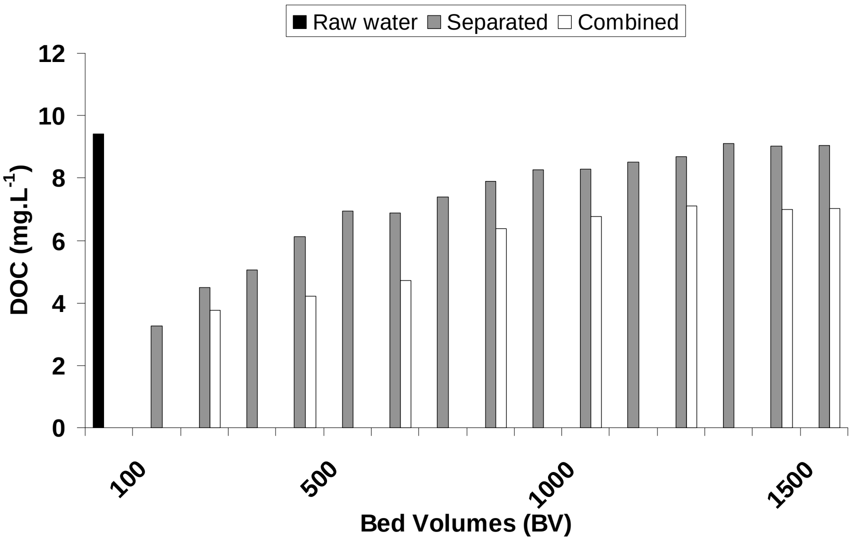


Figure 4.25 DOC residual after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) in Albert water.

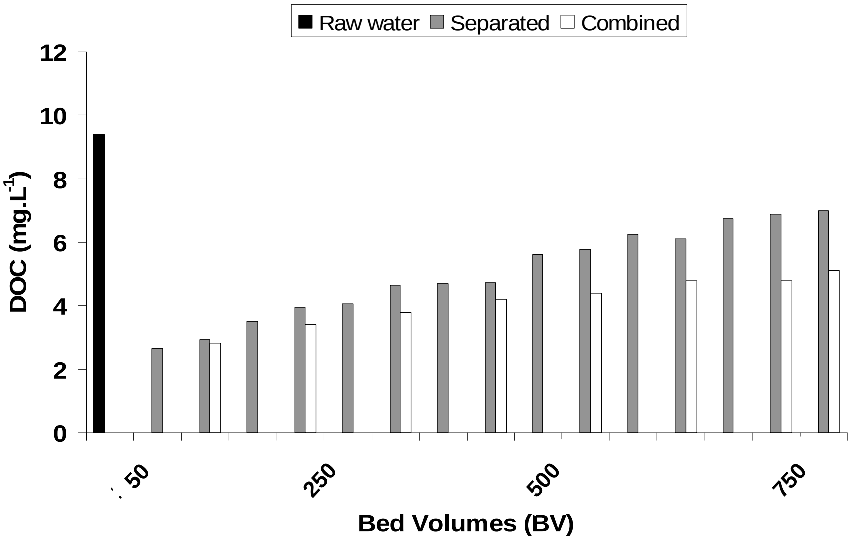


Figure 4.26 DOC residual after continuous magnetic resin treatment at bench-scale (20 mL.L^{-1}, 30 minutes contact time, 750 BV) in Albert water.

The HPSEC for Albert water showed a very similar trend to Penwhirn and Barcombe water with best removal of material between 5 to 1 kDa (Figures 4.27 and 4.28).

The first peak eluting after 6 minutes (indicating NOM >5 kDa), was reduced by 30, and 10 % after 100 and 1500 BV respectively which resulted in a 15 % reduction in the combined product water (Figure 4.27) when using 10 mL.L^{-1} magnetic resin. When using a 20 mL magnetic resin dose this same peak was reduced by 43 and 5 % after 50 and 750 BV respectively, resulting in a 10 % reduction in the combined water (Figure 4.28). The second and major peak eluting after 8.4 minutes elution time, which indicated NOM around 5 kDa approximately was reduced by 90 and 20 % after 100 and 1500 BV respectively, resulting in a 45 % reduction in the combined product water when using 10 mL magnetic resin. The higher resin dose of 20 mL.L^{-1} reduced this second peak by 100 % after 50 BV. After 750 BV this peak was reduced by only 70 %, resulting in an 80 % reduction in the combined water.

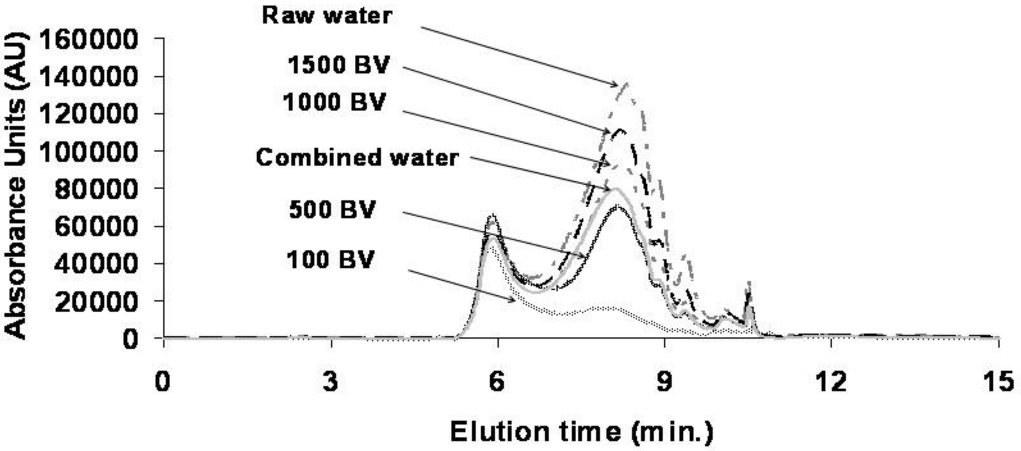


Figure 4.27 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) in Albert water.

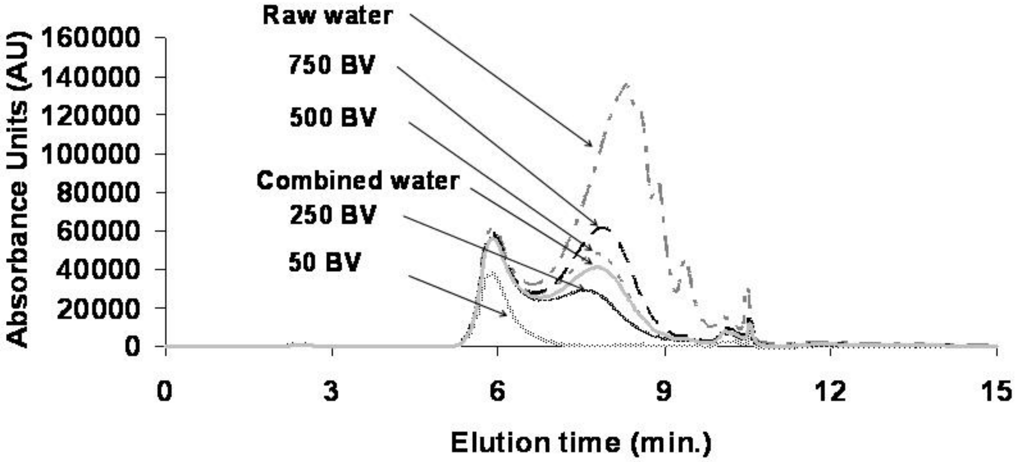


Figure 4.28 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (20 mL.L^{-1}, 30 minutes contact time, 750 BV) in Albert water).

The final peak eluting after 9.5 minutes and indicating NOM of approximately 1-2 kDa was reduced by 90 and 40 % after 100 and 1500 BV respectively, resulting in a 65 % reduction in the combined product water when using 10 $mL.L^{-1}$ magnetic resin. When using 20 $mL.L^{-1}$ magnetic resin the same peak was reduced by 95 and 85 % respectively after 50 and 750 BV respectively resulting in 90 % reduction in the combined water.

The charge load in Albert water was reduced by 45 % from 0.061 to 0.035 $meq.L^{-1}$ after magnetic resin treatment (10 $mL.L^{-1}$). A total charge of 0.390 meq was removed from the water, a value similar to that for Penwhirn water (0.465 meq). Similar levels of charge were removed after 1500 BV for both waters, but higher levels of DOC were removed in Penwhirn water than in Albert water. This was explained by the higher percentage of high MW NOM found in Albert water when compared to Penwhirn water. This was supported by the change in charge density throughout the trial which showed a preference of the magnetic resin to remove highly charged material, as the initial value of 6.5 $meq.g^{-1}$ was reduced by 25 %. This observation made exclusion of charged NOM due to preferential NOM removal by surface adsorption (Van der Waals forces) less probable and favoured the mechanism of size exclusion as being the limiting factor to NOM removal by magnetic resin. Nonetheless this conclusion generated the question why is the mid MW well removed despite the findings that high MW NOM is supposingly blocking the bead surface.

Although the removal of high MW organic compounds quickly deteriorates, the mid range MW compounds were effectively removed throughout the length of the trial. On coagulant flocs and GAC surfaces the balance of adsorbed organic material has been shown to be influenced by residual charge on the adsorbed molecules. Residual charge on adsorbed high MW NOM is here able to repel (steric repulsion) and reduce the affinity of further approaching molecules of high MW, preventing their adsorption. Smaller MW material is still able to adsorb to a certain degree on the GAC and coagulant flocs as it can more easily access the remaining exchange sites between the attached large molecules without encountering steric repulsion (Karanfil *et al.*, 1996; Avena and Koopal, 1999). Such a mechanism of steric repulsion could also promote the removal of mid to low MW material on magnetic resin.

To confirm the hypothesis that an increase of the resin dose which generates a higher exchange surface is the major factor for enhanced NOM removal a further investigation of the effect of dose increase only was undertaken using a second batch of Albert water collected in October 2006 (Section 4.2.3.1).

In addition the resin use was increased from 15 to 30 times to see whether further NOM could be removed and if an effect on the different MW peaks was noticeable.

When treating Albert water from October 2006 with 10 $mL.L^{-1}$ at 10 minutes contact time, the DOC was removed by 55 and 15 % after 100 and 1500 BV respectively, resulting in a 25 % DOC reduction in the combined product water (Figure 4.29). These results were very similar to those seen for treated Albert water collected in January 2006 (Figure 4.25). When increasing the number of times the resin was re-used 10 and 5 % DOC were removed after 2000 and 3000 BV respectively, resulting in a 15 % DOC removal in the final combined product water. When using a dose of 30 $mL.L^{-1}$ at 10 minutes contact time, the DOC was removed to 70 and 45 % after 33 and 495 BV respectively, resulting in a 50 % reduction in the combined product water (Figure 4.30). After 660 and 990 BV, the DOC was removed by 40 and 35 % respectively resulting in a final combined water with a 45 % DOC reduction. As tripling the resin dose increased the final DOC removal by 30 %, an increase in the applied dose was confirmed to be the major factor for enhanced NOM removal, rather than increased contact times. However these results also showed that NOM removal cannot be expected to increase equally to the increase of the resin dose. For example the first use of magnetic resin showed that 10 $mL.L^{-1}$ could remove 55 % DOC, while 30 $mL.L^{-1}$ removed 70% DOC. This is only 15 % increase in removal and most likely because not all NOM present in a water was removable by anion exchange.

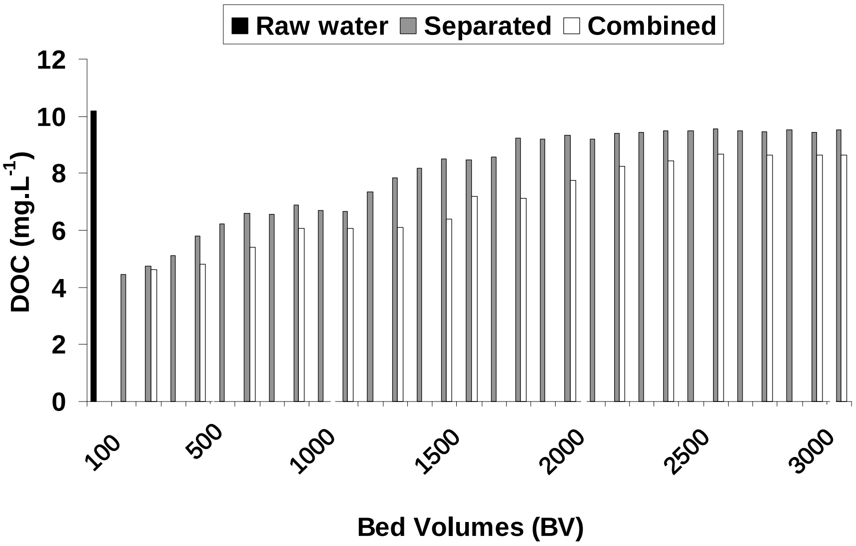


Figure 4.29 DOC residual after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 3000 BV) in Albert water.

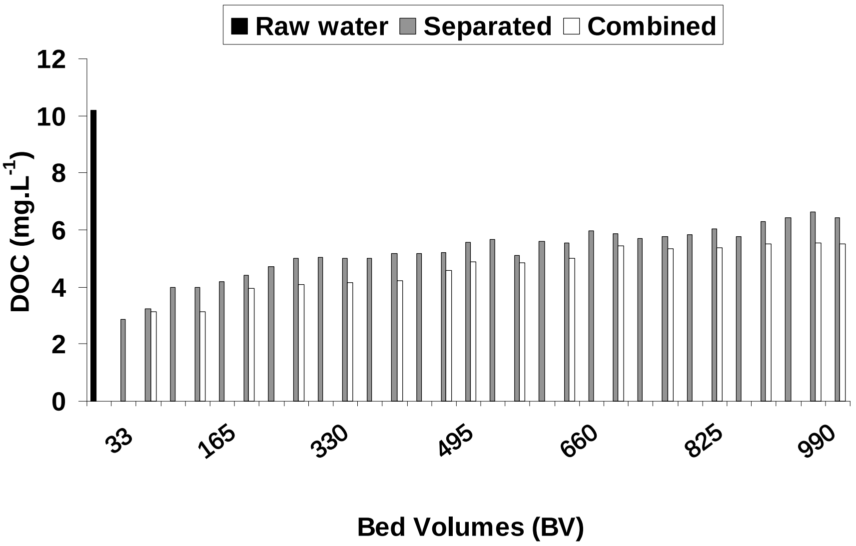


Figure 4.30 DOC residual after continuous magnetic resin treatment at bench-scale (30 mL.L^{-1}, 10 minutes contact time, 990 BV) in Albert water.

The HPSEC profiles for this water showed a similar removal trend as observed for the sample treated in January 2006. The first peak eluting after 5.6 minutes and representing high MW material >5 kDa was removed by 40 and 5 % after 100 and 3000 BV respectively using 10 mL.L^{-1} magnetic resin. This resulted in a 15 % reduction in the combined water (Figure 4.31). The 30 mL.L^{-1} magnetic resin dose removed the first peak by 95 and 20 % after 33 and 990 BV respectively which resulted in a 30 % removal in the combined water (Figure 4.32). This showed that magnetic resin was able to remove high MW NOM material, but that its removal rate decreased quickly. The second peak at 8 minutes elution time was removed by 98 and 40 % after 100 and 3000 BV respectively when using a resin concentration of 10 mL.L^{-1}. This resulted in a 60 % reduction in the combined water. The 30 mL.L^{-1} magnetic resin dose was able to remove the same peak by 100 and 80 % after 33 and 990 BV respectively resulting in 85 % reduction in the combined water.

The material eluting at 9.3 minutes was removed by 80 and 60 % after 100 and 1000 BV using 10 mL.L^{-1} of magnetic resin. However the absorbance was seen to increase by 130 and 115 % at 2000 and 3000 BV. From this trend, it was concluded that at 2000 BV, when the resin was strongly loaded with NOM, the lowest MW material was leaking from the resin in favour of material eluting at 8 minutes which had shown the best removal levels throughout the trial.

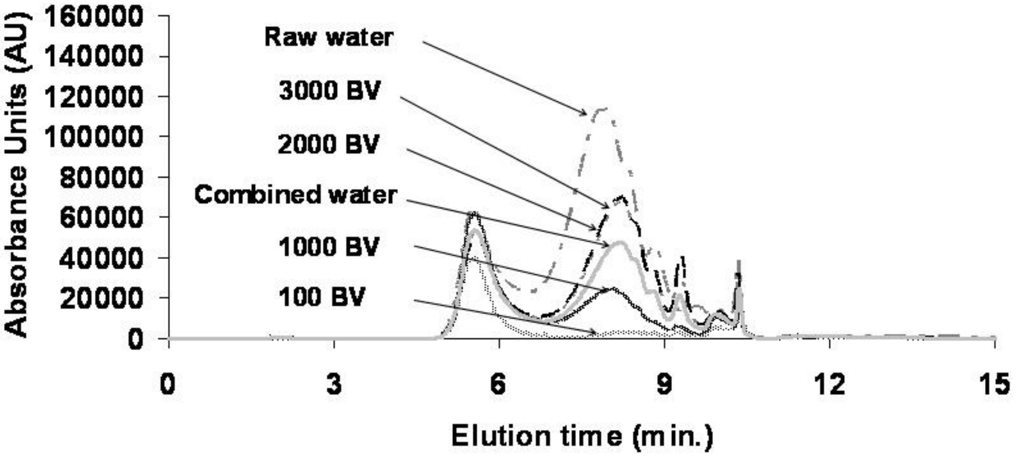


Figure 4.31 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 3000 BV) in Albert water.

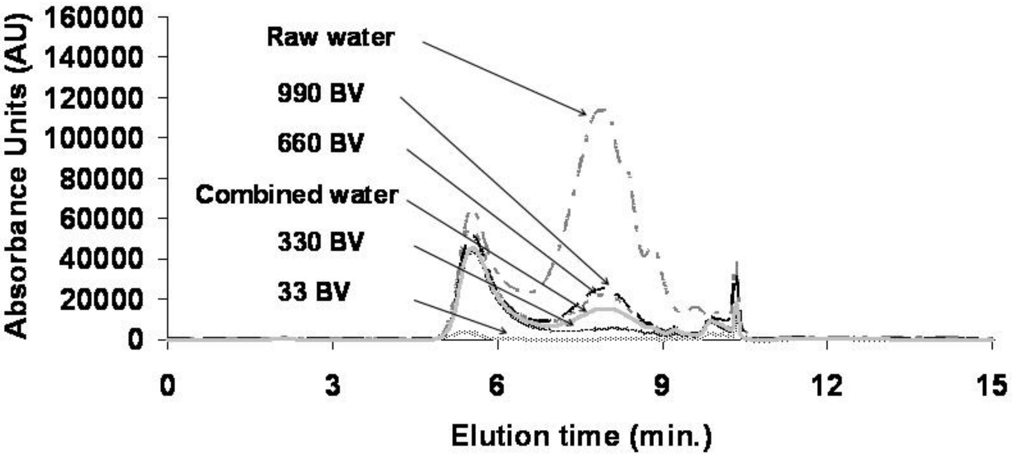


Figure 4.32 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (30 mL.L^{-1}, 10 minutes contact time, 990 BV) in Albert water.

The 30 mL.L^{-1} magnetic resin dose removed the material eluting at 9.3 minutes by 95 and 65 % at 33 and 990 BV, which resulted in a 70 % reduction in the combined water. The fact that no low MW material was seen to leak off the resin in favour of higher MW material was again related to the increased resin dose which allowed increased DOC removal due to its larger available surface area.

4.2.6 Removal of different organic model compounds

4.2.6.1 Separate model compounds

The removal of humic acid using a resin dose of 10 mL.L^{-1} and 10 minutes contact time is shown in Figure 4.33. The DOC removal decreased from 40 to 15 % after 100 and 1500 BV respectively, resulting in an overall 15 % reduction in the combined product water. In comparison a 30 mL.L^{-1} magnetic resin dose reduced the DOC by 62 and 26 % after 33 and 495 BV respectively which resulted in a 35 % reduction in the combined product water (Figure 4.34). Hereby the removal pattern consisting of a rapid DOC removal with on-going resin use, which could be eased by increasing the applied resin concentration, was similar to that observed for the high SUVA waters of Penwhirn and Albert water (Figure 4.11).

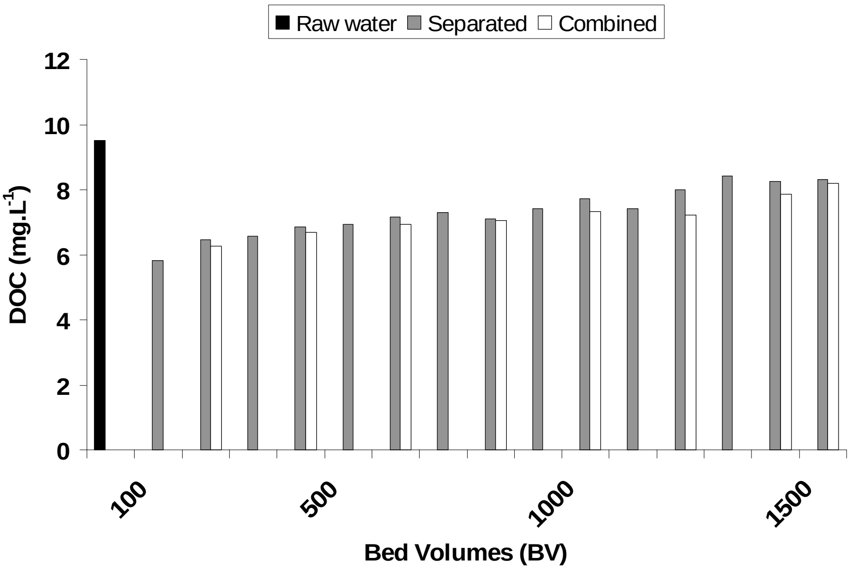


Figure 4.33 DOC residual after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) on humic acid.

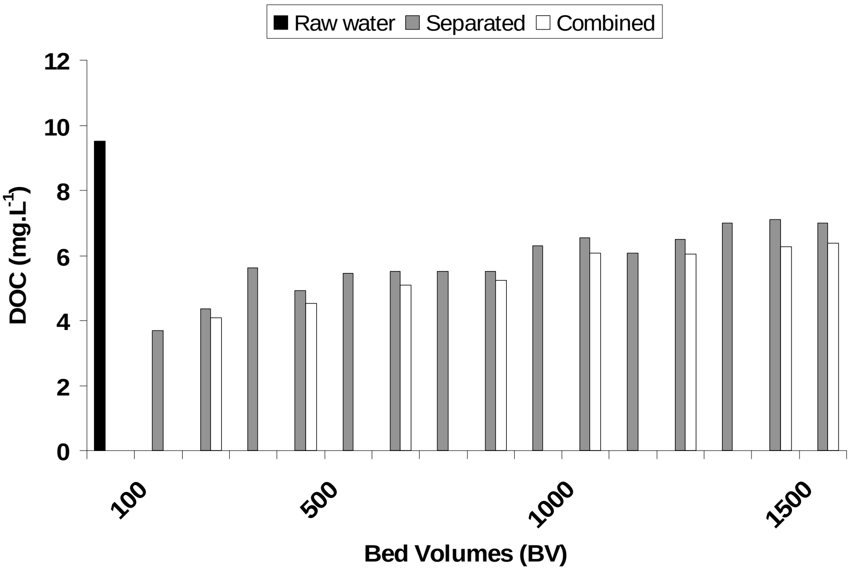


Figure 4.34 DOC residual after continuous magnetic resin treatment at bench-scale (30 mL.L^{-1}, 10 minutes contact time, 495 BV) on humic acid.

HPSEC profiles of the treated humic acid solutions are shown below. The first detectable peak at 6 minutes elution time representing NOM >5 kDa could not be removed by either applied magnetic resin dose (Figure 4.35 and Figure 4.36).

The second major peak at 7.8 minutes elution time was reduced by 35 % and 0 % at 100 and 1500 BV resulting in a 5 % reduction in the combined product water when applying a 10 mL.L^{-1} magnetic resin dose. The 30 mL.L^{-1} magnetic resin removed the same peak at 7.8 minutes elution time from 95 to 5 % after 33 and 495 BV respectively, resulting in a 10 % reduction in the combined water.

The peak at 10.7 minutes elution time, representing NOM of approximately 1-2 kDa was removed from 90 to 10 % at 100 and 1500 BV respectively, resulting in a reduction of 30 % in the combined product water when applying a 10 mL.L^{-1} magnetic resin dose. A 30 mL.L^{-1} magnetic resin dose removed this last peak by 85 and 40 % after 33 and 495 BV respectively resulting in a 50 % reduction in the combined water.

Again, the results show good capacity of the resin for removing material eluting between 8 and 11 minutes as previously observed for natural sources. However, it also confirms that the presence of high MW NOM quickly reduces the removal capacity of the resin and further NOM removal can only be achieved by increasing the resin dose applied to the water.

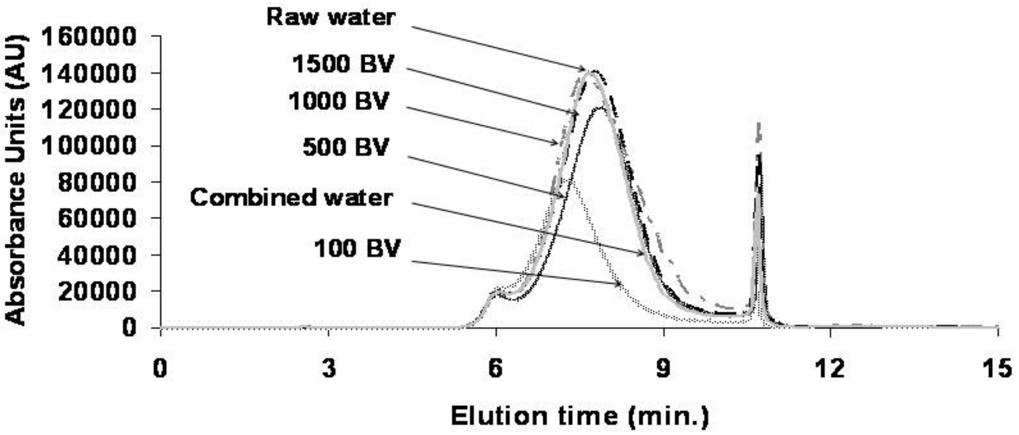


Figure 4.35 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) on humic acid.

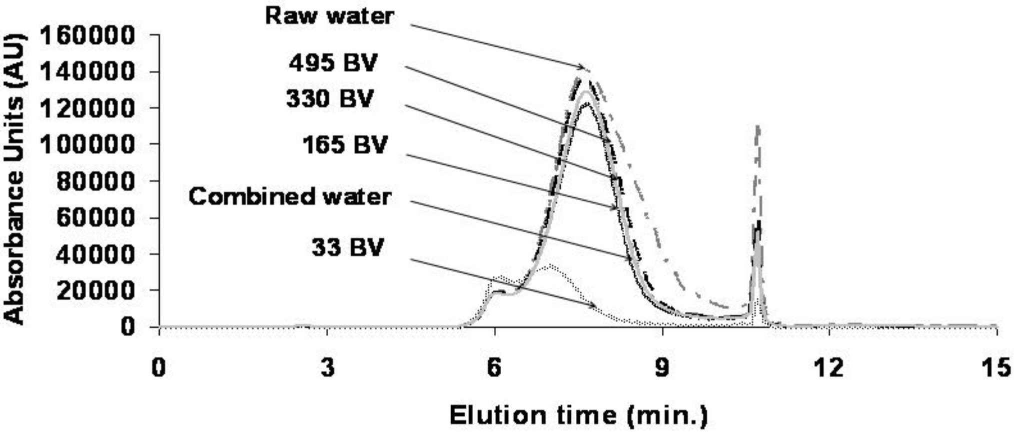


Figure 4.36 HPSEC Profiles after continuous magnetic resin treatment at bench-scale (30 mL.L^{-1}, 10 minutes contact time, 495 BV) on humic acid.

For tannic acid treated with 10 mL.L^{-1} magnetic resin at 10 minutes contact time, DOC removal was reduced by 92 and 55 % after 100 and 1500 BV respectively which resulted in a 75 % DOC reduction in the combined product water (Figure 4.37).

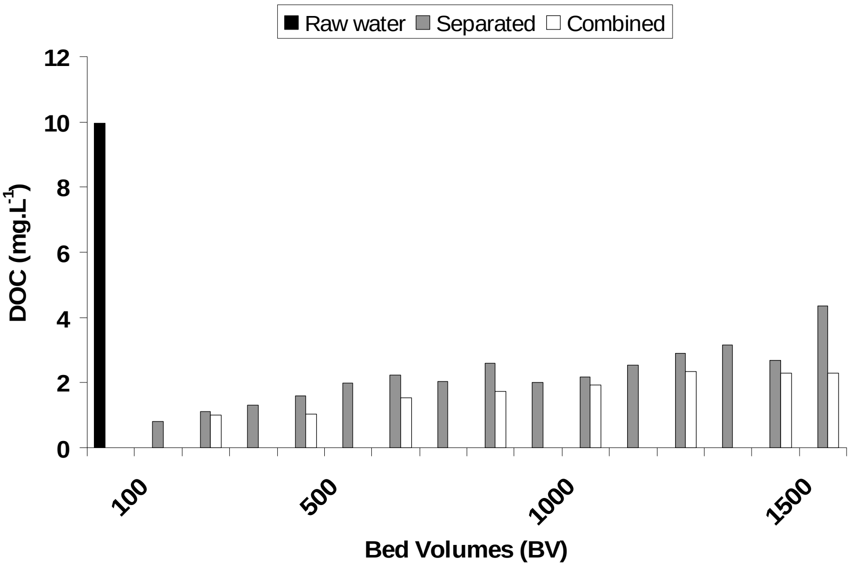


Figure 4.37 DOC residual after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) on tannic acid.

In a L-glutamic acid solution 10 mL.L^{-1} magnetic resin removed DOC by 55 and 15 % after 100 and 1500 BV respectively, which resulted in a 25 % reduction in the combined product water (Figure 4.38). This was regarded as unusual because L-glutamic acid has a MW of 147.1 Da which is more than ten times smaller than tannic acid with 1701.2 Da, yet its removal behaviour was similar to that of humic acid which contains NOM >5 kDa.

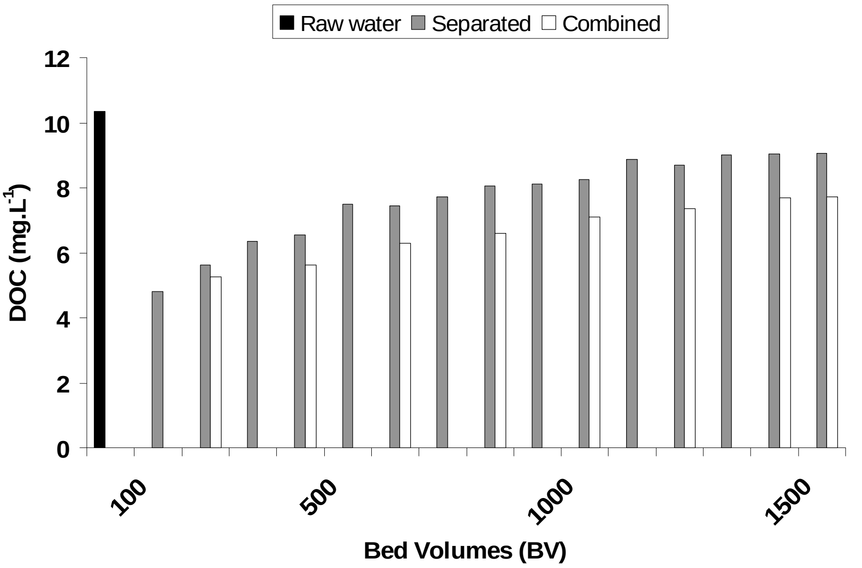


Figure 4.38 DOC residual after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) on L-glutamic acid.

The four remaining model compounds resorcinol, D-mannose, D-xylose and PEG were not removed by magnetic resin. For these four model compounds DOC removal rates were between 0 and 5 %. This very low removal percentage was within the limit of error on the instrument used for DOC analysis (5 %) and making it difficult to confirm whether any of these compounds had been removed.

The difference in the removal of all the selected model compounds, ranging from 75 to 0 % in the combined product waters, was attributed to the functional groups of the different molecules. Humic acid, tannic acid and L-glutamic acid have functional groups (Supposedly carboxylic) which dissociate at low pH values below 6 (Figure 4.8 and Figure 4.9) and thus would be charged during the experiment. Resorcinol, D-mannose, D-xylose and PEG have phenolic functional groups that dissociate at pH levels above 8 and hence would not be charged (Collins *et al.*, 1986). The presence of dissociated functional groups in organic molecules, such as humic acid, tannic acid and L-glutamic acid was observed to be independent of the hydrophobicity or MW of NOM the factor regarding the removal by magnetic resin. This conclusion is in agreement with Bolto *et al.*, (2004) who reported anion exchange resins to have the potential to remove all types of charged organic material. This confirms the data previously presented in this thesis (4.2.5.4) demonstrating that ion exchange, with a preference for highly charged material is the main removal path for NOM by magnetic resin. However this data is not in accordance with other studies (Kim *et al*., 2005; Boyer and Singer, 2006; Zhang *et al*., 2006) which have reported a good removal efficiency by magnetic resin for hydrophilic neutral NOM isolated from river waters (36-69.1 % DOC reduction). Nonetheless, these studies have not proven that the NOM characterised as hydrophilic neutral acids, did not contain a certain charge level.

During 15 repetitive uses the 10 mL of the magnetic resin was in contact with 150 mg of DOC. The resin removed 33, 115 and 40 mg of DOC when treating humic acid, tannic acid and L-glutamic acid solutions respectively. A similar total removal level for humic acid and L-glutamic acid, which are the biggest and the smallest removable model compounds respectively. . Nevertheless due to this large difference, in terms of MW both model compounds were thought to saturate the exchange capacity of magnetic resin by different mechanisms.

First if we compare humic acid and tannic acid there is evidence that surface blockage may be limiting the overall capacity for the former molecule in addition to steric repulsion (Avena and Koopal, 1999) (Figure 4.39 (A)). Tannic acid is significantly smaller and is able to attach to the resin without blocking up the surface area leaving space for more molecules to attach (Figure 4.39 (B). L-glutamic acid, consisting of a myriad of small molecules having two functional groups can quickly ‘fill-up’ the resin surface; using up the exchange sites of the resin instead of blocking the surface as for humic acid (Figure 5.39 (C)). A comparison of the removal rates presented in terms of the number of removed molecules, as opposed to molecule mass, support this mechanism. It was observed that 666.7 μmol of L-glutamic were removed by the resin, which was much more than what was observed for tannic acid (17.1 μmol).

A comparison of the charge removal can approve these different mechanisms. Humic acid, tannic acid and L-glutamic acid have charge density values of 6.2, 3.8 and 5.5 meq.g^{-1} DOC respectively. It was however seen that while treating the tannic acid solution a total charge of 0.45 meq had been removed, while for the more charged humic acid a total charge removal of only 0.28 meq was measured. This showed that the saturation of the resin by humic acid cannot be related to the exhaustion of the 5 meq exchange capacity, but is more likely due to blockage of the resin surface. For L-glutamic acid a total charge of 0.55 meq had been removed, which is far below the exchange capacity of the resin. Considering that the highest charge level was found for L-glutamic acid it is more likely that the low removal is due to the blockage by attachment of a large amount of small molecules.

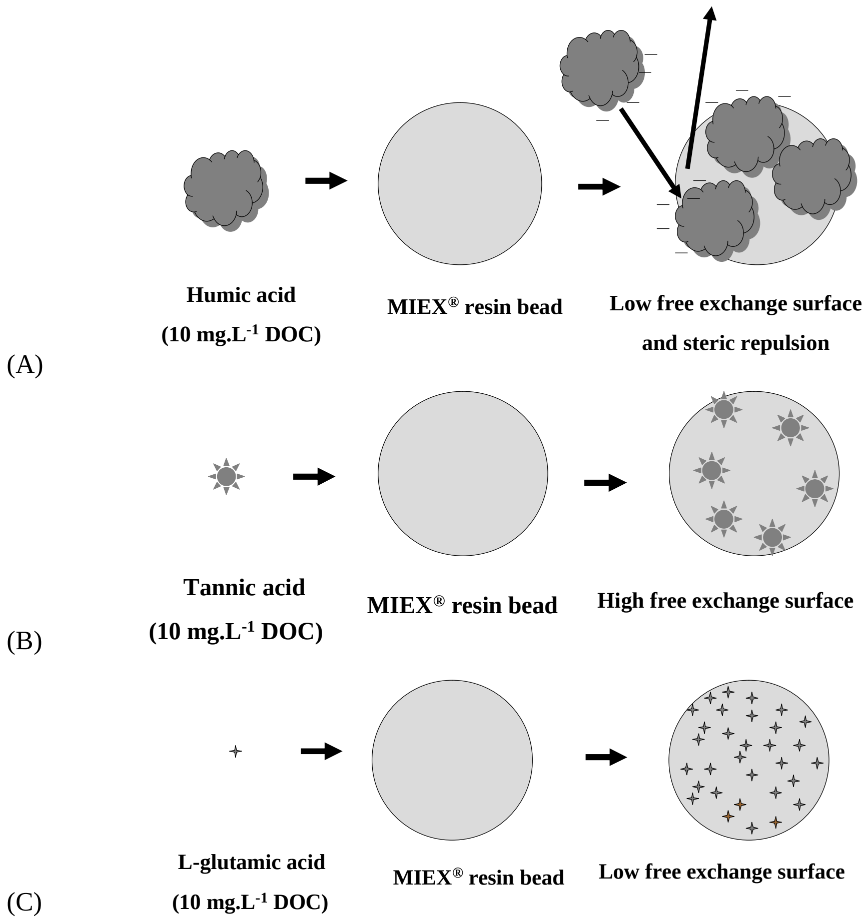


Figure 4.39 Impact of molecular weight on available surface exchange area of magnetic resin (A) Humic acid, (B) Tannic acid, (C) L-glutamic acid.

From this data it can be concluded that source waters containing charged NOM of moderate MW are the most amendable to treatment using magnetic resin. The effective treatment of sources dominated by high or low MW NOM, was shown to require higher resin inventories or regeneration rates which imply that sufficient and easily accessible exchange surface is provided on the outer bead surface for the DOC reduction.

As well it was seen that non-UV_{254} absorbing organic material, such as the low MW, hydrophilic acid compound of L-glutamic acid could be well removed (55 % DOC reduction). This showed that although magnetic resin had been previously seen to have a preference for organic material of a high UV_{254} absorbance, it was not a crucial criteria for selection, in contrary to MW and especially dissociated functional groups. The increased UV_{254} absorbance reduction in natural source waters was therefore related to the effective removal of highly aromatic NOM, disposing of high charge density (Ussiri and Johnson, 2004), without excluding the good removal of highly charged non-UV_{254} absorbing material.

When comparing the DOC reduction in the different natural sources, high alkalinity levels and therefore the presence of negatively charged carbonates were not expected to impact on the efficiency of magnetic resin, reported to allow the removal of inorganic anions (Humbert *et al.*, 2004), by competing for exchange sites. This was because for Draycote water, disposing of the highest level of alkalinity, a high level of DOC removal (55-70 %) was obtained throughout the trial, in comparison to the other investigated sources. This statement was confirmed by previous studies of Johnson and Singer (2004) and Humbert *et al.*, (2005), who removed 93 and and 80 % DOC respectively from source waters containing alkalinity levels of 176 and 20 $mg.L^{-1}$ $CaCO_3$ respectively.

4.2.6.2 Effect of pH variation on removal of organic model compounds

It was reported by Collins *et al.*, (1986) that the carboxylic functional groups dissociate above a pH of 6 and phenolic functional groups at a pH above 8. Therefore the impact of increasing or decreasing the pH to above and below the dissociation pH on the removal of the different model compounds by magnetic resin was investigated. The tested pH ranges were set from 2 to 12 and from 4 to 13 for the model compounds containing carboxylic and phenolic functional groups respectively.

For humic acid, tannic acid and L-glutamic acid the best removal range was between pH 4 to 10. This gave a removal of up to 45 %, 95 % and 75 % of DOC from the humic acid, tannic acid and L-glutamic acid solutions respectively (Figure 4.40). At pH 2, the DOC removal level was 35, 30 and 15 % for humic acid, tannic acid and L-glutamic acid respectively. This was attributed to the suggestion by Collins *et al*., (1986) that at the lowest pH investigated, the lowest level of dissociation was seen. At pH 12, the DOC was reduced to 40, 30 and 50 % from the humic acid, tannic acid and L-glutamic acid solutions respectively, which is probably due to carbon being released from the polyacrylic resin structure under such aggressive alkaline conditions. This acrylic polymer in magnetic resin has been classifed by the Department of Health and Ageing of the Australian Government as non-hazardous due to its high MW and low solubility in water (NICNAS, 2004). The monomer constituents of the polymer have however been classified as being of moderate toxicity following acute exposure by oral, dermal and inhalation routes. It should be considered here, that aggressive pH conditions can therefore release the monomer constituents into drinking water and be a health hazard. However such aggressive pH conditions (pH 12) are not expected to be found in natural water sources, seen in this thesis and previous studies to have a pH level between 5.2 and 8.1 (Pianta *et al*., 2000; Fearing *et al*., 2004; Kim *et al*., 2005; Nestlerode *et al*., 2006b), making a release of monomeric constituents from magnetic resin improbable.

For the model compounds containing phenolic groups only resorcinol showed a change in removal with increasing pH. At pH values of 4 to 8 the DOC was reduced by 0 and 10 % respectively, whilst it was reduced by 80 % at pH 10. Resorcinol has a pKa of 9.3 and a theoretical charge density of 1.8 meq.g^{-1} at pH 10. This confirms that the main removal path for NOM on magnetic resin was anion exchange. For D-mannose, D-xylose and PEG, DOC removal varied from 0 to 6 % over the pH range of 4 to 13 (Figure 4.41). These variations were thought to be more related to experimental error as they were close to the described 5 % error of the DOC analyser, rather than differences in actual removal, as D-mannose and D-xylose have pKa values of 12.1. Also, no changes in the removal were observed for high MW of PEG compared to low MW of

D-mannose and D-xylose. However a minor level of DOC removal through other mechanisms such as Van der Waals forces could not be totally excluded for all three compounds. Considering that increased pH values above 12 lead to a dissolution of magnetic resin, no potential DOC removal could be monitored above this.

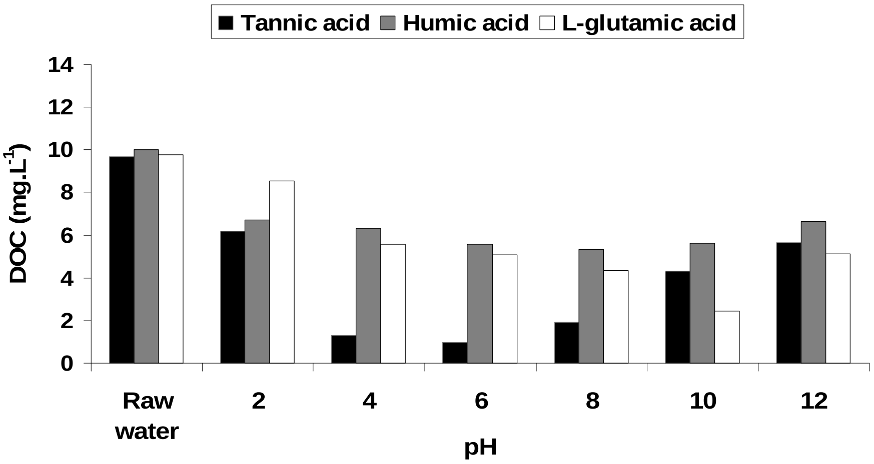


Figure 4.40 Effect of pH variation on DOC reduction by magnetic resin treatment on tannic acid, humic acid and L-glutamic acid.

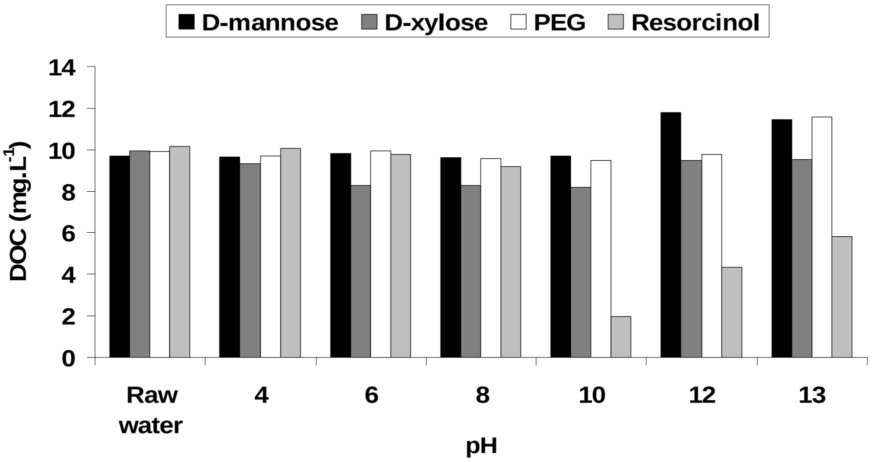


Figure 4.41 Effect of pH variation on DOC reduction by magnetic resin treatment on D-mannose, D-xylose, PEG and resorcinol.

4.2.6.3 Model compounds mixtures

Mixtures of the different model compounds were investigated to simulate the combinations of organics found in natural waters to see whether NOM removal could be influenced by interactions between different molecules. The selected mixtures of tannic acid and L-glutamic acid, tannic acid and D-mannose, resorcinol and L-glutamic acid and resorcinol and D-mannose were investigated under the same conditions as for the single model compounds (Section 4.2.6.2). The pH values of the different solutions ranged from 4.5 to 4.9. The measurable DOC in the water before treatment was 10 mg.L^{-1} and contained 50 % of each of the model compounds in the different solutions. D-xylose was not used in either mixture as it was expected to behave similarly to D-mannose due to its similar properties. PEG was not used as it was chosen at the end of the trial to investigate the impact of an increased MW on removal by magnetic resin. Humic acid was also ignored, as the range of different molecule species in this compound would have made the detection of an interaction with other molecules impossible with our equipment.

For the first investigated mixture of tannic acid and L-glutamic acid a DOC reduction of 85 and 40 % was measured after 100 and 1500 BV respectively resulting in a DOC reduction in the combined product of 45 % (Figure 4.42). The removal trend, as well as the removal percentage in the combined product water, was seen to lie in between the removal trend observed for tannic acid (Figure 4.37) and L-glutamic acid (Figure 4.38), which showed a 75 and 25 % DOC removal (50 % reduction on average) respectively in their final combined waters.

From these findings it appears as if both model compounds were following similar removal trends as when treated separately. In total 84 mg of DOC were removed during this trial. The magnetic resin tests on separate tannic acid and L-glutamic solutions saw removal of 115 and 40 mg DOC respectively. Halving the sum of those numbers gave a theoretical value of 77.5 mg DOC, which is very close to the measured DOC of 84 mg removed from the mixed solution (8 %) (Table 4.3). From this, it is likely that the DOC removal in the mixed solution was not influenced by interactions between both compounds. Furthermore, considering that 84 mg of DOC had been removed, it did not appear that either compound was not removed at all. This is because each compound only provided 75 mg DOC in the initial untreated mixed compounds solution.

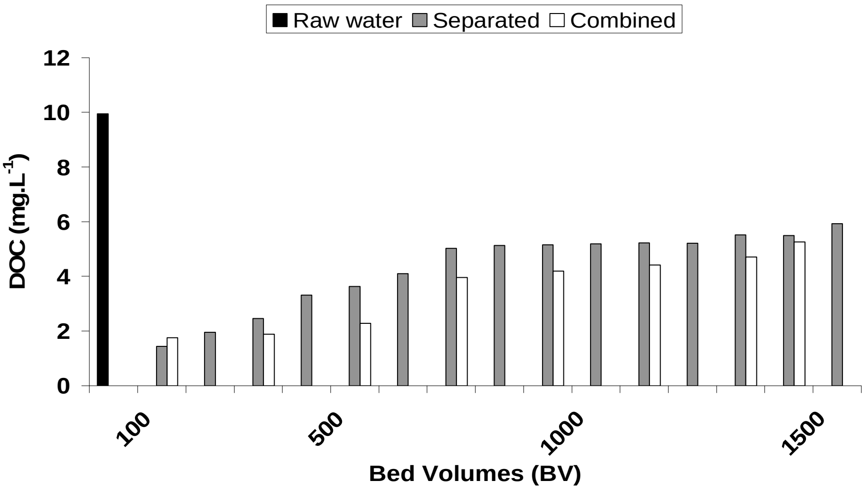


Figure 4.42 DOC residual after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) on tannic acid and L-glutamic acid mixture.

When mixing tannic acid with D-mannose a DOC removal of 35 and 8 % was measured after 100 and 1500 BV respectively, resulting in 27 % reduction in the combined product water (Figure 4.43). In total, 39 mg DOC were removed from the mixed water. The magnetic resin tests on the separated model compounds showed a removal of 115 and 3.1 mg DOC for tannic acid and D-mannose. Halving the sum of these numbers gave a value of 59 mg DOC as a theoretical removal value. These are 20 mg more than the actual measured value (35 % reduction). This was also less than half the amount of DOC removed from the tannic acid and L-glutamic acid mixture (84 mg DOC). It however cannot be concluded how much tannic acid or D-mannose were contained in the removed DOC. However, as tannic acid had been well removed by magnetic resin, when tested as a single compound solution (Figure 4.37) in contrary to D-mannose, and it was not obstructed by L-glutamic acid (Figure 4.42), it can be suggested that D-mannose could have a detrimental effect on the removal of tannic acid.

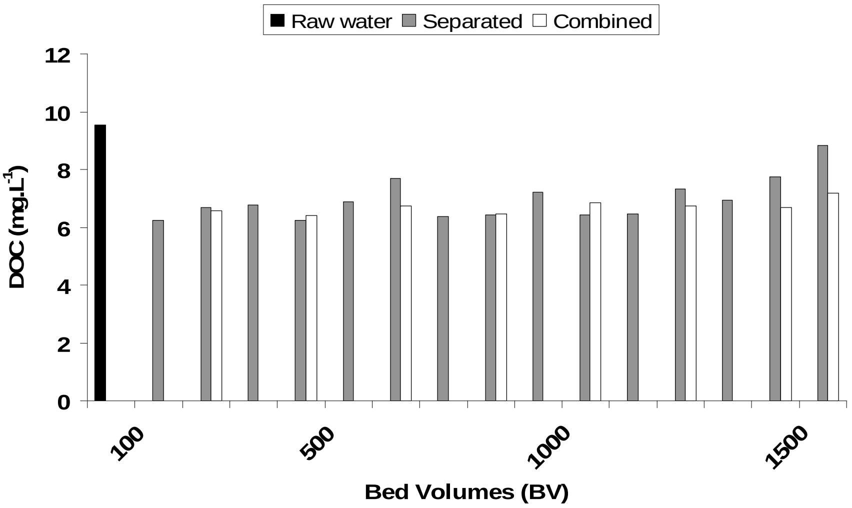


Figure 4.43 DOC residual after continuous magnetic resin treatment at bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) on tannic acid and D-mannose mixture.

Although it can only be hypothesised about the exact nature of the interaction mechanism, it was interesting that a charge load of 0.0018 meq.L^{-1}, was measured in the mixed solution before magnetic resin treatment. Considering that the charge was supposed to result only from the 5 mg DOC from the tannic acid in the solution, a charge density of 2.4 meq.g^{-1} DOC was calculated. This was 35 % lower than the charge density measured for the single tannic acid solution (3.8 meq.g^{-1} DOC). In comparison a charge density of 3.5 meq.g^{-1} DOC was measured for the tannic acid contained in the tannic acid and L-glutamic acid solution. Considering the lower charge density of tannic acid when mixed to D-mannose, a potential mechanism of charge neutralisation was suggested. However it should be reminded that this is only a potential mechanism which could explain the reduced removal efficiency of magnetic resin in this solution.

When combining resorcinol and L-glutamic acid, a DOC removal of 55 and 20 % was measured after 100 and 1500 BV, resulting in a removal of 35 % in the combined product water (Figure 4.44). In total 60 mg DOC was removed, but removal tests on the single compounds had shown a total removal of 0.9 and 40 mg DOC for resorcinol and L-glutamic acid respectively. The division of the sum of these values gives a theoretical DOC removal of 20.5 mg, which is 185 % less than the measured value.

It was also seen that in total 40 mg DOC had been removed from the combined product water, when treating L-glutamic acid only and that this amount had quickly saturated the exchange capacity of the resin. A mechanism of interaction between both model compounds that potentially allowed resorcinol to be removed was suggested. Nie *et al.*, (2005) observed in a simulation that L-glutamic and aspartic acid, found in active protein sites, were able to form a hydrogen bond with the phenolic group of methanol over their carboxylic functional groups. As with this reaction, the phenolic group can be proton donor or receptor, an interaction between either one of the carboxylic functional groups of L-glutamic acid or its amine group with a phenolic group of resorcinol was possible. Potentially such a mechanism could have allowed removing resorcinol from the solution. However this can only be hypothesised in this instance.

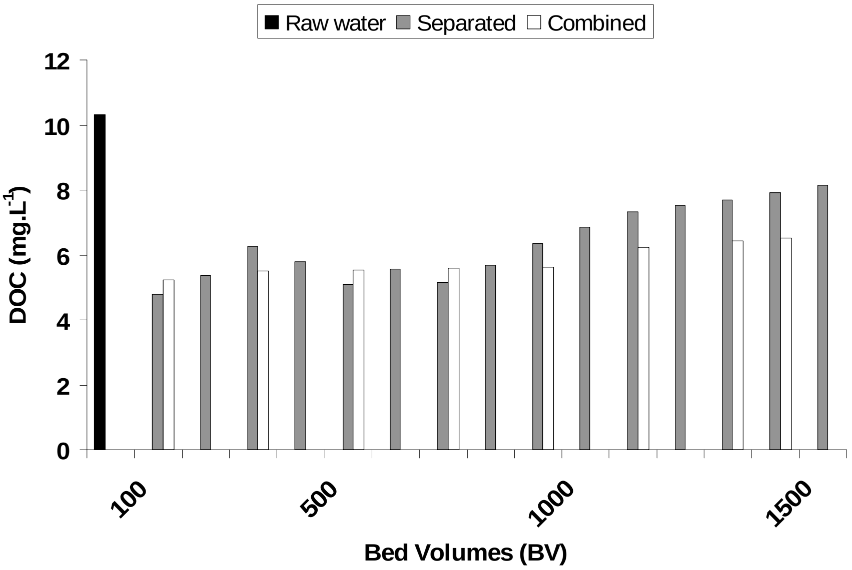


Figure 4.44 DOC residual after continuous magnetic resin treatment in bench-scale (10 mL.L^{-1}, 10 minutes contact time, 1500 BV) on resorcinol and L-glutamic acid mixture.

A combination of resorcinol with D-mannose showed after 100 and 1500 BV a DOC removal,<5 % which resulted in a DOC removal level of <5 % in the combined water. In total 1.5 mg DOC were removed from this solution. This was close to the theoretical 2 mg DOC removal calculated when halving the sum of DOC removed in separate solutions (0.9 mg for resorcinol and 3.1 mg for D-mannose). This confirmed the already observed trend that neither resorcinol nor D-mannose was removable by magnetic resin at low pH levels. No potential interactions between both these molecules could be suggested from these results.

Once more it was confirmed that anion exchange was the main removal path for NOM by magnetic resin, as removal only occurred in mixtures containing one or more molecules with dissociated functional groups.

Table 4.3 Difference between measured and theoretical DOC removal in model compounds mixtures.

Single/Mixed compounds solution	Theoretical DOC removal (mg)	Measured DOC removal (mg)	Difference: Measured DOC removal over theoretical DOC removal (%)
Tannic acid	/	115	/
L-glutamic acid	/	40	/
Resorcinol	/	0.9	/
D-mannose	/	2.1	/
Tannic acid and L-glutamic acid	77.5	84	+8
Tannic acid and D-mannose	59.6	39	-35
Resorcinol and L-glutamic acid	20.9	60	+185
Resorcinol and D-mannose	3	1.5	-100

In summary the work from this section allowed to show that the continuous bench-scale method was more appropriate for mirroring the NOM removal efficiency of magnetic resin in bench-scale than the single resin test widely used in previous studies. Although the magnetic resin had shown to remove hydrophilic and hydrophobic NOM, the strong presence of the latter fraction had shown to result in decreasing removal levels with on-going resin use; a trend which cannot be deduced from a single resin test. This was explained by a mechanism of physical surface blockage and steric repulsion by high

MW NOM, abundant in high SUVA waters dominated by hydrophobic fractions. This trend of surface blockage was confirmed by testing different model compounds to simulate the different NOM fractions present in natural sources and showed that it could be reduced by using higher magnetic resin doses providing larger external surface areas. It also showed that magnetic resin could effectively remove low MW, hydrophilic acids. However a rapid saturation was also seen here, which was related to the myriad of small molecules present in the tested solution that rapidly use up all easily accessible exchange sites on the resin beads. Beside MW, the most important characteristic allowing NOM to be successfully removed by magnetic resin was the presence of dissociated functional groups that impart negative charge on the organic material and allow it to exchange with chlorine onto the exchange sites of the resin. This was because tested model compounds with undissociated functional groups could not be removed by magnetic resin.

Furthermore it was seen that NOM of a high UV_{254} absorbance was preferentially removed from natural waters sources, however this was not regarded as a criteria for removal by magnetic resin because it was seen from the model compounds that hydrophilic, non UV_{254} absorbing NOM was also well removed. Therefore the increased reduction of UV_{254} absorbance can be related to the high charge density present in highly aromatic NOM and thereby affecting the level of UV_{254} absorbance, without excluding the removal of non-UV_{254} absorbing charged material. The increased presence of negatively charged carbonates was as well not expected to affect the removal efficiency of organic material by magnetic resin, considering that consistently high DOC removal levels were seen in the natural source water with the highest alkalinity.

From the model compounds it was also concluded that beside charge and MW, interactions between molecules can affect the removability of NOM. However this is a parameter impossible to quantify in source waters.

4.3 Magnetic resin vs. Coagulation and Combined treatment

4.3.1 Aim

The aim of the research reported in this section was to compare the NOM removal efficiency by magnetic resin compared to that of coagulation using ferric sulphate. This was undertaken for both high and low SUVA water sources and the model compounds.

4.3.2 Coagulant dose and pH optimisation in raw waters

Coagulant doses of 6 to 10 mg.L^{-1} as Fe at a pH of 4.5 were used in the different raw waters as optimum treatment conditions. For combined treatment, consisting of coagulation of magnetic resin pre-treated waters, Fe doses of 2 to 4 mg.L^{-1} (60 to 80 % Fe reduction) and again pH 4.5 were found as optimal conditions (Section 3.2.2.3).

The magnetic resin pre-treated water used for combined treatment with coagulation was the one collected into one large final sample during the continuous bench scale tests and denominated as combined product water (Section 3.2.2.1). Both these terms shall therefore not be confused.

Magnetic resin pre-treatment has already been shown to give a significant reduction of the required subsequent coagulation dose down to 50 and 85 % when compared to the optimised coagulant dose for the treatment of raw water (Drikas *et al*., 2003; Boyer and Singer, 2005). This coagulant reduction is possible because magnetic resin removes a part of NOM which would otherwise require coagulant for removal (Budd *et al*., 2004; and Jefferson *et al*., 2004). In the treated model compounds mixtures the coagulant doses were optimised to obtain DOC to Fe mass ratios of 1:1 in order to investigate the impact of magnetic resin pre-treatment on floc formation (Section 4.4). The pH in these solutions was regulated to 4.5 during coagulation. The Fe doses used were 10 mg.L^{-1} for all untreated model compound solutions, and of 8.2, 5.6, 7.1, 9.8 and 10 mg.L^{-1} for the magnetic resin pre-treated humic acid, tannic acid and L-glutamic acid, tannic acid and D-mannose, resorcinol and L-glutamic acid and resorcinol and D-mannose solutions respectively.

4.3.3 Draycote

In the low SUVA source of Draycote (1.3 L.m^{-1}.mg^{-1} DOC) magnetic resin treatment doses of 10 and 20 mL.L^{-1} showed a DOC reduction of 55 and 60 % respectively

(Figure 4.45). Comparative coagulation alone with 10 mg.L^{-1} Fe removed 65 % DOC and slightly increased the DOC reduction when compared to magnetic resin (5-10 %). However combined treatment gave the highest removal level with 70 and 75 % DOC reduction for the samples pre-treated with 10 and 20 mL.L^{-1} magnetic resin respectively.

The UV$_{254}$ absorbance was reduced by 65 and 70 % with 10 and 20 mL.L^{-1} magnetic resin. Coagulation alone reduced the UV$_{254}$ absorbance by 65 %, while combined treatment increased the UV$_{254}$ absorbance reduction to 70 % in the sample pre-treated with 10 mL.L^{-1} magnetic resin. No improvement was seen for the sample pre-treated with 20 mL.L^{-1} magnetic resin.

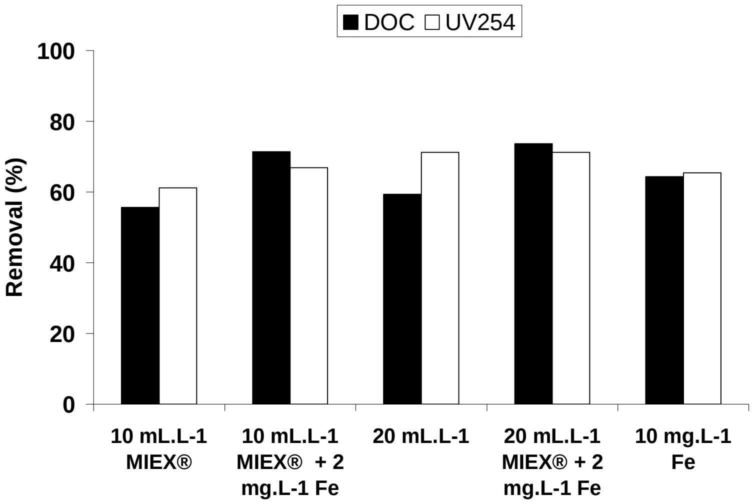


Figure 4.45 DOC and UV$_{254}$ removal by magnetic resin treatment, combined treatment and coagulation in Draycote water.

The HPSEC profiles of the different treatment options show a similar trend to the DOC removal. Coagulation reduced the major peak at 9 to 10 minutes elution time (approximately 5 to 1 kDa) to a similar degree as magnetic resin treatment, whilst the best reduction level was achieved for the combined treatment (Figure 4.46). However caution should be applied when comparing the different MW profiles as well as the DOC and UV$_{254}$ absorbance measurements, as the very small differences between the results of the different treatment options were close to the limit of error on the instruments used. This was 5 % for the DOC and UV$_{254}$ absorbance apparatus while differences below 2000 absorbance units between two measurements for the HPSEC was described as too imprecise to state a difference (Patterson, 2006; Shimadzu, 2006).

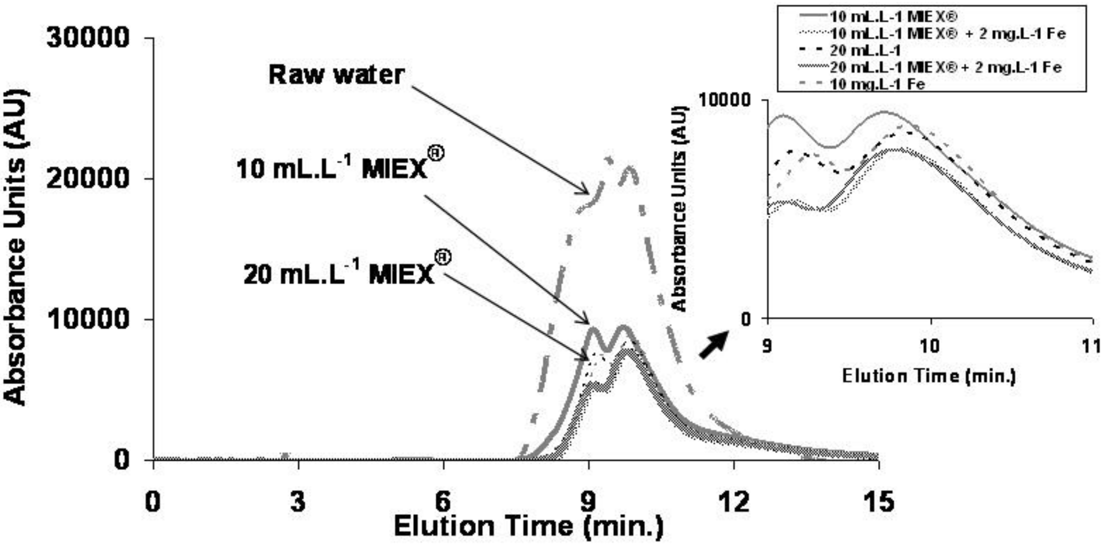


Figure 4.46 HPSEC Profiles after magnetic resin treatment, combined treatment and coagulation in Draycote water.

From these results it can be concluded that magnetic resin can compete with coagulation alone in terms of DOC removal efficiency for Draycote water. Given that NOM in Draycote water is primarily of hydrophilic nature (60 % HPIA and 20 % HPINA), this is not surprising as coagulation is poor at removing these fractions (Babcock and Singer, 1979; Jekel, 1985; Sharp *et al.*, 2006c), and stands in contrast to anion exchange processes (Anderson and Maier, 1979; Croué *et al.*, 1999, Bolto *et al.*, (2004). Nonetheless the fact that magnetic resin had only removed DOC to a similar extent like coagulation was not in accordance with Drikas *et al.*, (2003) who had treated another low SUVA water (1.3 $L.m^{-1}.mg^{-1}$DOC) with magnetic resin in full-scale. While magnetic resin removed 56 % of DOC in that study, comparative coagulation had only been able to remove 35 %. Combined treatment was not seen by Drikas *et al.*, (2003) to be able to improve the DOC removal level of magnetic resin, making the anion exchange process the most efficient treatment for that water. The HPSEC analysis of the water investigated by Drikas *et al.*, (2003) showed however a different MW distribution when compared to Draycote water, as only one peak indicating a MW of approximately

1-2 kDa could be detected. Magnetic resin was able to reduce this peak by 95 %, while coagulation alone reduced it by 65 % only. Such water contained only detectable NOM in the sub 3 kDa range which is described by Sharp *et al*., (2006c) to be the fraction least well removed by coagulation, whilst Draycote water had shown to contain NOM >5 kDa.

4.3.4 Barcombe

In the low SUVA source of Barcombe (1.7 $L.m^{-1}.mg^{-1}$ DOC) magnetic resin treatment with doses of 10 and 20 $mL.L^{-1}$ had resulted in a DOC reduction of 33 and 45 % respectively (Figure 4.47). Comparative coagulation with 10 $mg.L^{-1}$ Fe resulted in a significant DOC reduction of 78 %, while combined treatment increased the DOC removal from the sample pre-treated with 10 $mL.L^{-1}$ magnetic resin to comparable 80 %.

Monitoring of the UV_{254} absorbance reduction in contrary showed much less difference between the different treatment systems. Magnetic resin treatment with 10 and 20 $mL.L^{-1}$ reduced the UV_{254} absorbance by 65 and 74 % respectively, while both coagulation alone and combined treatment reduced the UV_{254} absorbance by 75 %.

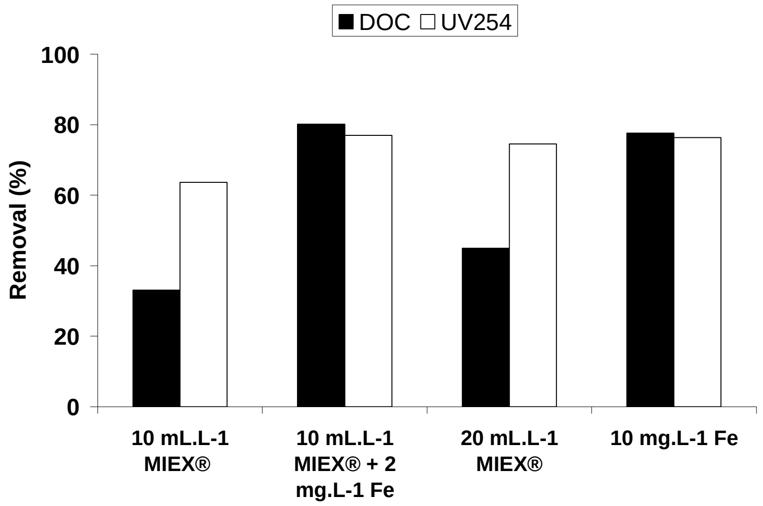


Figure 4.47 DOC and UV_{254} removal by magnetic resin treatment, combined treatment and coagulation in Barcombe water.

HPSEC profiles showed that coagulation alone or used in combination with magnetic resin, was necessary to reduce the first peak at 7 minutes elution time (>5 kDa) by 100 % (Figure 4.48). The magnetic resin doses of 10 and 20 mL.L^{-1} had shown to reduce this peak only by 40 and 45 % respectively. When comparing the removal of the material eluting between 9 to 11 minutes (approximately 3.5 to 1 kDa), no significant difference was observed between the different treatment options.

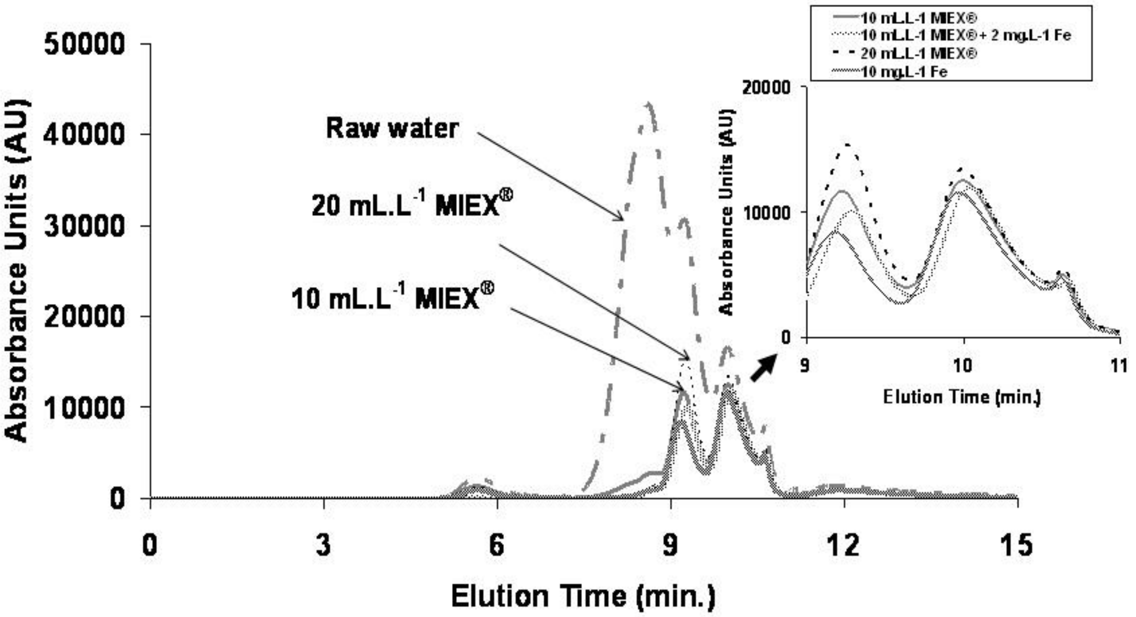


Figure 4.48 HPSEC Profiles after magnetic resin treatment, combined treatment and coagulation in Barcombe water.

The removal data obtained from Barcombe water showed that in terms of UV_{254} absorbance no significant difference could be measured between the samples treated by magnetic resin, coagulation alone or combined treatment. The same observation of similar removal rates was made for the removal of the material eluting between 9 to 11 minutes (approximately 3.5 to 1 kDa). However it was seen that coagulation alone or in combined treatment improved the DOC reduction by up to 35 % when compared to magnetic resin, which showed that a high level of non-UV_{254} absorbing organic material had been removed by the former treatment options.

This observation was related to the previously made statement (Section 4.2.5.2) that Barcombe water was likely to contain due to the presence of green algae some EOM.

EOM had been reported to be of low SUVA (0.5 to 1.5 $L.m^{-1}.mg^{-1}$ DOC) (Nguyen *et al*., 2007; Henderson *et al*., 2007), making it difficult to detect by HPSEC, but has also high MW (16 to 100 kDa) (Henderson *et al*., 2006; Pivokonsky *et al*., 2006) and thus reduces its removability by magnetic resin (Section 4.2.5.2). However, Henderson *et al*., (2006) had been able to remove 94.8 % of the DOC resulting from the EOM of green algae by coagulation and related this to a mechanism of EOM entrapment in the coagulant flocs. From this comparative data it can be concluded that coagulation, based on charge neutralisation, entrapment, adsorption and complexation with metal ions into insoluble aggregates (Dempsey *et al*., 1984; Vilgé-Ritter *et al*., 1999) is a more efficient treatment method for the removal of high MW NOM in Barcombe water. Evidence for this can be seen on the total reduction of the small peak eluting at 7 minutes in Barcombe water (approximately >5 kDa) when using coagulation.

4.3.5 Penwhirn

In the high SUVA water of Penwhirn (5.6 $L.m^{-1}.mg^{-1}$ DOC) the same trend of increased DOC removal after coagulant addition was observed as for Barcombe water.

Magnetic resin treatment with a 10 $mL.L^{-1}$ dose removed 30 % of DOC, while coagulation alone and combined treatment removed 80 and 85 % of DOC respectively (Figure 4.49). A further water sample, obtained from a magnetic resin pilot plant located at Pewnhirn WTW during the period when raw water was collected, was compared to these results. This water was treated onsite by Orica with 30 $mL.L^{-1}$ magnetic resin for 20 minutes contact time at a regeneration rate of 4.5 % and equates to 741 BV service (Equivalent to 22 re-uses of the resin) (Section 3.4.1). The fact that the DOC removal level in this sample was equal to that obtained in bench-scale with 10 $mL.L^{-1}$ magnetic resin was related to these longer service periods in the pilot plant; a procedure seen to reduce the NOM removal capacity of the resin (Section 4.2.5.4). Combined treatment of the sample pre-treated with 30 $mL.L^{-1}$ magnetic resin removed DOC by 85 %.

The UV_{254} absorbance was reduced 35 and 55 % using 10 and 30 $mL.L^{-1}$ magnetic resin. Coagulation alone reduced the UV_{254} absorbance to 93 %, while combined treatment reduced the UV_{254} absorbance to 95 and 98 % in the samples pre-treated with 10 and 30 $mL.L^{-1}$ magnetic resin.

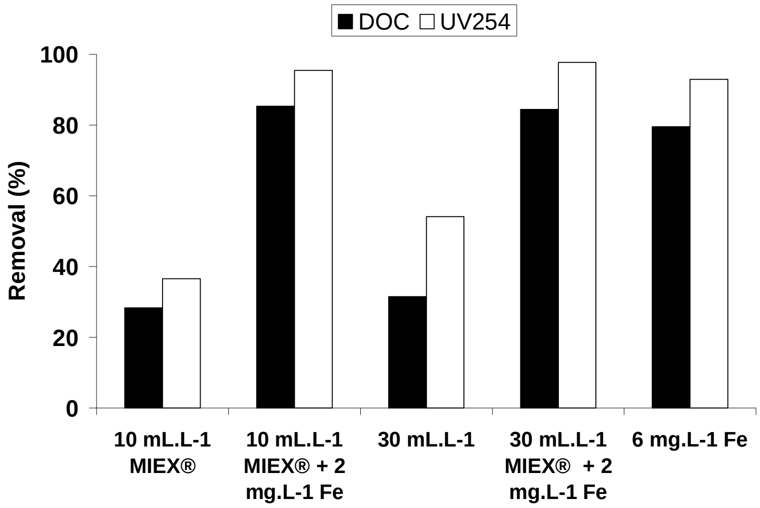


Figure 4.49 DOC and UV_{254} removal by magnetic resin treatment, combined treatment and coagulation in Penwhirn water.

An investigation of the HPSEC profiles showed that combined treatment and coagulation were able to remove by 100 % the first shoulder and first major peak at 6 and 8 minutes elution time (approximately >5 kDa) (Figure 4.50). This observation confirmed the trend observed for Barcombe water that coagulation is more efficient to remove high MW NOM, than magnetic resin due to the physical blockage mechanisms by large molecules occurring on its surface. The 30 $mL.L^{-1}$ magnetic resin dose was however seen to have reduced the major peak at 8 minutes elution time to a higher extent than the 10 $mL.L^{-1}$ magnetic resin dose. This was thought to be due to more strongly UV_{254} absorbing, high MW NOM able to exchange onto the larger external surface area and thereby resulting into the previously seen lower UV_{254} absorbance. However this cannot be confirmed, especially because the magnetic resin dose had been used extensively and cannot be directly compared to the results obtained in bench-scale.

Removal of the lower MW material of approximately 3.5-1 kDa eluting between 9 to 11 minutes, was similar for magnetic resin (10 $mL.L^{-1}$) and coagulation alone. At higher magnetic resin dose (30 $mL.L^{-1}$) there was an increased removal of this material, only exceeded by combined treatment.

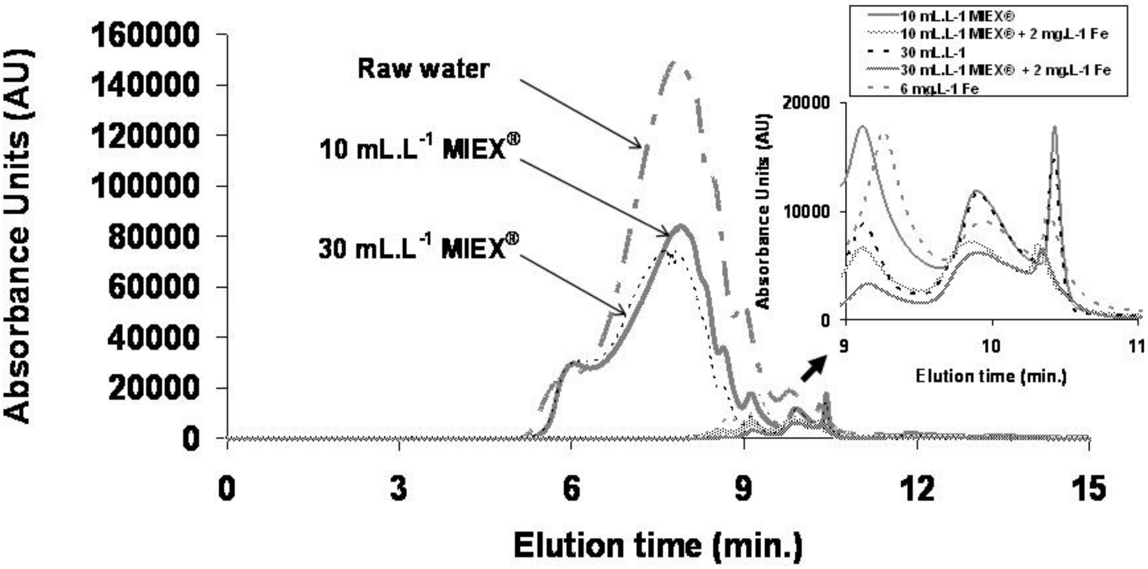


Figure 4.50 HPSEC Profiles after magnetic resin treatment, combined treatment and coagulation in Penwhirn water.

The removal data obtained from Penwhirn water showed that coagulation was essential to efficiently remove the DOC and UV_{254} absorbance. However it could not be stated whether combined treatment could enhance DOC removal. This was because coagulation only had been able to remove DOC by 80 %, while combined treatment removed DOC by 85 %, which resulted in a 5 % difference, a value close to the limit of error of the measurement device.

From the HPSEC profiles it was seen that coagulation removed all high MW NOM eluting between 6 and 8 minutes (MW approximately >5 kDa). However, for the material eluting between 9 and 11 minutes the combined treatment allowed the highest removal. Exactly the same trend showing that coagulation is essential for the removal of high MW NOM and combined treatment results in the highest reduction of low MW NOM was reported by Fearing *et al*., (2004) and Jefferson *et al*., (2004) who tested the efficiency of NOM removal by magnetic resin in high SUVA waters. The combined treatment had however not clearly shown to result in an increased DOC removal and it was suggested that the different peak heights in the low MW area could result from the removal of different types of NOM by magnetic resin and coagulation, without however having resulted in an improved DOC reduction.

4.3.6 Albert

Treatment of the high SUVA Albert water (6.4 L.m^{-1}.mg^{-1} DOC) with 10 and 20 mL.L^{-1} magnetic resin reduced the DOC by 25 and 45 % respectively (Figure 4.51). Combined treatment of the sample treated with 10 mL.L^{-1} magnetic resin increased the DOC removal to a level of 90 %, while coagulation alone reduced the DOC by 80 %. The UV$_{254}$ absorbance was reduced by 30 and 50 % by the 10 and 20 mL.L^{-1} magnetic resin doses. Combined treatment of the sample treated with 10 mL.L^{-1} magnetic resin and coagulation alone removed the UV$_{254}$ absorbance by 95 %.

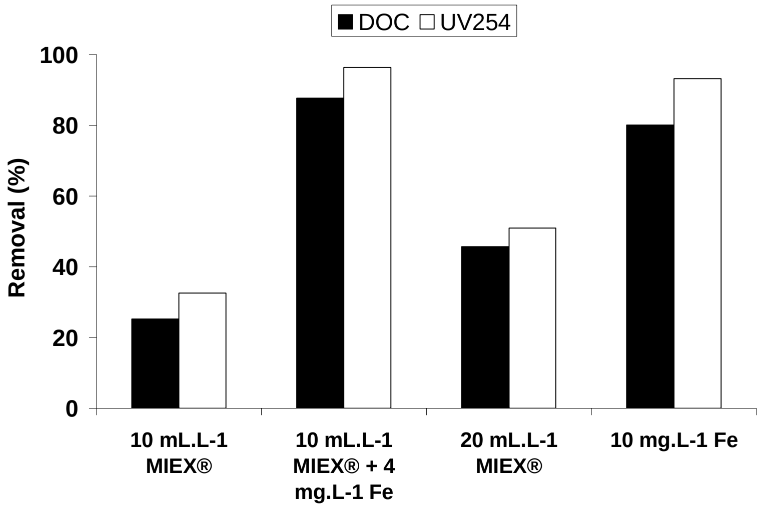


Figure 4.51 DOC and UV$_{254}$ removal by magnetic resin treatment, combined treatment and coagulation in Albert water.

The HPSEC profiles showed a similar trend as observed for Penwhirn, because combined treatment and coagulation removed 100 % of the peaks at 6 and 8 minutes elution time, indicative of NOM with a MW approximately >5 kDa (Figure 4.52). The low MW material of approximately 3.5-1 kDa eluting between 9 and 11 minutes was removed to a similar extent by coagulation alone and by 10 mL.L^{-1} magnetic resin. Treatment with 20 mL.L^{-1} magnetic resin showed improved removal of this MW material to a similar level to that seen for combined treatment

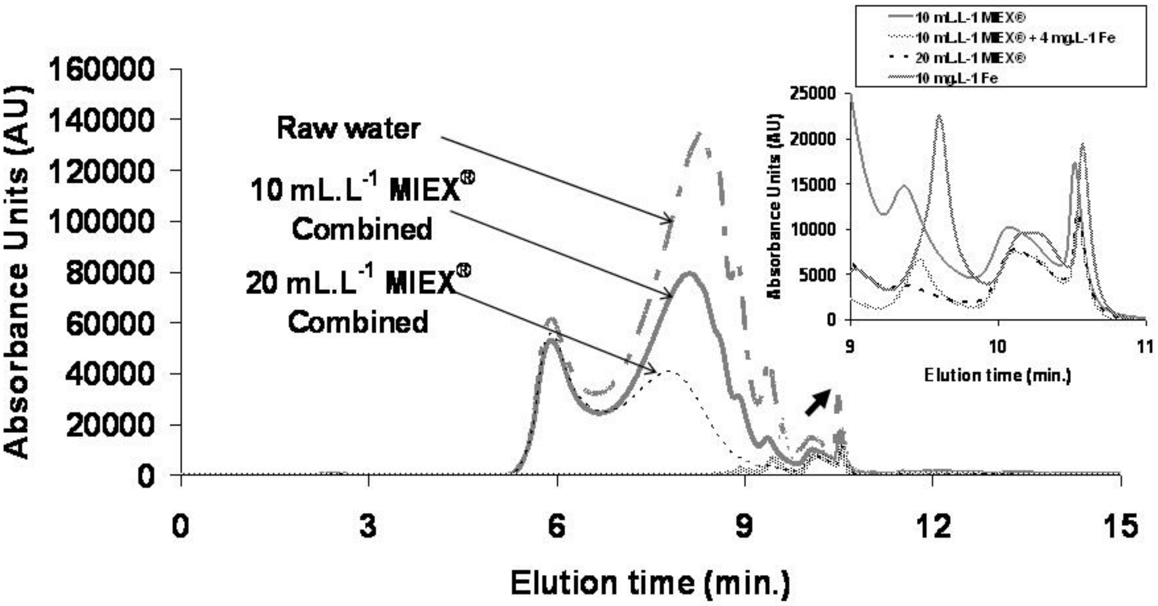


Figure 4.52 HPSEC Profiles after magnetic resin treatment, combined treatment and coagulation in Albert water.

The removal data obtained from Albert water confirmed the trend seen for Penwhirn water, that coagulation is crucial to successfully remove the high MW NOM eluting between 6 and 8 minutes (MW approximately >5 kDa), and combined treatment is the most efficient treatment option for the removal of low MW NOM (approximately 3.5-1 kDa). Considering that combined treatment had removed 10 % more DOC than coagulation alone, it was suggested that beside the possibility of magnetic resin removing a different type of low MW NOM simply resulting in a different peak height another possibility has to be considered. That is, that magnetic resin can remove low MW NOM in general to a higher extent than coagulation, which would be supported by the previously observed good removal of that material by magnetic resin (Section 4.2).

4.3.7. Model compounds

4.3.7.1 Removal of single model compounds by magnetic resin and coagulation alone

The aim of this section is to further investigate whether magnetic resin and coagulation remove different types of organic material and enable higher DOC removal by broadening the range of removable NOM species. In order to achieve this different single model compounds previously described (Section 4.2.3.2) were treated in a comparative test sequence by magnetic resincoagulation alone and combined treatment..

Repetitive use of magnetic resin had previously shown (Section 4.2.6.1) to reduce DOC by 15, 75 and 25 % in the combined product waters of humic acid, tannic acid and L-glutamic acid respectively (Figure 4.54). In contrast, the treatment of resorcinol, D-xylose and D-mannose by magnetic resin was inefficient with DOC reduction levels <5 %. Coagulation alone was seen to reduce the DOC content in the solutions containing humic acid, tannic acid and L-glutamic acid by 85, 82 and 10 % respectively. For resorcinol, D-xylose and D-mannose coagulation alone was seen of the same inefficiency as magnetic resin with a DOC reduction level <5 % for all three compounds.

This comparative data showed that both processes were of similar efficiency for removing tannic acid, which has a hydrophobic, charged molecule of moderate size. For the humic acid solution coagulation was seen necessary to successfully reduce the DOC level. When comparing the HPSEC profiles after treatment it was seen that coagulation had, in contrary to magnetic resin, been able to totally remove the first shoulder and major peak eluting at 6 and 8 minutes retention time (MW >5 kDa) (Figure 4.55). This confirms the observation made for the source waters, that coagulation was essential to remove high MW NOM. Magnetic resin had however seen to remove 15 % more DOC from the L-glutamic solution than coagulation alone, showing that anion exchange was more suitable to remove low MW material, containing dissociated functional groups.

Sharp *et al*., (2006c) who coagulated different fractions of HAF, FAF, HPIA and HPINA showed removal trends similar to those seen for humic acid, tannic acid and L-glutamic acid, characterised by XAD fractionation as HAF, FAF and HPIA respectively. Sharp *et al*., (2006c) removed HAF, FAF and HPIA by 84, 64 and 14 % respectively, showing the same trend of high efficiency of coagulation to remove hydrophobic NOM, while confirming its low capacity for HPIA removal.

Sharp *et al*., (2006c) was as well able to remove HPINA by 17 %, which is a much higher level than that seen for magnetic resin and coagulation when treating D-mannose and D-xylose solutions (<5 %), characterised by XAD-fractionation as HPINA. It was suggested that this difference could result from the source water HPINA fraction of Sharp *et al*., (2006c) containing polysaccharides, that might have been easier entrapped into the floc matrix during coagulation (Freese *et al*., 2001) than the tested low MW model compounds. Nonetheless the removal data of Sharp *et al*., (20006c) confirmed that HPINA was only poorly removed by coagulation, when compared to HAF and FAF. It follows from the above comparative data that tannic acid was representative in terms of DOC removal efficiency by coagulation. The same conclusion could not be made for resorcinol, which had been defined as FAF by XAD fractionation. The very low removal by coagulation of resorcinol (<5 %) was related, beside its very low MW, to an observation made by Guan *et al*., (2006). That study reported that phenolic functional groups only govern the binding of NOM to metal hydroxides at increased pH levels at which these functional groups are dissociated. However at pH 4.5, which was used in this work for coagulation of the model compounds, the functional groups of resorcinol were not dissociated (Section 4.2.6.1).

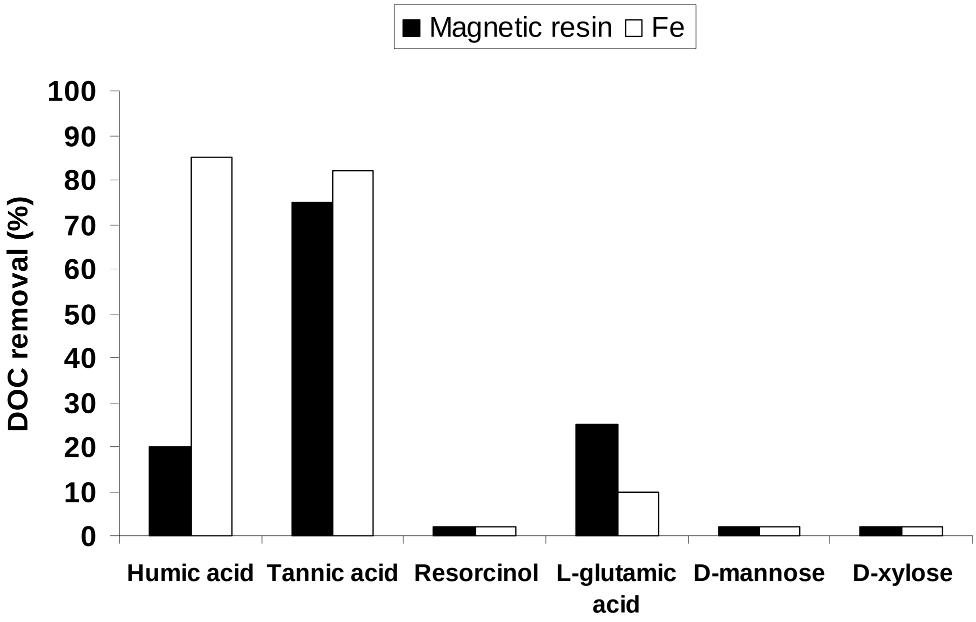


Figure 4.53 Comparison of removal efficiency of the different single model compounds by magnetic resin and coagulation.

4.3.7.2 Comparison of removal efficiency of magnetic resin, coagulation and combined treatment in mixed compound solutions

Treatment of mixed compound solutions had previously shown differences in terms of DOC removal efficiency by magnetic resin, when compared to the respective single compound solutions. This difference had been related to interactions between the different model compound molecules in the mixtures, either enhancing or reducing the removal efficiency of DOC by magnetic resin. Coagulation alone and combined treatment were applied to investigate whether the DOC removal levels in the magnetic resin pre-treated solutions could be enhanced as observed for the source waters.

Combined treatment of humic acid was included here, because it contained a large range of different MW fractions, making it rather similar to both investigated source waters of Albert and Penwhirn. Combined treatment of the humic acid solution also revealed a similar removal trend as seen for Albert and Penwhirn, by increasing the DOC reduction to 85 %. This value is similar to that obtained by coagulation alone (83 %). Investigation of the HPSEC profiles showed that after the combined treatment the first shoulder and major peak eluting at 6 and 8 minutes retention time (approximate MW >5 kDa) (Figure 4.55) were completely eliminated.

Comparison of the HPSEC profiles showed that, as seen for Penwhirn and Albert water, coagulation alone or combined treatment were necessary to reduce the first shoulder by 100 % and first major peak detectable for humic acid at 6 and 8 minutes elution time indicating NOM of an approximate MW of >5 kDa (Figure 4.54). The removal level of lower MW material eluting between 9 and 11 minutes (approximately 3.5-1 kDa) was higher after coagulation than after magnetic resin treatment. However combined treatment allowed, as previously observed for Albert and Penwhirn water, the highest removal rate for that material.

In a mixture containing tannic acid and L-glutamic acid 45 % DOC were removed using the magnetic resin dose of 10 $mL.L^{-1}$. Combined treatment increased the DOC removal in that solution to 62 %, while coagulation alone removed 47 % DOC. Considering that coagulation alone had shown a low ability to remove L-glutamic acid, it was expected that it had mostly removed tannic acid, which resulted in the removal of half the DOC contained in the solution. The initial solution was comprised of equal parts of each compound and thus a reduction of 62 % DOC after combined treatment can only mean that both compounds have contributed towards the DOC removal. This increased removal rate after combined treatment showed that magnetic resin was advantageous when applied as an additional treatment in waters dominated by low MW material, which could help explain the increased DOC reduction seen in Draycote water by combined treatment. It also explains the increased removal of low MW material in waters dominated by high MW NOM such as Albert and Penwhirn.

In a mixed solution containing tannic acid and D-mannose, magnetic resin reduced the DOC by only 27 %. As magnetic resin had previously shown to remove tannic acid to a high extent in a single compound solution (75 %), this low removal level in the mixed solution was related to an interaction between tannic acid and D-mannose which had shown to be inefficiently removed by magnetic resin in a single compound solution (<5 % DOC reduction). Combined treatment and coagulation alone reduced the DOC level by 41 and 47 % respectively from this solution. This improved removal showed that coagulation was less affected by an interaction between both molecules and was more efficient in this solution. It was suggested that the molecules might have been entrapped inside the floc structure (Vilgé-Ritter *et al.*, 1999; Duan and Gregory, 2003), however no evidence could be given for this.

In a mixture containing resorcinol and L-glutamic acid, magnetic resin removed 35 % DOC. Combined treatment did not show any real improvement with a total DOC reduction of 37 %, while coagulation alone resulted in a DOC reduction < 5 %. For this mixture magnetic resin was clearly the most efficient treatment method due to its ability to remove L-glutamic acid.

In the final mixture containing resorcinol and D-mannose, magnetic resin, coagulation and combined treatment gave a DOC removal level < 5 %. This was expected as both compounds were removed very inefficiently by coagulation (<5 %) or magnetic resin treatment.

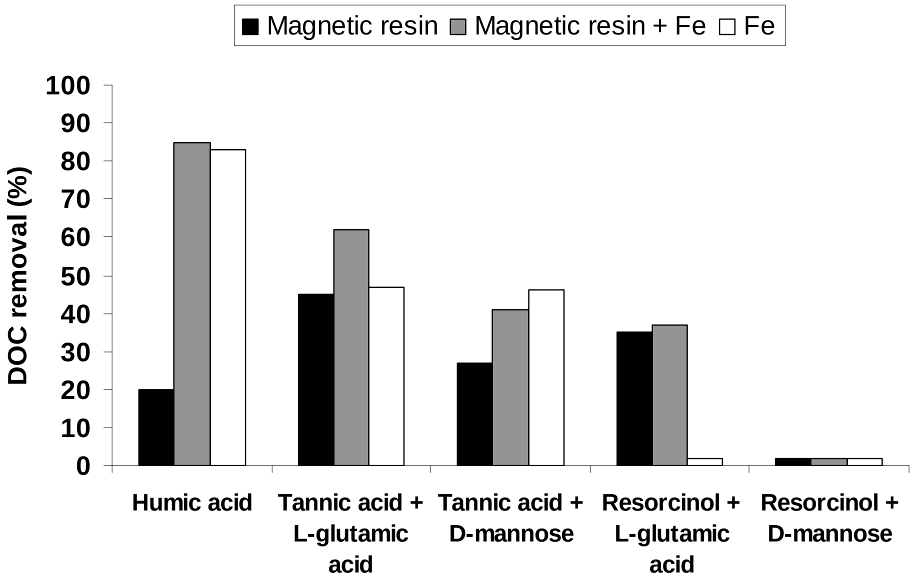


Figure 4.54 Comparison of DOC removal efficiency of the different model compounds mixtures by magnetic resin, coagulation and combined treatment.

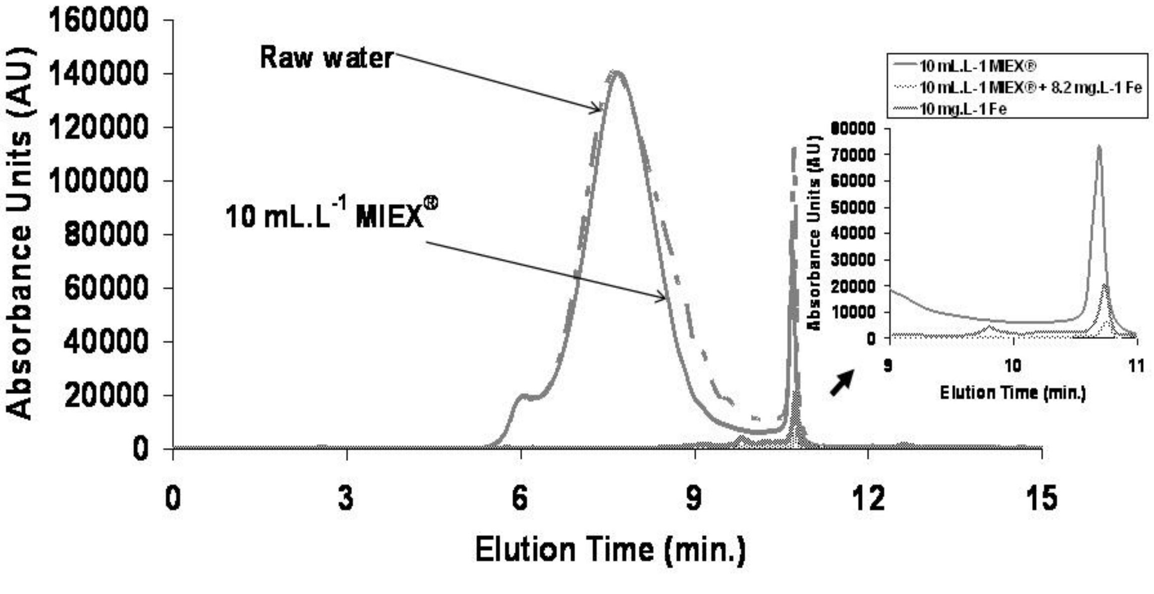


Figure 4.55 HPSEC Profiles after magnetic resin treatment, combined treatment and coagulation on humic acid.

In summary it was observed that magnetic resin can compete with coagulation in sources dominated by hydrophilic, low MW NOM. This was confirmed by treatment of different model compounds either in single or mixed solutions by magnetic resin, coagulation and combined treatment. Magnetic resin had been able to enhance DOC removal in all tested solutions containing low MW, hydrophilic acids.

In moorland waters dominated by high MW NOM, previously observed to reduce the removal efficiency of magnetic resin by physical surface area blockage, coagulation was necessary for effective DOC reduction. Nonetheless combined treatment could enhance the removal of DOC and low MW material in these waters.

Magnetic resin treatment was however not an efficient treatment option for algae water. This was related to the potential presence of high MW EOM making its removal by magnetic resin difficult. Combined treatment of algae laden water enabled however a reduction by 80 % in the required coagulant dose; a beneficial effect seen for all investigated source waters.

4.4. Impact of magnetic resin pre-treatment on floc properties

4.4.1 Aim

The aim of the research reported in this section was to investigate the impact of combined treatment on the quality of flocs formed in the source waters and synthetic waters presented in Sections 4.2 and 4.3.

4.4.2 Raw waters

During drinking water production coagulant flocs can experience elevated levels of shear stress compared to conditions under which they were formed such as in dissolved air flotation units (DAF) or during transfers through pipes and pumps (McCurdy *et al*., 2004). The impact of any elevated shear stress is to reduce the size of the formed aggregates as a result of breakage. The importance of any changes to the floc size are that removal efficiencies decrease in most solid-liquid separation processes as the particle size decreases. Smaller particles settle slower than larger particles and are less likely to be captured by air bubbles in DAF units (Boller and Blaser, 1998). Currently no standardised method for floc strength measurements has been established. However, a range of methods to characterise the flocs have been presented in the literature, such as microscopy (Li and Ganczarczyk, 1986), exposure to different shear levels (Francois, 1987), erosion by ultrasonics (Chu *et al*., 2001), micromanipulation (Zhang *et al*., 1999) and settling rate (Huang, 1994). The methods used in the current study follow the approach as outlined by Jarvis *et al*., (2004) who measured changes in floc size distribution over time as the shear rate in a bench flocculator was increased. For this thesis the floc strength was measured in the following terms:

- Floc size: The median floc size reached during exposure to the normal shear rate levels found in a flocculator. The strength of a floc is directly related to the size reached whereby larger flocs are considered to be stronger (Parker *et al*., 1972; Matsuo and Unno, 1981; Muehle, 1993; Spicer and Pratinsis, 1996; Mikkelsen and Keiding, 2002).
- Settling rate: The rate of settlement of an individual floc. Positive characteristics are shown by increased settling rate at a given floc size and consequently an increased effective density (Boller and Blaser, 1998; Schwoerbel, 1999; Aguilar *et al*., 2003).

- Response to shear: Change in the median floc size upon exposure to elevated shear rates. The data is presented as a log-log plot of median floc size against shear rate. The plot is interpreted in terms of its gradient whereby stronger flocs exhibit a shallower gradient. (Parker *et al*., 1972; Leentvaar and Rebhun, 1983; Bache and Rasool, 2001). An alternative method is to measure the floc strength factor which represents the percentage change in the median floc size from one shear rate to another (Francois, 1987)

Analysis of the floc data in this thesis revealed that the impact of magnetic resin pre-treatment on floc properties was not consistent for all waters and appeared to be related to the compositional make up of NOM. To illustrate, for coagulation and combined treatment median floc sizes (d_{50}) of 938-990 µm and 1051-1072 µm were observed for the low SUVA waters of Draycote and Barcombe respectively (1.3-1.7 m^{-1} L mg^{-1} DOC) (Figure 4.57 (A), (B)). Whereas in the case of the high SUVA waters of Penwhirn and Albert (5.6-6.4 m^{-1} L mg^{-1} DOC respectively) treatment by coagulation alone resulted in a d_{50} of 478 ± 3 µm and 577 ± 8 µm respectively (Figure 4.57 (C), (D)). While for combined treatment median floc sizes increased to 667 ± 7 µm and 946 ± 7 µm for Penwhirn and Albert respectively.

Measurement of the settling velocity of the floc size distribution supported the previous measurements of floc size in that no differences were observed in terms of the settling velocity of the flocs from coagulation and combined treatment for the low SUVA waters. To illustrate, the settling velocity for a 500 and 1000 µm floc was compared with the median value at each size (taken from the power equation calculated for each set of data) as well as the range held within the 95% confidence limits, (shown below in brackets). In the case of Draycote, the settling velocity for the 500 and 1000 µm flocs was 409 (230-640) $\mu m.s^{-1}$ and 660 (430-1040) $\mu m.s^{-1}$ respectively for coagulation alone (Figure 4.56 (A)), compared to 420 (270-660) and 750 (480-1180) $\mu m.s^{-1}$ respectively when combined treatment was applied. Similar data was observed in the case of Barcombe where the 500 and 1000 µm flocs settled at 1680 (884-3177) and 2360 (1203-4416) $\mu m.s^{-1}$ respectively for coagulation alone, compared to 1590 (840-3020) and 2420 (1260-4600) $\mu m.s^{-1}$ respectively for combined treatment (Figure 4.56 (B)).

In the case of high SUVA waters combined treatment generated a significant improvement in the settling rate. Such observed increases in settling rate are in addition to the increase in size as they are compared at the same floc size. For instance, in the case of water from Penwhirn the settling rate of a 500 and 1000 μm floc was 480 (280-820) and 920 (530-1500) μm.s^{-1} respectively for coagulation and 1180 (700-2010) and 1560 (920-2260) μm.s^{-1} respectively for combined treatment (Figure 4.56 (C)). An even greater increase was observed in the case of Albert water whereby the settling rate of a 500 and 1000 μm floc were of 790 (500-1250) and 1260 (900-1880) μm.s^{-1} respectively for coagulation and of 2100 (1350-3300) and 3500 (2230-5470) μm.s^{-1} respectively for combined treatment (Figure 4.56 (D)). Combined treatment increased thereby the median settling velocity of a 1000 μm floc by 118% for Albert water as opposed to 70% for Penwhirn water. In comparison combined treatment of the two low SUVA waters increased the median settling velocity of a 1000 μm floc by 2.5 % and 14 % for Barcombe and Draycote respectively.

The data above reports cases where water pre-treated by magnetic resin was filtered before coagulation to remove any resin carry-over. If such filtration was not adopted increased floc settling velocities, resulting from fast settling magnetic resin carry-over (Section 4.1.4) being entrapped inside the floc matrix, were observed.

For example, in the case of Barcombe water, inclusion of carry-over increased the settling velocity of the 1000 μm flocs from the previously reported value to 3650 (1902-6695) μm.s^{-1}; a 55 % increase in settling velocity (Figure 4.56 (B)). In the case of the experiments conducted on high SUVA water inclusion of fines increased the settling velocity by 26-27 %. Differences were not always observed and in the case of Draycote a much lower resin carry-over was observed. Whilst the reasons for such a different carry-over are unclear the results indicate that resin carry-over can affect the settling behaviour of flocs, which could lead to a misinterpretation of the results.

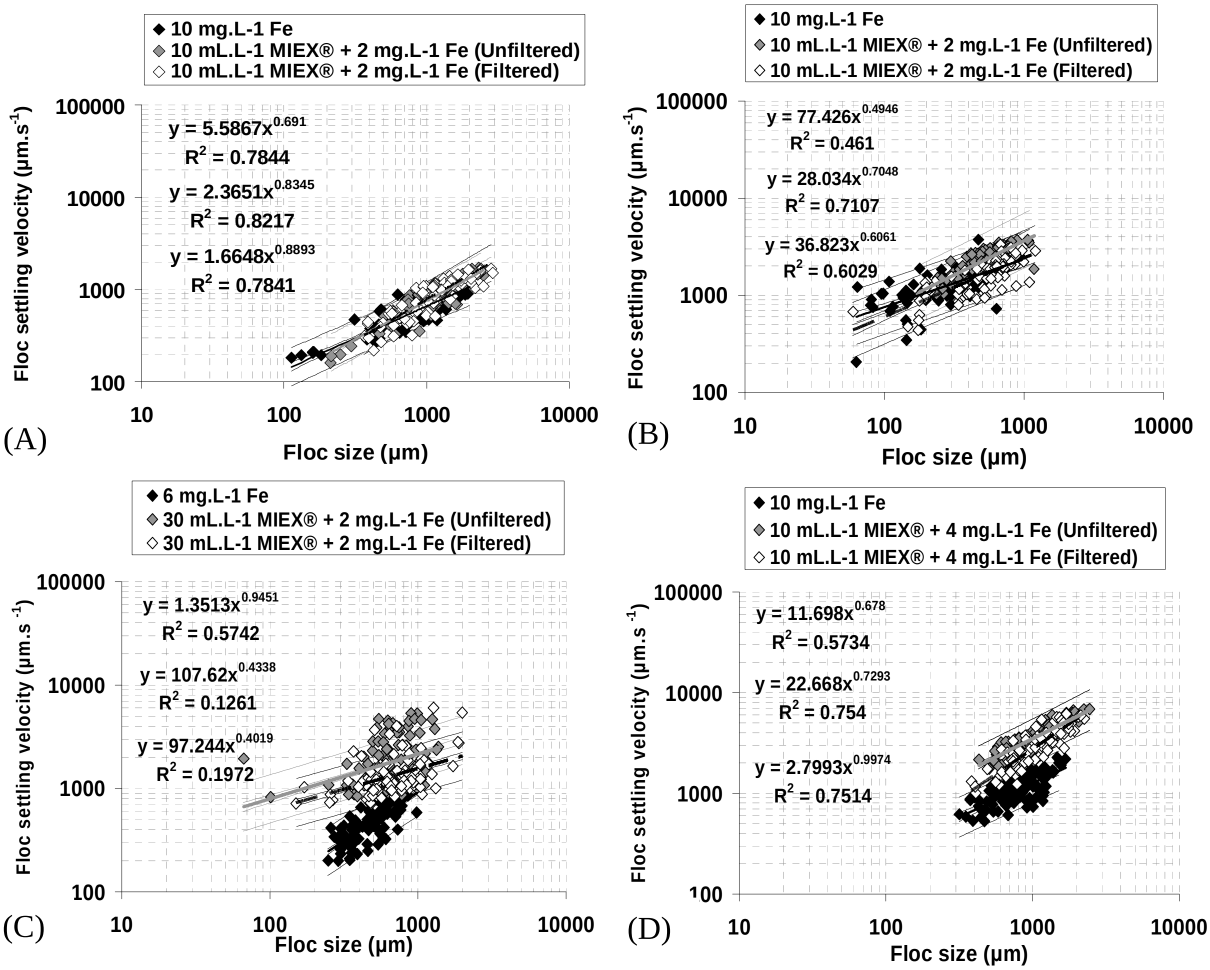


Figure 4.56 Floc settling velocity profiles for the coagulated source waters: (A) Draycote water, (B) Barcombe water, (C) Penwhirn water, (D) Albert water.

Differences in settling velocity at comparative sizes are related to differences in the effective density of the flocs as result of changes in the structure of the aggregates. The settling rate data can be utilised to quantify such changes through the calculation of the fractal dimension (d_f) (Jefferson and Jarvis, 2006). Flocs with a fractal dimension close to 1 have in that study been described as having an open, weak and porous structure, whereas a value of 3 indicates a strong and compact structure. The d_f values after coagulation alone and combined treatment were 1.69-1.89, 1.49-1.61, 1.95-1.40 and 1.68-1.99 for Draycote, Barcombe, Penwhirn and Albert respectively (Figure 4.56). Consequently, the application of a pre-treatment stage with magnetic resin is shown to increase the d_f of three (making the flocs more compact) of the water and decrease the d_f of one (make the flocs more open). As such there is no direct correlation between fractal dimension and the settling properties observed. Explanation of structural changes in the flocs was also attempted by visually comparing flocs under an optical microscope (Section 3.7.5).

Combined treatment of the high SUVA waters appeared to generate flocs with a more distinct structure, which would explain their higher settling velocity (Appendix 1). Filtration of combined treatment appeared however to result again in more open floc structures, but which had not appeared to have a detrimental affect. A visual comparison of the flocs showed for Draycote water independently of the treatment system flocs of similar appearance characterised by an open floc structure (Appendix 2). For Barcombe water no real difference could be seen as well between the coagulation flocs and the flocs from unfiltered magnetic resin pre-treated water. However this was difficult to judge as the flocs contained high levels of suspended algal material. Filtration of the magnetic resin pre-treated water showed after combined treatment pale flocs which appeared to be of a more open structure. Nonetheless visual comparison did not qualify as an additional investigation method, to investigate floc density, as only 10 pictures had been taken for each system, making them subjective to the eye of the observer.

The trend for improved floc properties in terms of size and settling rate after combined treatment in high SUVA waters is in agreement with the work of Jefferson *et al*., (2004) and Bursill *et al*., (1985). Jefferson *et al*., (2004) who investigated water with a SUVA level of 6 m^{-1} L mg^{-1} DOC reported floc sizes of 720 ± 84 μm and 1000 ± 200 μm for coagulation and combined treatment respectively. Settling rate was also shown to increase after combined treatment. For example the settling rate of a 500 μm floc increased from 382 $\mu m.s^{-1}$ after coagulation to 977 $\mu m.s^{-1}$ after combined treatment. Jefferson *et al*., (2004) indicated d_f values of 1.76 and 1.75 for flocs from combined treatment and coagulation alone. This confirmed as seen above that there was no direct correlation between fractal dimension and increased settling velocity for combined treatment.

Similarly, Bursill *et al*., (1985) who analysed a source with a SUVA level of 12 m^{-1} L mg^{-1} DOC reported coagulation and combined treatment to produce flocs of 300-750 μm and 1000-3000 μm respectively. Floc settling rate as measured by the time necessary for all the flocs to settle after the stirring in the jar tester had stopped indicated, that flocs formed from combined treatment water settled 3-9 times more quickly than those directly after coagulation.

To investigate the floc response to stress, particles were exposed to increased shear rates, ranging from 30 to 200 rpm. It was seen from these tests that the floc sizes in all investigated sources and systems were reduced to a certain extent. As with many of the previous characteristics the impact of combined treatment could be related to the initial SUVA of the raw water. In the case of low SUVA water at Draycote no significant difference was observed in terms of the floc strength factor (Section 3.7.1) whereby coagulation and combined treatment flocs broke down on average (average value calculated from the different shear rates) by 25% (Figure 4.57 (A)). For Barcombe, the flocs were observed to break less for coagulation (20 %) than for combined treatment (35 %) (Figure 4.57 (B)). In part this appears to be due to the water containing a high concentration of algal material during the trial. This suspended material was measured to remain independently of the applied shear rate of a d_{50} value of 580 ± 85 µm. Magnetic resin was seen on the other hand to be contaminated with algal material after 5 minutes settling time, indicating that a large part of the suspended material had settled before the coagulation step. A d_{50} of 280 ± 65 µm measured after magnetic resin had settled confirmed that less large fragments of suspended material able to interfere with the measurement were present in this solution.

For the high SUVA waters at Penwhirn and Albert the initially larger flocs from combined treatment were able to remain larger than coagulation flocs until a shear rate of 100 rpm beyond which they converged to a common floc size of 180-230 µm and 270-330 µm in Penwhirn and Albert water respectively (Figure 4.58 (C), (D)). For Penwhirn water flocs had broken down by 60 % after coagulation compared to 50 % after combined treatment based on 10 $mL.L^{-1}$ of magnetic resin and 60 % based on 30 $mL.L^{-1}$ of magnetic resin, which did not support the trend of increased floc strength after combined treatment for Penwhirn water (Figure 4.57 (C)). Nevertheless, it was expected that this trend related in part to the fact that combined treatment had allowed flocs to grow to an initially larger size than coagulation only. In such case caution isrequired for the interpretation of the data, as initially larger flocs have a greater natural tendency to break (Argaman and Kaufman, 1970; Thomas *et al*., 1999).

Overall, post the period of increased shear an average d_{50} floc size of 400 ± 12 µm and 205 ± 5 µm was measured for combined treatment and coagulation respectively, demonstrating that on average the former treatment still generates larger floc sizes. The same trend was seen for Albert water where floc sizes were on average reduced by 40 and 50 % after shear application for coagulation alone and combined treatment respectively (Figure 4.57 (D)). Combined treatment flocs remained however on average larger at a size of 490 ± 12 µm compared to 335 ± 11 µm after coagulation alone.

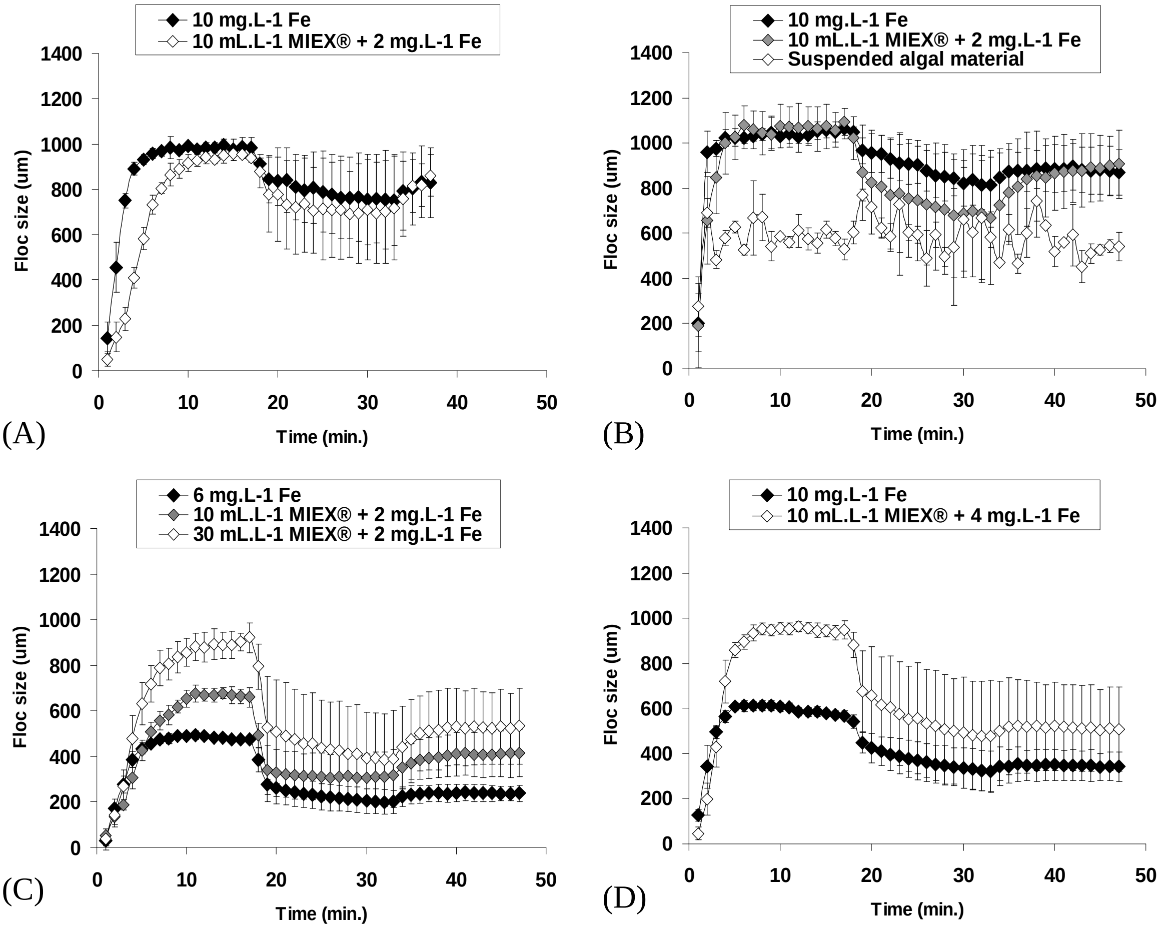


Figure 4.57 Average floc growth, breakage and re-growth profiles for the source waters: (A) Draycote water, (B) Barcombe water, (C) Penwhirn water, (D) Albert water.

A more complete picture of the impact of exposure to elevated shear rates is observed by constructing the floc strength plots (Figure 4.58). Analysis of such data normally involves calculation of the gradient whereby smaller gradients are considered to indicate stronger flocs. However, some caution is required as mentioned above because of the greater natural tendency of large flocs to break and hence generate a larger gradient (Argaman and Kaufman, 1970; Thomas *et al*., 1999).

In the case of low SUVA waters no difference was observed between coagulation and combined treatment. In Draycote water floc strength gradients of -0.48 and -0.51 were observed after coagulation and combined treatment respectively (Figure 4.58 (A)). For Barcombe combined treatment generated a floc less resistant to elevated shear rates, though the initially floc sizes were similar. To illustrate the floc strength gradient was -0.23 after coagulation alone compared to -0.73 after combined treatment, indicating the flocs from the latter treatment to be weaker (Figure 4.58 (B)). Nonetheless for this source it was as already stated, difficult to define whether coagulation flocs were really stronger than flocs from combined treatment or if the suspended algal material had obstructed the measurement.

For both high SUVA sources the flocs from combined treatment were observed to be more sensitive to elevated shear rates as evidenced by floc strength gradients of -0.44 (coagulation alone), -0.64 (resin dose: 10 $mL.L^{-1}$) and -1.01 (resin dose: 30 mL^{-1}) for Penwhirn (Figure 4.58 (C)) and -0.38 and -0.72 for Albert after coagulation and combined treatment respectively (Figure 4.58 (D)). In these cases flocs grew to an initially larger size making them generally more susceptible to breakage. Thus it is difficult to separate out the influence of the combined treatment purely on the resistance for each flocs to elevated shear rates. However, in each case floc sizes tended to converge at larger elevated shear rates for both combined treatment and coagulation alone, indicating that the differences observed may be mainly due to the initially larger sizes.

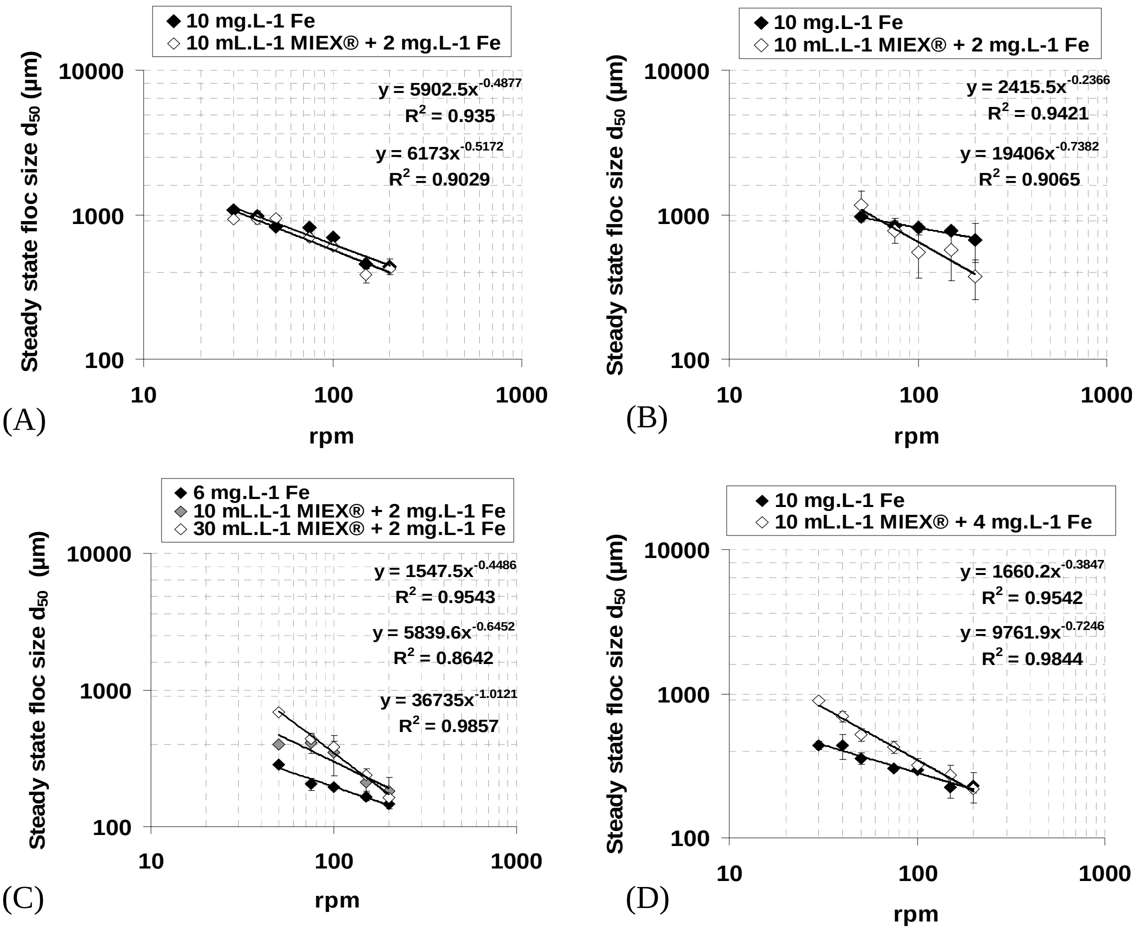


Figure 4.58 Floc strength profiles for the source waters after different levels of shear: (A) Draycote water, (B) Barcombe water, (C) Penwhirn water, (D) Albert water.

Despite the contradictory trend arising from the floc strength profiles when compared to floc size and settling velocity combined treatment in high SUVA sources was still evaluated as advantageous. This was because the increased settling velocity of flocs in high SUVA waters would allow WTW's that use solid-liquid separation by sedimentation to obtain faster clarification rates. The effect of increased settling rates has already been observed at full-scale plants. For example at Green Valley WTW (California, USA) which treated a water of a more moderate SUVA level (2.7-3.5 m^{-1} L mg^{-1} DOC) by combined treatment based on a 30 % coagulant reduction, increased floc settling velocities were also seen as well as reduced solids loading on the filters (Nestlerode *et al.*, 2006b). This observation however implies that increased floc properties in terms of settling velocity is not totally restricted to sources of such high SUVA as Penwhirn and Albert and can also occur in waters of more moderate SUVA.

In practice elevated shear rates occur for relatively small periods of time and so an important component of any investigation is to understand what capacity the floc system has for regrowth. The previously reported inability of flocs to be able to re-grow to their original size was tried to be explained by levels of applied shears that change the floc surfaces to a more compact structure by which they loose their bonding capacity (Serra *et al.*, 1997; Spicer *et al.*, 1998). Supportive data for this was given by Yukselen & Gregory (2004) who exposed alum flocs to a shear rate of 400 rpm for different time periods and saw that the re-growth potential decreased with increasing periods of stress. In this study the regrowth potential was determined by reducing the shear rate back to 30 rpm for 15 minutes and comparing the new size to that developed under elevated shear (average calculated from all different shear rates). For Barcombe water the flocs re-grew by 20 % after coagulation alone, compared to 50 % after combined treatment. A similar trend of differing results was observed for Penwhirn water where regrowth by 10 % for coagulation compared to 30 % for combined treatment. While no differences could be seen for both Albert and Draycote water (Figure 4.57), indicating that increased regrowth-potential cannot be related to the initial SUVA of the raw water, suggesting that this mechanism is of a more complex nature. Further work is suggested to be done in this area.

Overall, the application of combined treatment has been shown to enhance the physical properties of flocs, especially those derived from high SUVA waters. At a conceptual level the improvement in floc properties is likely to be caused by either a change in the ratio of organic to inorganic components within the floc, removal of specific components from the organics or a combination of both. The former is supported by the general view that incorporation of NOM produces weaker flocs (Bache *et al.*, 1999). This could be supported by comparative treatment of Albert raw water with 5 and 10 mg.L^{-1} Fe. From the measured residual DOC concentrations after treatment DOC:Fe mass ratios of 1.46:1 and 2:1 were seen to be contained inside the matrix of the flocs resulting from 10 and 5 mg.L^{-1} Fe respectively. Median floc sizes of 577 ± 8 µm and 445 ± 10 µm were measured for the flocs resulting from 10 and 5 mg.L^{-1} Fe respectively and indicating that a higher DOC content can affect the size to which a floc can grow.

However, during the trials with the different waters flocs grown after combined treatment had DOC:Fe ratios in the range 1.46-3.36:1 compared to 0.75-1.56:1 when coagulation alone was applied (Table 4.4). In such cases all flocs formed after combined treatment showed improved physical characteristics even though they had significantly more NOM within the floc structure.

Table 4.4 DOC: Fe mass ratio in flocs formed by combined treatment and coagulation alone.

	DOC : Fe mass ratio in floc matrix (mg:mg)	
	Magnetic resin and Fe	Fe
Draycote	0.95:1	0.69:1
Barcombe	2.25:1	0.75:1
Penwhirn	3.36:1$^{(A)}$/3.13:1$^{(B)}$	1.56:1
Albert	1.46:1	0.75:1

$^{(A)}$ 10 mL.L^{-1} magnetic resin, $^{(B)}$ 30 mL.L^{-1} magnetic resin

Jefferson *et al.*, (2004) suggested that the beneficial impact of combined treatment on floc properties in high SUVA waters could be relatable to the reduced presence of NOM of lower MW which had been preferentially removed by magnetic resin. This would result in the incorporation of more NOM of high MW in the flocs and thereby potentially enhance the floc structure, showing that the character of NOM included affects floc properties (Collins *et al*., 1986; Jarvis *et al*., 2004). This suggestion could be confirmed by the data shown in this thesis. Under section 4.2 it was seen that magnetic resin preferentially removed the mid to low MW material eluting between 8 and 11 minutes (approximately 5 to 0.5 kDa). In high SUVA sources this was seen to result in a higher concentration of high MW material eluting around 6 minutes (approximately >5 kDa), which had been described to have polymeric characteristics (Hayes *et al*., 1989). By increasing the proportion of high MW polymeric type molecules within the floc structure a greater number of binding points are made available as well as an increase in the bridging potential and the capacity to form flocs by electrostatic patch mechanisms (Ray and Hogg, 1987; Gregory and Li, 1991; Bolto, 1995; Gregory, 1996; Aguilar *et al*., 2003). Electrostatic patch coagulation is based on charge neutralisation induced by formation of positively charged precipitate that can induce coagulation of NOM by electrostatic interactions. This can generate fairly strong attraction between particles leading to more compact floc structures (Chowdhury and Amy, 1991). Jefferson *et al*., (2004) had also compared flocs from combined treatment to polymer flocs and had reported that both systems resulted in larger flocs but that the settling properties of the second system were rather poor. Hence it could be suggested that the larger floc sizes would result from the bridging effect of NOM, while the compact structure would be based on another mechanism such as electrostatic patch coagulation. However this could not be proven and further work concerning the impact of NOM character on floc formation is suggested here, especially as knowledge of improved floc structure would be crucial for WTW's.

4.4.3 Single model compounds

It has been suggested above that the presence of different NOM molecules in terms of MW can influence the properties of flocs. Therefore the characteristics of the flocs resulting from treatment of the different analytical model compounds were compared. Flocs formed during the coagulation of model compounds were compared to precipitate (Ferric hydroxide) flocs formed under the same conditions (10 mg.L^{-1} Fe and pH 4.5). Those precipitate flocs were seen to grow to a d_{50} value of 891 ± 35 µm, which was very close to the d_{50} value of 901 ± 90 µm reported for ferric hydroxide precipitate flocs by Jarvis *et al*., (2006).

Coagulation of tannic acid generated a floc with a d_{50} of 1943 ± 1398 µm; the largest flocs measured for this study. The size was measured manually by optical microscopy (Section 3.7.1 and 3.7.3), as the diameter of the flocs exceeded the upper detection limit of the dynamic laser diffraction instrument. In comparison, flocs formed from resorcinol, L-glutamic acid, D-mannose and D-xylose solutions all grew to a similar size to that of the precipitate flocs with d_{50} values of 800-912 µm.

Greater differentiation was observed in terms of settling velocities of the different systems. In the case of tannic acid the settling rate of a 500 and 1000 µm floc was 1580 (835-3000) µm.s^{-1} and 3220 (1700-6120) µm.s^{-1} respectively (Figure 4.59 (A)). In comparison the settling rates for the other compounds were lower. For resorcinol standardised 500 and 1000 µm flocs were calculated to settle at 1490 (790-2840) and 2330 (1220-4421) µm.s^{-1} respectively, while values of 1610 (850-3050) and 2340 (1120-4030) µm.s^{-1} respectively were calculated for standardised 500 and 1000 µm L-glutamic acid flocs (Figure 4.59 (B), (C)). These results showed that resorcinol and L-glutamic acid could affect the floc properties. D-mannose and D-xylose flocs however were seen to settle at rates nearly identical with precipitate, where standardised 500 and 1000 µm flocs were calculated to settle at 680 (360-1310) µm.s^{-1} and 1220 (650-2360) µm.s^{-1} (Figure 4.59 (D), (E)).

When visual comparison of the different flocs was undertaken the particles formed in the tannic acid solution looked different in colour and appeared to be more compact than precipitate (Appendix 3). The observed black colour of tannic acid flocs is thought to result from the interaction of the di-gallic acid moieties that constitute the tannic acid molecules with the iron in the coagulant (Simon *et al*., 1994; Budnar *et al*., 2006). For the flocs formed in resorcinol, L-glutamic acid, D-mannose and D-xylose no structural differences were observed when compared to the precipitate flocs.

Overall, the data obtained from the separate model compounds confirmed the trend seen previously (Section 4.4.2) that the incorporation of NOM does not necessarily result in weaker flocs. This was because flocs from tannic acid contained the highest DOC: Fe ratio in their floc matrix (0.81 : 1), when compared to the other model compound flocs (0.02:1-0.11:1). Furthermore it was confirmed that the NOM type included in the floc was important. This was as tannic acid showed with the highest MW and the highest DOC removal (82 %) the best floc properties, while the low DOC removal of L-glumatic acid (10 %) and resorcinol (<5 %) had also shown to affect the flocs in contrary to D-mannose and D-xylose.

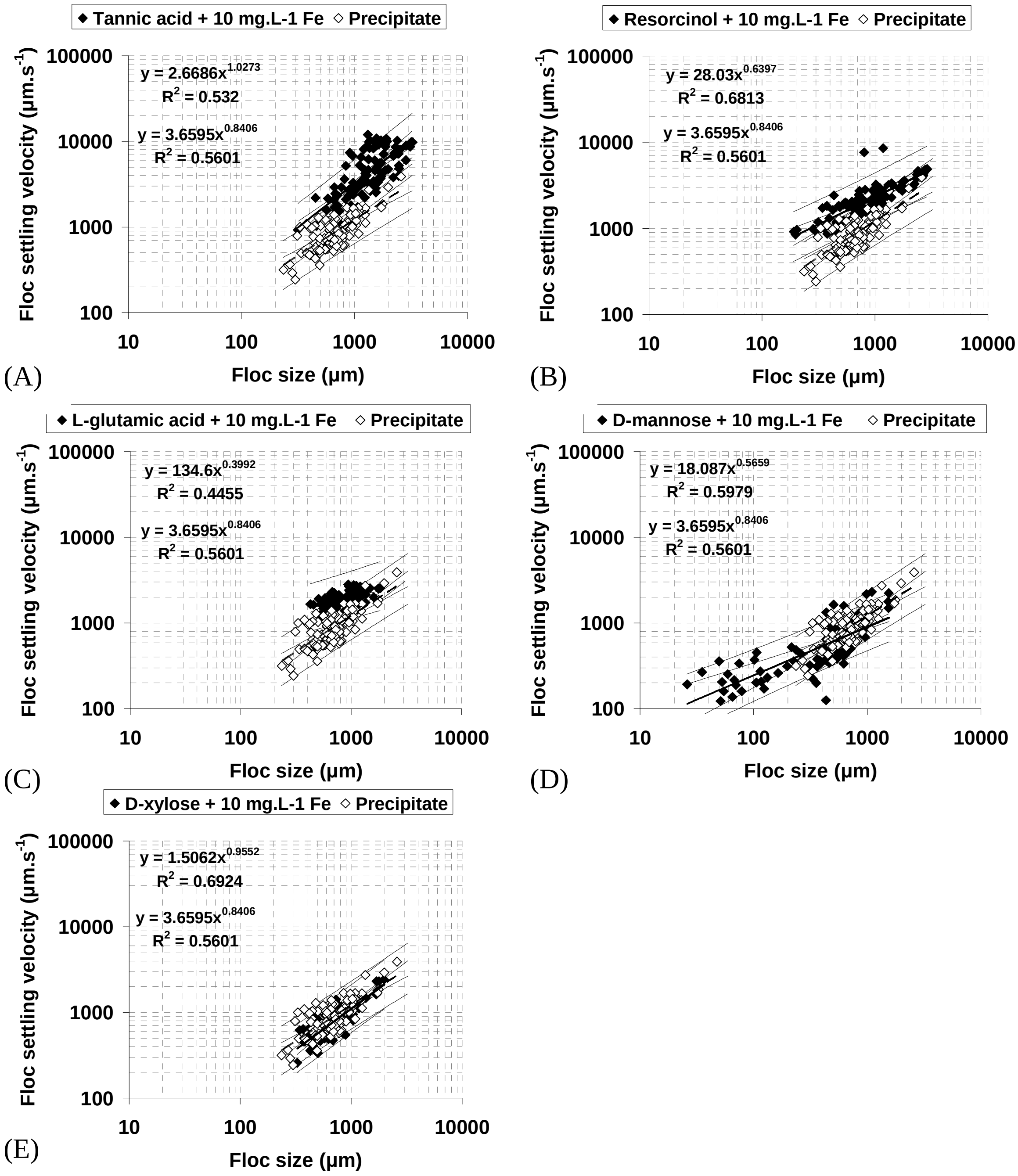


Figure 4.59 Floc settling velocity profiles for the coagulated model compound solutions: (A) Tannic acid, (B) Resorcinol, (C) L-glutamic acid, (D) D-mannose, (E) D-xylose.

As previously reported Sharp *et al*., (2006c) removed the DOC contained in the FAF, HPIA and HPINA fraction by 64, 14 and 17 % respectively (Section 4.3.7.1). This removal data showed the same trend of high efficiency of coagulation to remove hydrophobic NOM, while confirming its low capacity to remove HPIA, as observed in this thesis (Tannic acid: 82 %, L-glutamic acid: 10 %). Sharp *et al.*, (2006c) had however been able to remove the DOC contained in the HPINA fraction by 17 %, while the DOC contained in D-xylose and D-mannose had been removed < 5%.

In contrary to our work where tannic acid had produced the largest flocs Sharp *et al.*, (2006c) found that FAF produced the smallest flocs (523 µm) when compared to HPIA (759 µm) and HPINA (668 µm). The same trend was seen for Sharp *et al.*, (2006c) when measuring settling velocities of 710, 1152, 1385 $\mu m.s^{-1}$ for standardised 1000 µm FAF, HPIA and HPINA flocs respectively, showing in contrary to our data that FAF flocs settle the slowest. The d_f values were of 2.02, 1.63, 1.39, 1.56 and 1.95 respectively for tannic acid, resorcinol, L-glutamic acid, D-mannose and D-xylose respectively. Sharp *et al.*, (2006c) calculated d_f values values of 2.24, 1.90 and 1.88 for FAF, HPIA and HPINA respectively. For both data sets it was seen that FAF (in this thesis tannic acid), had the highest value. This demonstrated that the FAF fraction produced the most compact flocs and is in agreement that FAF flocs have the narrowest microporosity (Alvarez- Puebla *et al.*, 2005). However this did not agree for resorcinol (d_f: 1.63). As well Sharp *et al.*, (2006c) showed that the lower the d_f value, the higher the settling velocity, a trend not seen for the model compounds as the highest and lowest d_f values were seen for tannic and L-glutamic acid, which produced the fastest settling flocs. Again it was seen that no correlation between d_f value and settling velocity, could be observed in this thesis. These different trends occurring between flocs formed with different NOM fractions from a real water and those formed with model compounds are difficult to explain. Although the different single model compounds confirmed that different NOM types lead to differences in floc formation, they do not seem to simulate behaviour of a specific raw water fraction containing a large range of different molecules.

Floc strength calculations after application of different levels of shear stress reduced the d_{50} floc size for the precipitate as well as for all model compound solutions by 50 % on average, excepted for tannic acid (60 %) (Figure 4.60 (B)). However the tannic flocs were seen to remain with an average d_{50} floc size of 780 ± 200 µm larger than all the other flocs (430 ± 200 µm) (Figure 4.60 (A)).

Regrowth potential for all the model compounds was relatively poor compared to that observed for the real waters. All the compounds except tannic acid regrew by 10 % which was equivalent to the regrowth potential observed for precipitate. Tannic acid was less able to regrow with a factor <5 %. Visual observation of the tannic acid flocs indicated that they were rounder and less dendritic, compared to the others providing less opportunity for reconnection and thereby reformation (Serra *et al*., 1997).

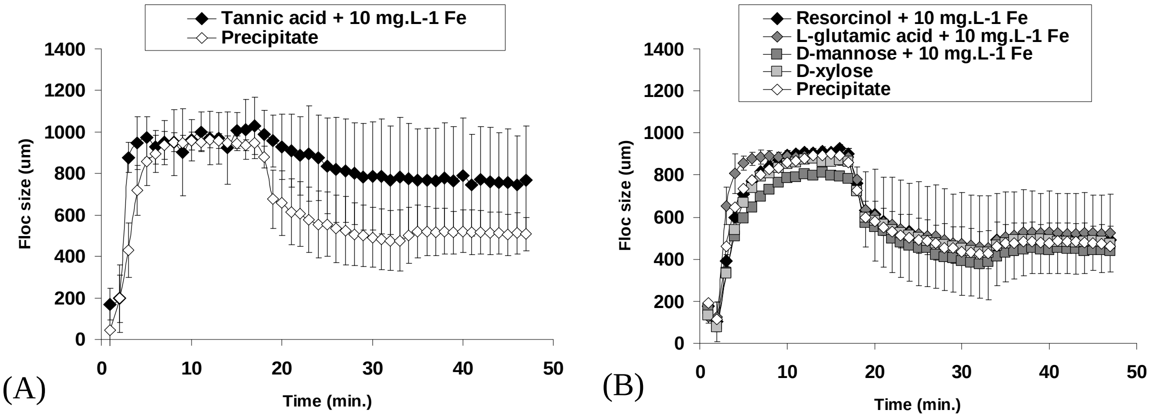


Figure 4.60 Average floc growth, breakage and re-growth profiles for the coagulated model compound solutions: (A) Tannic acid vs. precipitate, (B) Resorcinol, L-glutamic acid, D-mannose and D-xylose vs. precipitate.

Comparing the floc strength profiles confirmed that tannic acid flocs remained larger at all the shear rates when compared to the precipitate alone (Figure 4.61 (A)). As explained above the floc size reached by tannic acid at 30 rpm was determined by optical microscopy whilst the other measurements were made by laser diffraction. Comparison of the data sets revealed three main observations. In the case of resorcinol, D-mannose and D-xylose no difference was observed between the test and the precipitate system indicating that the DOC uptake <5 % of the compounds was insufficient to cause any change to the aggregate properties in terms of resistance to shear. Whereas in the case of L-glutamic acid a 10 % DOC uptake was seen to significantly change the properties of the systems. In this case the initial floc size for both L-glutamic acid and precipitate were similar enabling more direct comparison of the gradients which were -0.61 and -0.81 respectively and indicating that the flocs containing L-glutamic acid were more able to resist the impact of elevated shear rates. The floc strength gradient of the tannic acid system was -0.78 indicating it to be very similar to that of the precipitate whilst the actual initial floc sizes were significantly different. In such cases as the gradient is consistent but the tannic acid flocs were much bigger it suggests that the tannic acid flocs were stronger as an increased gradient would have been expected due to the larger size as seen for Albert and Penwhirn after combined treatment.

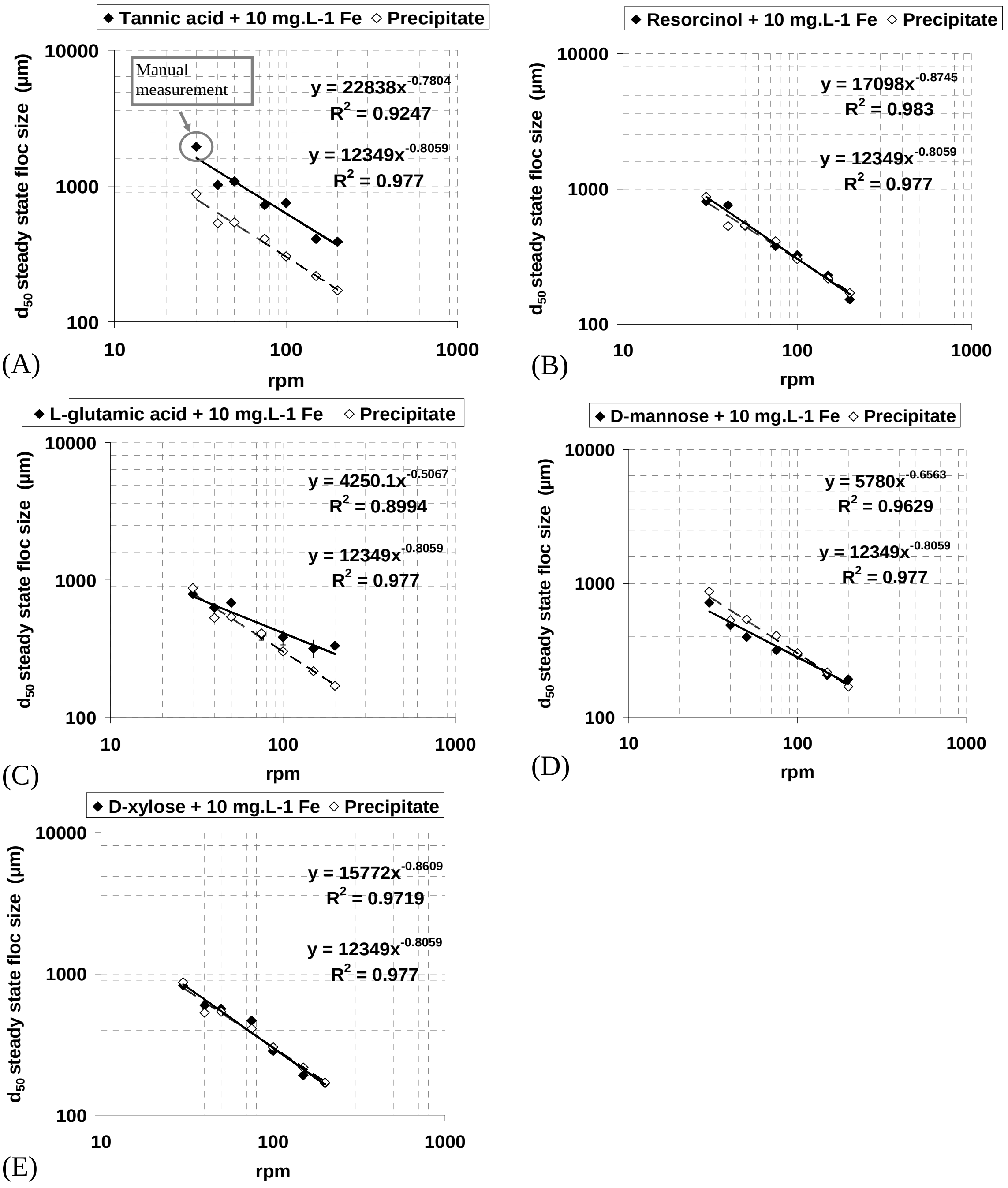


Figure 4.61 Floc strength profiles for the coagulated model compound solutions after different levels of shear: (A) Tannic acid, (B) Resorcinol, (C) L-glutamic acid, (D) D-mannose, (E) D-xylose.

In order to try to gain further understanding about how the low DOC removal levels of 10 and <5 % in L-glutamic acid and resorcinol solutions respectively had been able to influence the floc settling characteristics to such a high level, removal isotherms (Section 3.6.2) were plotted for the different model compounds (Figure 4.62).

It was seen that under addition of increasing DOC levels to the precipitate formed out of 10 mg.L^{-1} Fe after 15 minutes slow stir at pH 4.5, the solid-liquid phase concentration increased most for tannic acid and L-glutamic acid, indicating a better removal of these molecules onto precipitate. To illustrate, after addition of 7 mg.L^{-1} of DOC, the solid-phase concentration was of 0.15, 0.017, 0.028, 0.010 and 0.011 for tannic acid, resorcinol, L-glutamic acid, D-mannose and D-xylose respectively.

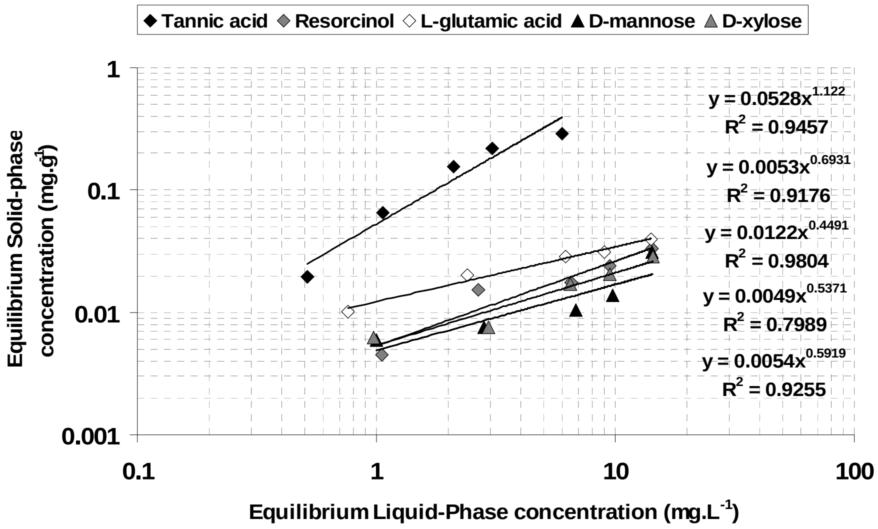


Figure 4.62 Model compounds isotherms.

Most researchers attributed NOM removal by precipitate flocs to surface coordination with carboxylic/phenolic functional groups of organic matter that exchange with oxide surface hydroxyl groups under acidic or slightly acidic pH conditions (Ochs *et al.*, 1994; Edwards *et al.*, 1996; Chen *et al.*, 2002). Other studies however claim that functional groups primary form surface oxide complexes (Gu *et al.*, 1994; Korshin *et al.*, 1997). Filius *et al.*, (2000) on the other hand found that the affinity for the ligand exchange of a carboxylate oxygen on fulvic acid and surface water groups was very low, which indicated a low chemical affinity but strong electrostatic interactions. Consequently physical adsorption (Van der Waals forces) should as well be considered as potential removal mechanism (Kummert and Stumm, 1980; Rohmann and Sontheimer, 1982).

Considering that tannic acid and L-glutamic acid have the highest removal efficiency it was concluded that the presence of dissociated functional groups could be the key for removal by precipitate. Furthermore as both model compounds had been seen to produce flocs with increased floc properties such as settleability and to a certain extent the resistance to shear the dissociated functional groups must have been able to enhance the floc structure. Interaction with the precipitate via complexation was thought to be the most probable mechanism for that. However it could not be stated which mechanism had allowed tannic acid and L-glutamic acid to produce flocs of a higher strength and settling rate, as well as how resorcinol which contained undissociated functional groups had been able to affect floc properties. Nonetheless this data confirmed at least the conclusion made that the nature of NOM enclosed in the floc can greatly influence the properties of the particle.

4.4.4 Model compound mixtures

To further investigate the impact of organic matter type on floc properties, mixtures of the model compounds were investigated. Humic acid is also included as it contains a range of molecules and has a similar HPSEC profile to that observed for the high SUVA waters of Albert and Penwhirn (Section 4.4.2).

Floc growth tests showed that after coagulation alone and combined treatment humic acid flocs grew to a d_{50} of 572 ± 43 and 993 ± 26 µm. This showed a clear improvement after magnetic resin pre-treatment in terms of floc size as observed during the trials with Albert and Penwhirn water. Sharp *et al.*, (2006c) had measured flocs containing HAF isolated from a source water to reach a d_{50} of 723 ± 33 µm after coagulation alone, which was higher than the value obtained for coagulation alone in this work but below those from combined treatment.

Comparison of flocs generated from mixtures revealed different trends. In the case of the tannic acid and L–glutamic acid mixture similar d_{50} values of 954 ± 91 µm and 882 ± 11 µm were measured after coagulation and combined treatment. Coagulation flocs were however seen to continue growing and reached a higher d_{50} value of 1050 ± 91 µm after 20 minutes, while combined treatment floc size had plateaued after 12 minutes. An opposite trend was seen in the case of tannic acid and D-mannose where the d_{50}

increased from 689 ± 181 µm for coagulation alone to 839 ± 140 µm for combined treatment. Mixtures of resorcinol with either L-glutamic acid or D-mannose resulted in d_{50} values of 879 ± 14 µm and 940 ± 83 µm respectively for coagulation and combined treatment respectively which were very similar to precipitate flocs as well as to the floc sizes obtained after coagulation of these model compounds in single solutions (Section 4.4.3). This first comparison showed that magnetic resin had influenced floc formation in the solutions containing tannic acid, however while larger flocs were formed in presence of D-mannose, smaller flocs were formed in presence of L-glutamic acid.

Floc settling tests showed that for the humic acid solution combined treatment resulted in increased floc settling velocity. Standardised 500 and 1000 µm flocs were calculated to settle at 920 (495-1770) and 1380 (730-2650) $\mu m.s^{-1}$ respectively after coagulation alone and at 3440 (1840-6600) and 4850 (2520-9100) $\mu m.s^{-1}$ respectively after combined treatment (Figure 4.63 (A)). The d_f values were of 1.68 and 1.49 after coagulation and combined treatment respectively, which would indicate a more open structure after combined treatment. From a visual comparison of the flocs in both systems it however appeared that combined treatment on humic acid resulted in denser flocs than coagulation, which were seen to consist of a myriad of smaller particles very loosely bound to each other (Appendix 4). These observations were also seen to correspond to those made for Albert and Penwhirn water (Appendix 1).

When comparing the mixed compounds it was seen that in both mixtures containing tannic acid the particles settled faster than those containing resorcinol. However it was also seen that in the mixtures containing tannic acid flocs were settling faster after combined treatment than after coagulation. To illustrate, in the case of treatment of tannic acid and L-glutamic acid solutions, standardised 500 and 1000 µm flocs were calculated to settle at 870 (470-1690) and 1880 (970-3400) $\mu m.s^{-1}$ respectively after coagulation and at 3750 (1990-5080) and 4510 (2360-8500) $\mu m.s^{-1}$after combined treatment respectively in the Figure 4.67 (A). A similar trend was seen for the tannic acid and D-mannose mixture. For this mixture standardised 500 and 1000 µm flocs were calculated to settle at 810 (430-1540) and 1540 (810-2900) $\mu m.s^{-1}$ respectively after coagulation and at 3020 (1600-5700) and 3800 (2000-7250) $\mu m.s^{-1}$ respectively after combined treatment. While in the mixtures containing resorcinol, combined treatment did not increase the settling velocity when compared to coagulation alone, resulting in settling velocities for all systems very similar to that measured for precipitate only.

The d_f values were of 1.26-2.11, 1.33-1.92, 1.82-2.03 and 2.63-2.26 after combined treatment and coagulation alone for the solutions of tannic acid and L-glutamic acid, tannic acid and D-mannose, resorcinol and L-glutamic acid and resorcinol and D-mannose. Although the d_f values were seen to decrease after combined treatment in both solutions containing tannic acid, they were seen either to increase or decrease in the solutions containing resorcinol without any alteration of the settling velocity. Therefore a correlation between d_f values and settling velocity after combined treatment could also not be made here.

The main observation made from investigating the settling velocity was that combined treatment had the same impact on increasing the settling velocity in both mixtures, while it had been seen above to result in different floc sizes depending on the presence of L-glutamic acid (reduced floc size) or D-mannose (increased floc size). When mixing Resorcinol with L-glutamic acid or Resorcinol with D-Mannose, the different impacts of L-glutamic acid and D-Mannose on floc settling velocity could not be observed.

From a visual comparison it was observed that the flocs were black after coagulation in the solutions containing tannic acid as observed for tannic acid only (Appendix 5). After combined treatment the flocs were of the same brown colour like precipitate, suggesting a lower content of tannic acid than in the flocs from coagulation only.

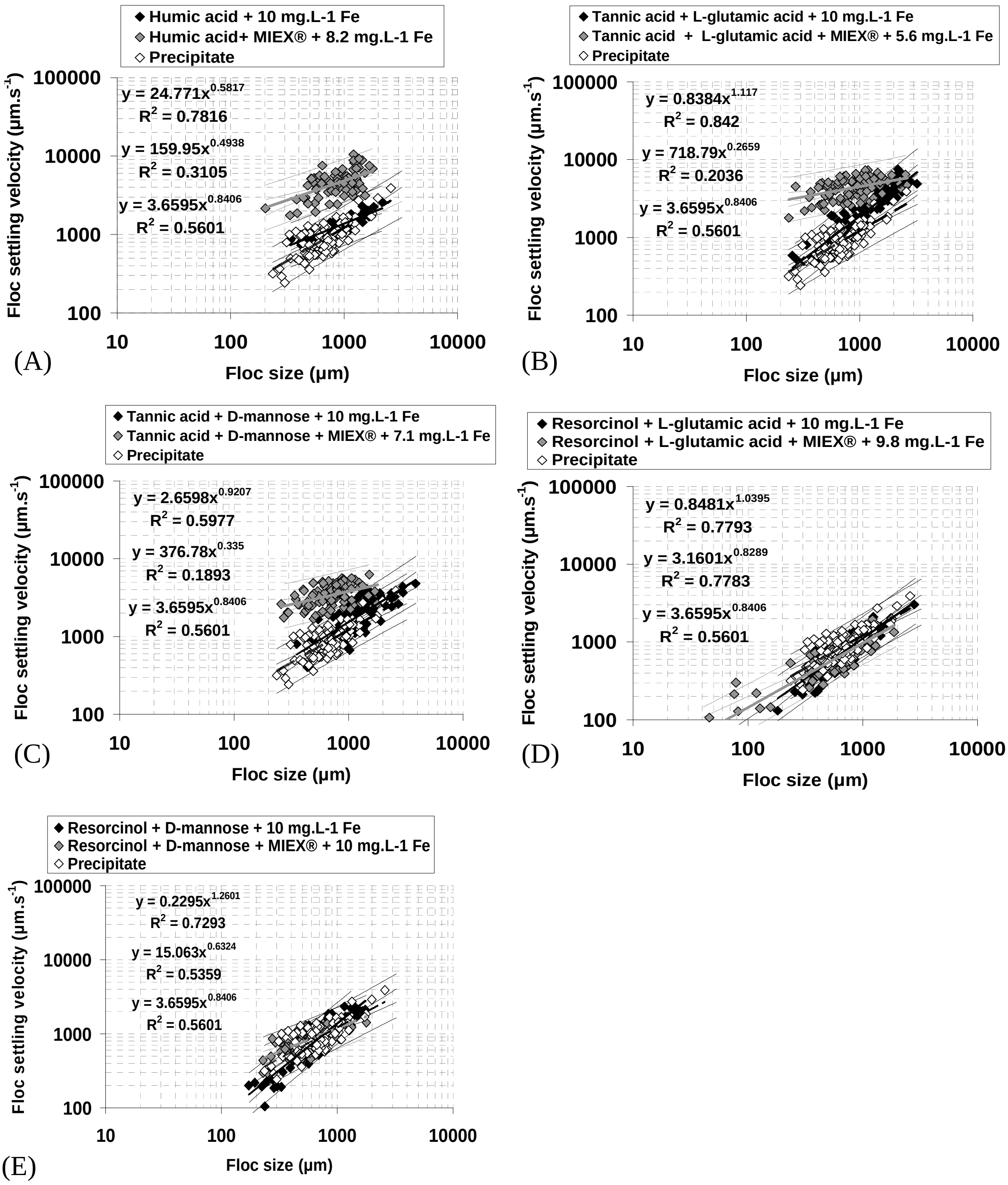


Figure 4.63 Floc settling velocity profiles for the coagulated model compound mixed solutions: (A) Humic acid vs. precipitate, (B) Tannic acid and L-glutamic acid vs. precipitate, (C) Tannic acid and D-mannose vs. precipitate (D) Resorcinol and L-glutamic acid, (E) Resorcinol and D-mannose vs. precipitate.

Floc strength factor calculations showed that humic acid flocs breakage was 50 % independently of magnetic resin pre-treatment or not. However, pre-treatment initiated the floc growth to larger size so that larger flocs were obtained upon breakage (d_{50}: 536 ± 247 μm) than after coagulation (d_{50}: 281 ± 113 μm) (Figure 4.64 (A)) as previously described for Penwhirn and Albert water. In the tannic acid and D-mannose solution flocs were seen to break down by 20 % after combined treatment and coagulation alone, while in the tannic acid and L-glutamic acid solution combined treatment resulted in a 50 % floc breakage compared to 20 % after coagulation alone (Figure 4.64 (B), (C)). This showed again that magnetic resin had influenced floc formation depending on the organic molecules present in the water. In the mixture of resorcinol and D-mannose flocs were seen to break down by 40 %, independently of combined treatment, while in the mixture of resorcinol and L-glutamic acid combined treatment flocs broke down by 40 and 35 % after coagulation alone and combined treatment (Figure 4.64 (D), (E)).

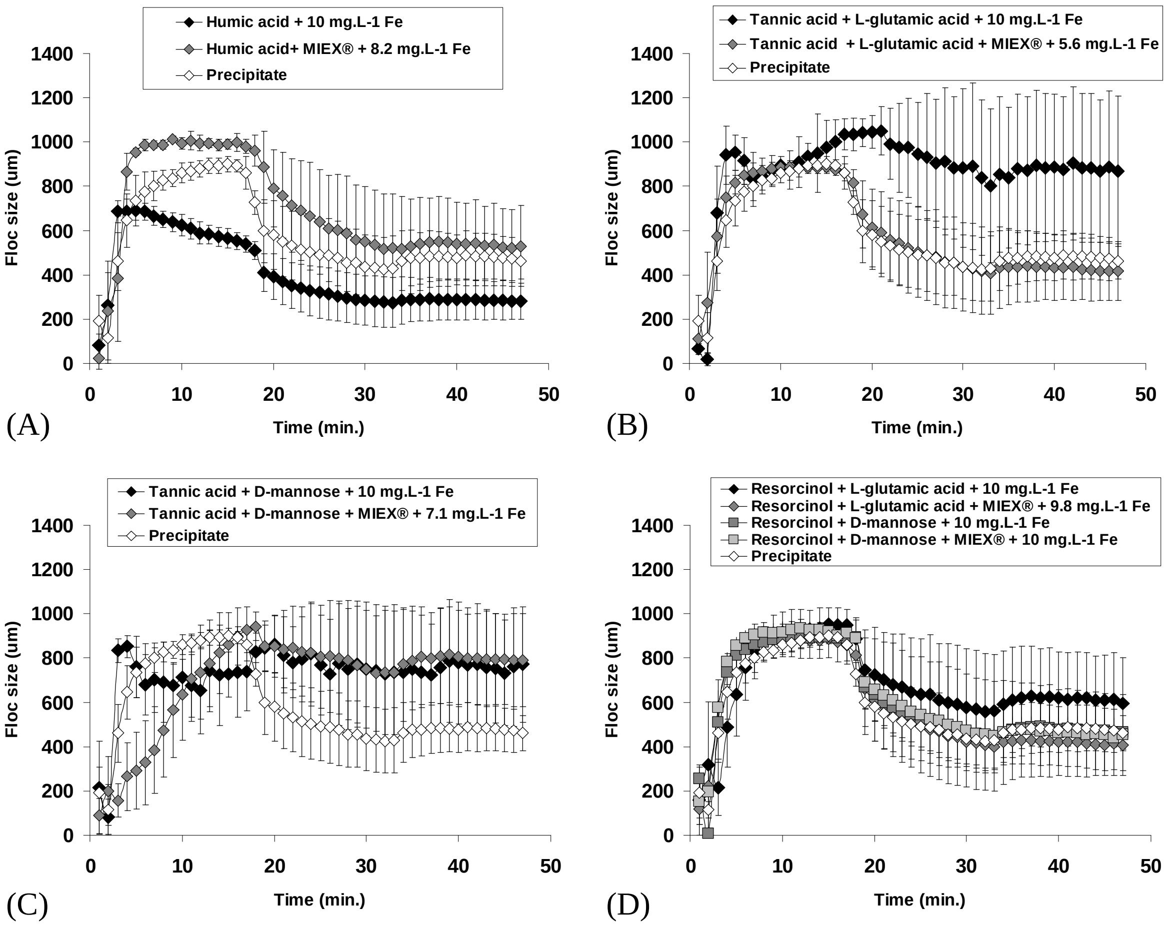


Figure 4.64 Floc growth, breakage (200 rpm) and re-growth profiles for the coagulated model compound mixed solutions: (A) Humic acid vs. precipitate, (B) Tannic acid and L-glutamic acid vs. precipitate, (C) Tannic acid and D-mannose vs. precipitate (D) Resorcinol and L-glutamic acid and resorcinol and D-mannose vs. precipitate.

Regrowth potential of all mixed systems was rather poor when compared to the source waters, as already noticed for the single compounds. All mixtures containing resorcinol were seen to re-grow to 10 % independently of pre-treatment as seen for precipitate only. The regrowth potential for all tannic acid mixtures, except tannic acid and L-glutamic acid, was <5 % after coagulation alone. Interesting was that tannic acid as a single model compound could inhibit the regrowth of the flocs (Figure 4.60 (A)) which was also reflected in the mixed systems.

Comparing the floc strength profile revealed that the presence of humic acid reduced the formed flocs size compared to the precipitate and that they remained smaller for all but the highest elevated shear rate levels (Figure 4.65 (A)). Combined treatment however resulted in larger floc sizes at all except the highest elevated shear level, as previously seen for the high SUVA source waters. Floc strength gradients of -0.55, -0.76 and -0.81 were observed for coagulation alone, combined treatment and precipitate respectively, indicating that larger flocs are less resistant to elevated shear rates and that under very high shear rates all the systems converge to a similar floc size.

No impact of the treatment on the floc size was observed for mixtures of resorcinol with either L-glutamic acid or D-mannose. Again it was noticed, that in mixture with Resorcinol, L-glutamic acid did not positively affect floc properties, in this case floc strength, in contrary to the observation made when used as a single compound (Figure 4.65 (D), (E)).

In cases of mixtures including tannic acid increased floc sizes were observed in all cases apart from the mixture with L-glutamic acid after combined treatment (Figure 4.65 (B), (C)). Comparison with the individual compounds revealed that when mixed with another compound tannic acid (L-glutamic acid and D-mannose) flocs grew to smaller size and exhibited a greater resistance to elevated shear rates than when tested as a single compound. To illustrate, the initial median floc size was 1943 μm for the tannic acid only solution compared to 882 μm when mixed with L-glutamic acid (coagulation alone). Corresponding floc strength gradients were -0.78 and -0.67 respectively. As was the case with the single compound the floc strength gradient was lower than that for the precipitate flocs and consequently the systems did not converge at high elevated shear rates indicating a higher strength.

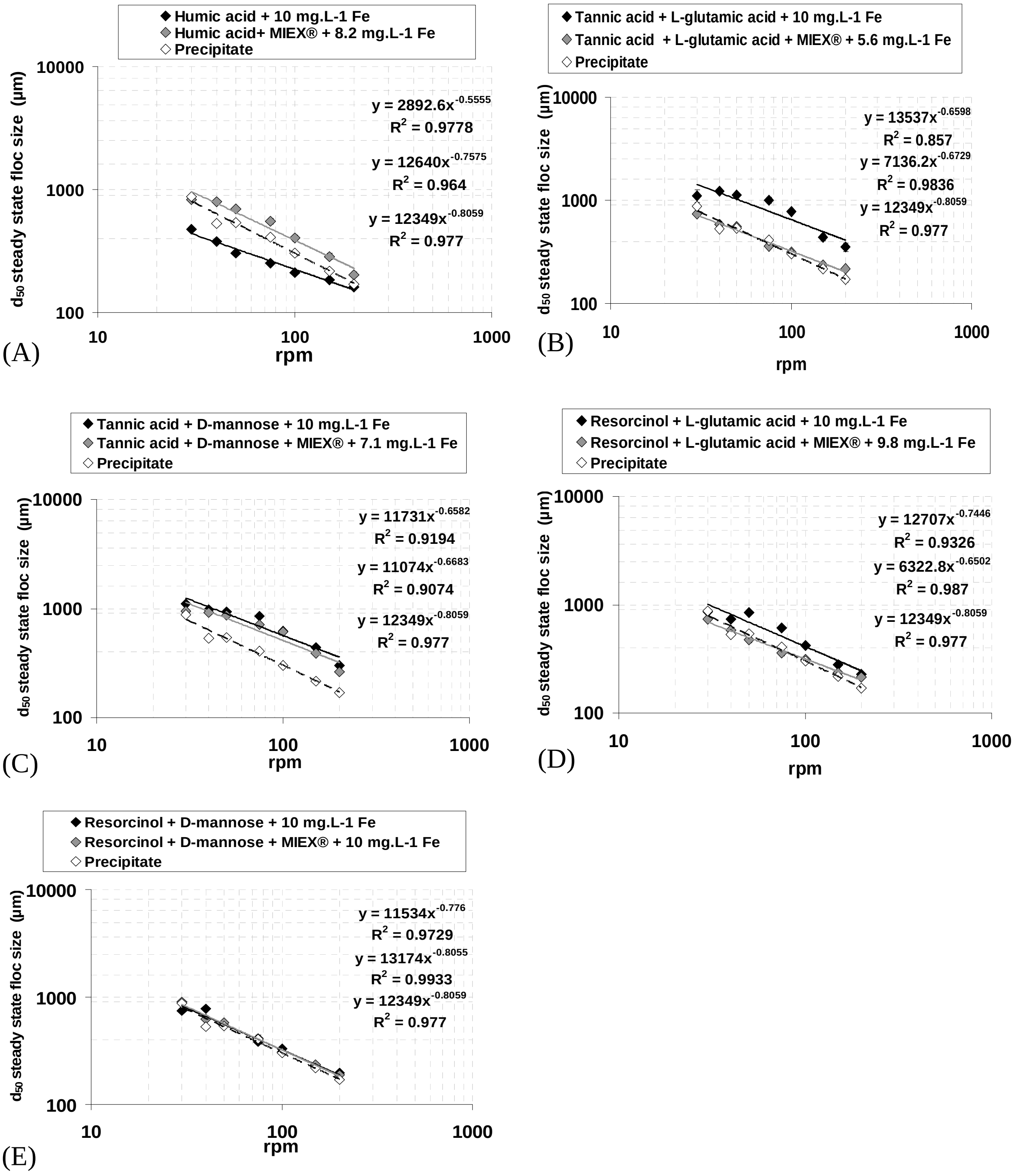


Figure 4.65 Floc strength profiles for the coagulated model compound mixed solutions after different levels of shear: : (A) Humic acid vs. precipitate, (B) Tannic acid and L-glutamic acid vs. precipitate, (C) Tannic acid and D-mannose vs. precipitate (D) Resorcinol and L-glutamic acid vs. precipitate, (E) Resorcinol and D-mannose vs. precipitate.

While this comparative data has shown that coagulation of humic acid with and without magnetic resin pre-treatment results in similar floc properties like in natural sources, the mixtures composed of two model compounds did not produce a trend directly relatable to the findings made for the source waters. However the data on the mixed model compounds supports the observation made for source waters and single model compounds that the nature of NOM affects floc properties. For example mixtures of tannic acid and D-mannose as well as tannic acid and L-glutamic acid increased the floc resistance to shear. Pre-treatment with magnetic resin however reduced the resistance of flocs to shear in the mixture containing tannic acid and L-glutamic acid, while having no impact in the mixture containing tannic acid and D-mannose. This suggested that magnetic resin had influenced the impact the organic material contained in the tannic acid and L-glutamic acid solution had on floc formation by removing a part of those compounds. Comparison of the DOC:Fe ratios showed that in both solutions combined treatment resulted in a lower content of organic material inside the flocs. To illustrate, the DOC:Fe ratios after coagulation alone and combined treatment were of 0.47:1-0.33:1 and 0.48:1-0.16:1 for tannic acid and L-glutamic acid mixture, and for tannic acid and D-mannose mixtures, excluding a potential detrimental effect of a higher organic content on floc strength. The different trends observed in terms of floc strength after combined treatment can be related to the character of the organic compounds mixtures before and after magnetic resin treatment. This was especially the case of tannic acid and L-glutamic acid which, in contrary to D-mannose, had been readily removed by magnetic resin. Also, the addition of D-mannose to tannic acid had reduced the removability of tannic acid, indicating a potential interaction between both compounds that could influence floc formation in another way, than both separate compounds. The same effect of different molecules influencing each others impact on floc formation could have resulted in the differing floc properties seen between mixtures containing resorcinol and L-glutamic acid and the solutions containing only one of those compounds. However this could not be proven in this work and further work is suggested to be done in this area.

In summary, it was seen in this section that the character of NOM is a crucial factor in the complex mechanism of floc formation by hydrolysing metal salts. This is a particularly important finding considering that easy separation of the flocs during water treatment is essential for good water quality. Magnetic resin was seen to significantly enhance floc properties in terms of floc size and settling velocity when used as a pre-treatment to coagulation in high SUVA waters. This was related to the partial removal of the low MW material by the magnetic resin and in the incorporation of a higher amount of high MW NOM into the floc matrix. Due to its polymeric structure it is possible that high MW NOM can increase the number of binding points within the floc structure as well as increase the bridging potential and the capacity to form flocs by electrostatic patch mechanisms. This would result in larger flocs with a higher effective density, allowing flocs to settle quicker. An increase of floc strength by this mechanism remains a debatable point. This was because flocs from combined treatment were able to remain on average larger than flocs formed by coagulation alone with increasing shear rates. However they broke to a higher extent and converged at one point to a similar size. Nonetheless the higher breakage rate could potentially only relate to the initial larger sizes of combined treatment flocs, making them more prone to breakage.

Parallel tests on model compounds confirmed that the character of NOM is crucial in determining the quality of flocs, but has also indicated that potential interactions between different compounds can affect floc formation. Further work is therefore suggested to be done to gain further understanding of the highly complex interactions between different organic compounds as well as their impact on floc formation.

4.5 Impact of magnetic resin treatment on downstream processes in pilot-scale

4.5.1 Aim

The aim of this section was to investigate if the impact of magnetic resin on flocs in bench-scale could be reproduced in a continuous pilot-scale system and how this would influence the downstream solid-liquid separation processes and THM formation.

4.5.2 Characteristics of raw water and magnetic resin pre-treated water

The pilot plant study carried out at Cranfield University used raw water from Albert WTW (Yorkshire Water) collected in June 2006 in addition to water pre-treated on-site with a magnetic resin pilot-plant (detailed description of both plants can be found in Section 3.4)

The raw water from Albert WTW was characterised by a high DOC level and a high UV_{254} absorbance of 7.3 $mg.L^{-1}$ and 40.4 m^{-1} respectively, but by a low turbidity of 1.7 NTU (Table 4.5). The ratio of UV_{254} absorbance to DOC level resulted in a high SUVA value of 5.5 $L.m^{-1}.mg^{-1}$ DOC indicating that Albert water contained NOM of high aromaticity and MW (Edzwald and Tobiason, 1999) as observed before.

The magnetic resin pre-treatment was carried out using an optimised dose of 30 $mL.L^{-1}$, at 13 minutes contact time and regeneration rate of 3.3 %. This treatment reduced the DOC and UV_{254} absorbance by 50 and 53 % respectively. The pre-treated water had a SUVA of 5.8 $L.m^{-1}.mg^{-1}$ DOC and was similar to that of the raw water. The turbidity of the resin treated water was 1.3 NTU, slightly lower than that measured in the raw water. This was unexpected as resin fines and fragments have been reported to increase the turbidity of the resin treated water (Nguyen *et al*., 1997). Nonetheless visual observation during continuous magnetic resin tests (Section 4.2) had shown that the amount of suspended resin in the settled water decreased rapidly with ongoing use of the resin (5-10 re-uses). This would result in a decreasing contribution of extensively used resin on the waters turbidity; however no evidence can be given for this.

When comparing the removal efficiency with those obtained from other studies on continuous pilot and full-scale magnetic resin treatment systems it was observed that it fits in with their reported DOC and UV_{254} reduction levels of 30 to 73 % and 46 to 76.7 respectively (Drikas *et al*., 2003; Allpike *et al*., 2005; Boyer and Singer, 2006; Shorrock and Drage, 2006).

Similar removal efficiency was seen for the magnetic resin pilot-scale treatment at a resin service of 1000 BV and the continuous bench-scale jar tests carried out on Albert water in October 2006 with a magnetic resin dose of 30 $mL.L^{-1}$ at 990 BV resin service, although the waters have been collected at different time periods.

This was because the 45 % DOC reduction seen in the combined product water at the end of the bench-scale test was regarded as giving a more realistic reflection of the 50 % DOC reduction seen in the pilot-scale study than a single resin treatment. In October 2006 a single use of magnetic resin in bench-scale had removed 70 % of DOC in Albert water. This would have given rise to false expectations in terms of removal efficiency if a single use of magnetic resin had been regarded as representative for the continuous process as previously done in the literature (Cook *et al*., 2002; Kim *et al*., 2005).

Table 4.5 Characteristics of Albert raw water and magnetic resin pre-treated water.

Parameters	DOC ($mg.L^{-1}$)	UV_{254} (m^{-1})	SUVA ($L.m^{-1}.mg^{-1}$ DOC)	Turbidity (NTU)	Zeta Potential (mV)
Raw water	7.3	40.4	5.5	1.7	-16.9 ± 1.9
Magnetic resin pre-treated water	3.7	21.5	5.8	1.3	-11.1 ± 3

XAD resin fractionation showed that the raw water and the magnetic resin pre-treated water were both dominated by hydrophobic NOM. (Figure 4.66). Considering that magnetic resin had removed 50 % of the DOC from the water and that the residual NOM was proportionally composed of the same mixture of fractions, no apparent preference for a specific NOM type was seen.

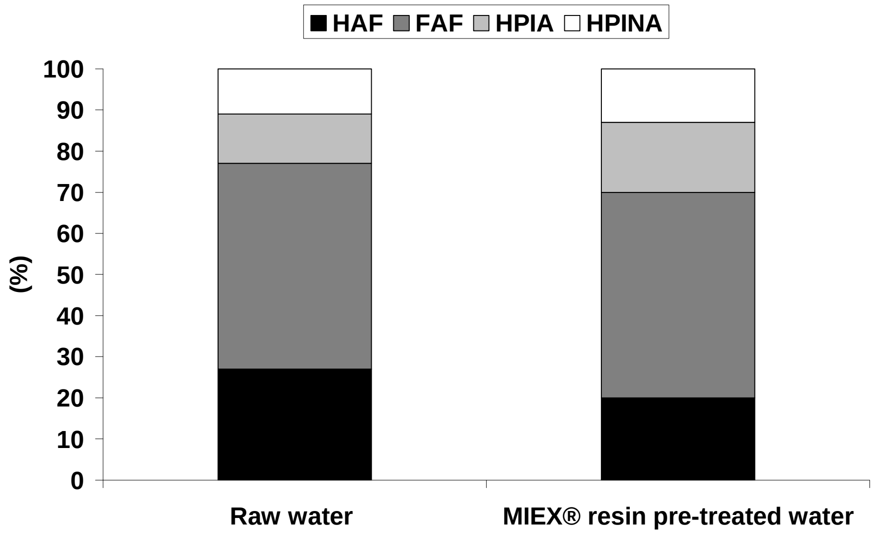
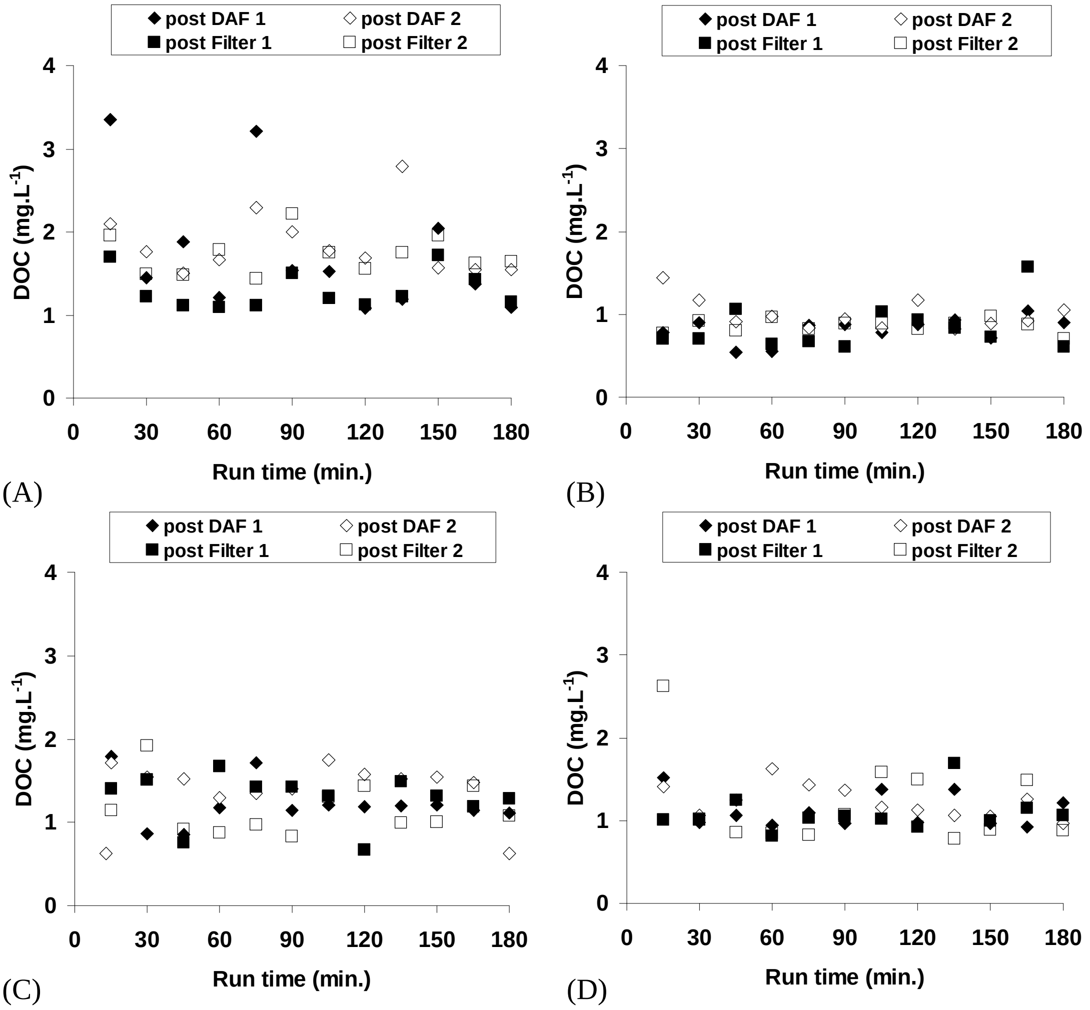


Figure 4.66 Fractionation of Albert raw water and magnetic resin pre-treated water.

4.5.3 Coagulation and combined treatment

Coagulation of Albert raw water was carried out at a Fe dose of 7.7 mg.L^{-1} Fe at a pH of 4.2 to be in accordance with the conditions used at the WTW during the time of abstraction. Combined treatment consisted of coagulation of the magnetic resin pre-treated water with Fe doses reduced by 50 (3.8 mg.L^{-1} Fe), 60 (3.0 mg.L^{-1} Fe) and 70 % (2.3 mg.L^{-1} Fe). No noticeable difference in terms of DOC reduction was observed post DAF and sand filtration for these three combined treatment systems. But differences in terms of DOC removal efficiency were observed when comparing combined treatment to coagulation alone. Coagulation alone gave a DOC reduction of 80 % with effluent values of 1.4 ± 0.3 mg.L^{-1} (Figure 4.67), while combined treatment using a 60 and 70 % coagulant reduction gave a slightly better removal of 83 % with residual DOC values of 1.2 ± 0.3 mg.L^{-1} and 1.1 ± 0.4 mg.L^{-1}. Combined treatment using the 50 % Fe reduction gave the best DOC removal with average values of 0.9 ± 0.2 mg.L^{-1} (88 % reduction).

The UV$_{254}$ absorbance showed similar trends, where coagulation alone gave a UV$_{254}$ absorbance reduction of 92 % giving a residual level of 2.9 ± 0.6 m^{-1}. Combined treatment with a 50, 60 and 70 % Fe reduction increased removal of the UV$_{254}$ absorbance to values of 1.3 ± 0.3 m^{-1} (97 %), 1.6 ± 0.6 (96 %) m^{-1} and 1.9 ± 0.8 m^{-1} (95 %) respectively. This resulted in SUVA levels of 2, 1.4, 1.3 and 1.7 L L.m^{-1}.mg^{-1} DOC for coagulation, magnetic resin + 3.8 mg.L^{-1} Fe, magnetic resin + 3.0 mg.L^{-1} Fe and magnetic resin + 2.3 mg.L^{-1} Fe respectively. While it was seen that the combined treatment increased the DOC removal in comparison to coagulation alone, it also showed to reduce the SUVA level of the water to a greater extent.



(A) (B)

(C) (D)

Figure 4.67 DOC of water treated by coagulation and by combined treatment (A) 7.7 mg.L^{-1} Fe, (B) Magnetic resin + 3.8 mg.L^{-1} Fe, (C) Magnetic resin + 3.0 mg.L^{-1} Fe, (D) Magnetic resin + 2.3 mg.L^{-1} Fe.

The HPSEC profiles showed that the raw water collected from Albert reservoir in June 2006 had a characteristic first peak eluting around 5.8 minutes elution time, as previously seen in Section 4.2.5.4, and indicated material of an approximate MW >5 kDa. This peak was followed by a major peak eluting at 8.3 minutes also indicating material of an approximate MW >5 kDa, which was however classified due to longer retention times as being of lower MW than the NOM of the first peak. This was followed by several smaller peaks between 9 and 10.5 minutes elution time, which indicated material of an approximate MW of 2 to 0.5 kDa (Figure 4.68 (A)).

Magnetic resin treatment removed the second peak at 8.3 minutes elution time, while the first peak at 5.8 minutes elution time was only slightly reduced as previously seen for Albert water (Section 4.2.5.4). Combined treatment was able to completely remove the first peak as well as to increase the removal of the second peak when compared to coagulation alone.

For the low MW material, eluting between 9 and 10.5 minutes, coagulation alone was able to remove more NOM than magnetic resin (Figure 4.68 (B)). However combined treatment systems increased the removal of the low MW NOM, independently of the applied coagulant dose, as previously seen in high SUVA waters (Section 4.3.6), as well as by Fearing *et al*., (2004) and Jefferson *et al*., (2004).

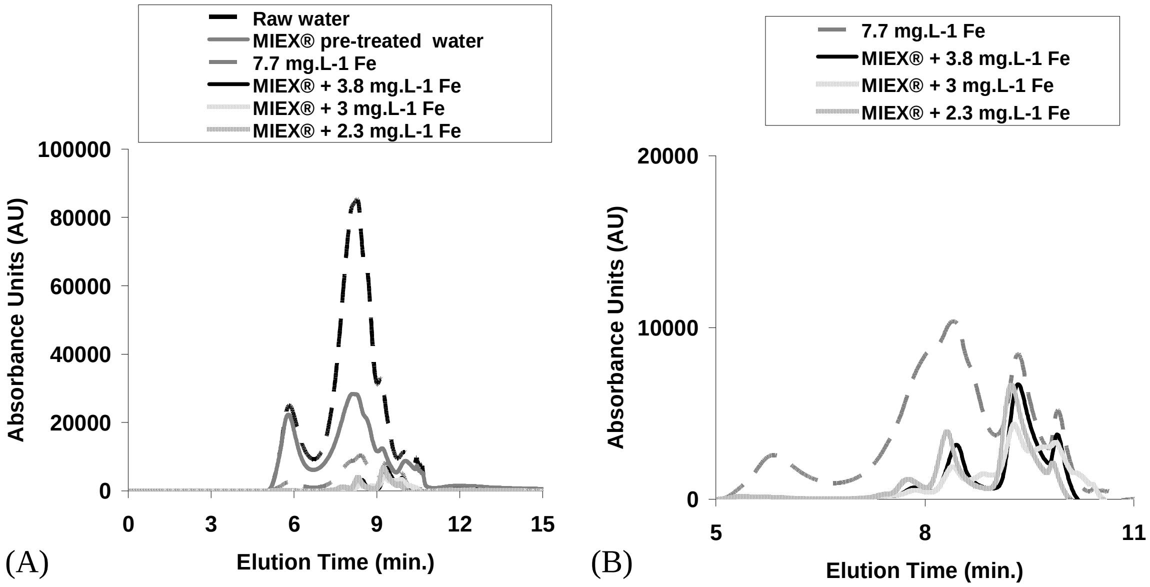
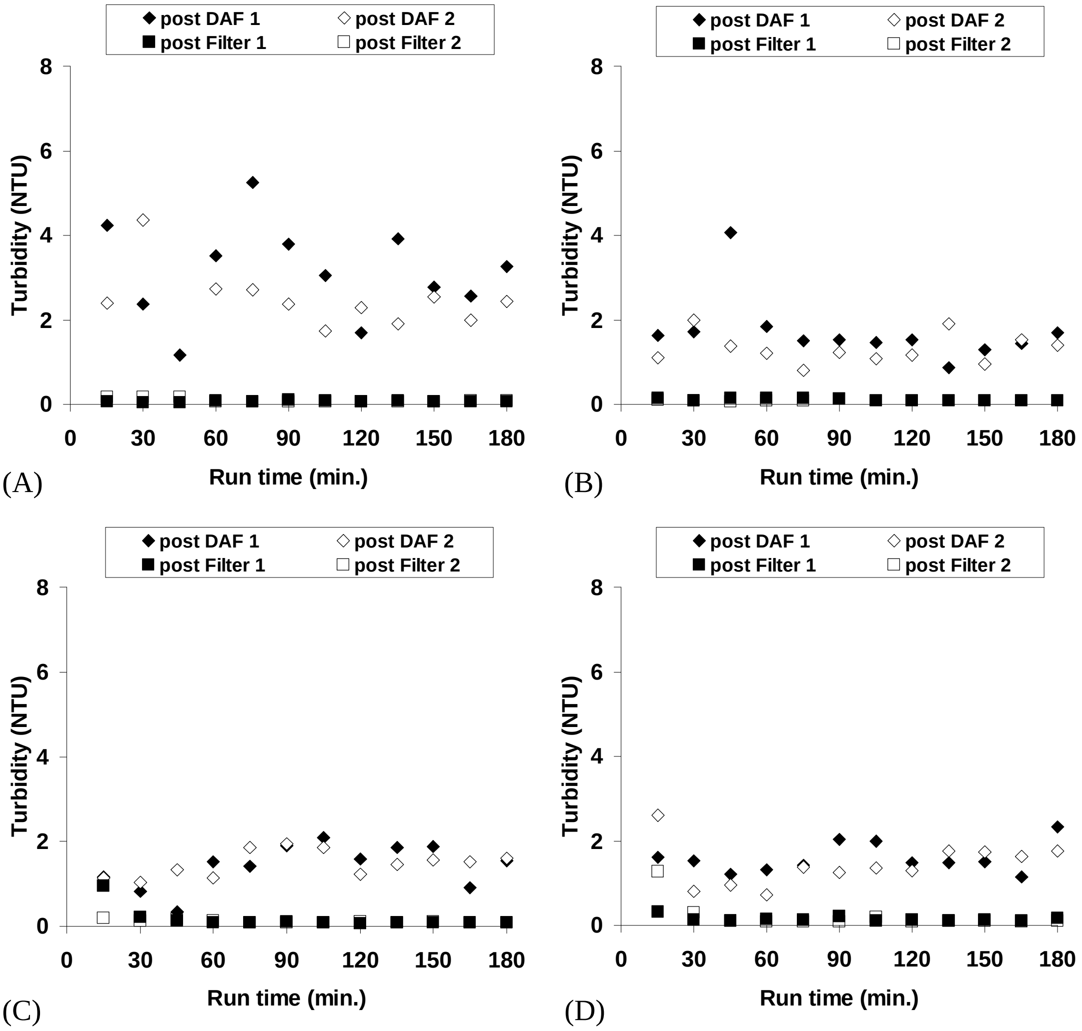


Figure 4.68 HPSEC Profiles of Albert raw water and investigated treatment systems (A) All treatment options, (B) Coagulation alone and combined treatment.

The turbidity after DAF was 3.8 ± 1.5 NTU for coagulation, whilst it was of 1.5 ± 0.6 NTU after combined treatment regardless of the reduced coagulant dose used (Figure 4.69). As an indication of particle removal efficiency the turbidity measured in the flocculator for coagulation was 19 NTU, whilst for combined treatment it was of 38 NTU, which showed a better clarification for the latter one.

Sand filtration for coagulation and combined treatment (50 % and 60 % coagulant dose reduction) gave similar average values of 0.04 ± 0.01 NTU and 0.03 ± 0.02 NTU respectively. Some deterioration and more unstable turbidity after sand filtration were seen for combined treatment using a 70 % coagulant reduction. This was reflected by an increased average residual of 0.06 NTU and higher standard deviation of ± 0.11 NTU.



(A) (B) (C) (D)

Figure 4.69 Turbidity of water treated by coagulation and by combined treatment (A) 7.7 mg.L^{-1} Fe, (B) Magnetic resin + 3.8 mg.L^{-1} Fe, (C) Magnetic resin + 3.0 mg.L^{-1} Fe, (D) Magnetic resin + 2.3 mg.L^{-1} Fe.

A comparison of the removal consistency of the compared treatment systems in terms of DOC and turbidity represented in curves indicating the 10 to 90 percentiles under the value shown on the x axis showed the same removal trends as seen in Figure 4.69 in time series. These curves indicating the 10 to 90 percentiles under the value give an indication of the robustness of the treatment. In the context of this thesis, the definition of a robust system has been taken from Huckey and Coffey (2004) as “a system that provides excellent performance under normal conditions and deviates minimally from this during periods of upset or challenge”. The robustness of the different treatment systems were evaluated here by looking at the mean residual values and the slope of the linear regression between the 10 to 90 percentiles of the samples. A steeper slope through the data across this range indicated a more robust treatment around the average than for a system with a widespread of data around the average.

Combined treatment using a 50 % coagulant dose reduction showed however to provide consistently the lowest DOC residuals after both DAF and sand filtration, as reflected by the steepest slopes of 231.1 and 285.1 respectively (Figure 4.70 (A), (B)). Combined treatment using a 60 % and 70 % coagulant reduction (slopes of between 101.9 and 136.8) was above coagulation which had the shallowest slopes (77.8 and 101.1). For turbidity removal a similar trend was seen after DAF where combined treatment gave a consistently better turbidity removal when compared to coagulation (Figure 4.70 (C)). This was reflected by the steep slopes of the data lines generated for combined treatment (83.5 to 119.1), whereas the data line for coagulation which spanned a greater range of turbidity provided a shallower slope (30.9).

Turbidity after sand filtration was more consistent across 80 % of the samples (Figure 4.70 (D)). This was particularly the case for coagulation and combined treatment using a 50 % and 60 % coagulant reduction where the slopes ranged from 638.7 to 982.8. Combined treatment using a 70 % coagulant dose reduction had a shallower slope of 446.2 indicating a higher average turbidity as well as a greater widespread of results. Beside this it was observed that filter ripening times of 15 to 20 minutes for coagulation and combined treatment using a 50 % and 60 % reduced coagulant dose increased to 30 to 40 minutes when using combined treatment with a 70 % coagulant dose reduction.

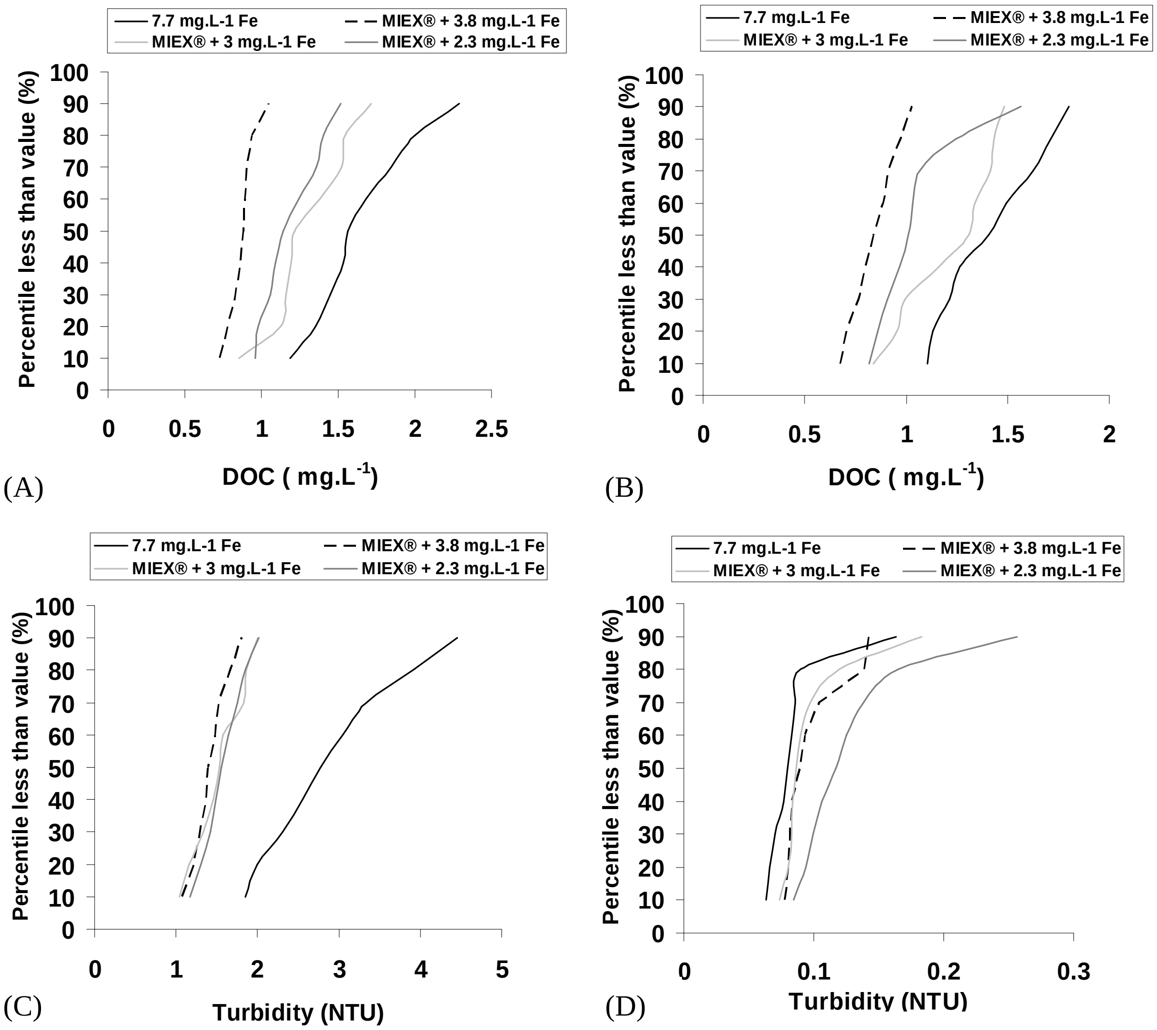


Figure 4.70 Robustness of water quality after treatment by coagulation and by combined treatment (A) Post DAF DOC , (B) Post Filter DOC, (C) Post DAF turbidity, (D) Post Filter turbidity.

This trend of reduced turbidity removal and increased filter ripening times when applying a low coagulant dose (70 % reduction) in combined treatment was because of insufficient removal of charged NOM. This was identified by a more negative zeta potential of -10.2 ± 3.9 mV of the coagulated suspension compared to values of between -1.6 ± 3.0 and -4.4 ± 5.9 mV for all the other coagulated systems.

Considering that Parsons *et al.*, (2004) and Sharp *et al.*, (2004) showed that optimum DOC removal occurs within a zeta potential window of +5 and -10 mV it was observed that the highest coagulant reduction (70 %) is on the edge of the lower limit of the zeta potential required for optimum charge neutralisation and destabilisation of NOM (Duan and Gregory, 2003). Particle capture mechanisms during filtration are however strongly dependent on charge as sand is predominantly negatively charged (Jegatheesan and Vigneswaran, 2005). Shaw *et al*., (2000) reported for sand a zeta potential of -25 mV at pH 4, which was close to the pH conditions used in the study (pH 4.2). Repulsion between sand and the negative suspension when coagulant was under-dosed would explain why the filter ripening period increased and higher filtered turbidities (0.06 ± 0.11 NTU) were seen after sand filtration. From this it was concluded that the adequate coagulant dose must be applied after magnetic resin pre-treatment to maintain robust treatment.

4.5.4 Floc characteristics

Further investigation of the improved turbidity removal by DAF for combined treatment were undertaken by analysing the structural characteristics of the flocs using the laboratory jar testing methods described in Section 3.7. It was decided to coagulate water at bench-scale for floc characterisation, rather than to extract flocs from the pilot plant as physical alteration of their properties during transport to the laboratory could not be guaranteed. Raw water was coagulated in a jar tester under the same conditions as used in the pilot–scale testing and compared to water pre-treated in the magnetic resin pilot-plant and coagulated in a jar tester using a 60 % coagulant reduction. This dose was chosen because significantly improved turbidity was seen at this dose reduction using the pilot plant compared to coagulation, whilst similar DOC removal and a large coagulant saving could be achieved.

A comparison of the median floc size (d_{50}) after 15 minutes growth time showed that combined treatment led to substantially larger flocs (d_{50}: 970 ± 15 µm) in this high SUVA water than coagulation alone (d_{50}: 620 ± 15 µm) (as already seen in Section 4.4.2) (Figure 4.71). This indicated that flocs from combined treatment are stronger, as the strength of a floc has previously been described to be directly related to its size (Parker *et al*., 1972; Matsuo and Unno, 1981; Muehle, 1993; Spicer and Pratinsis, 1996; Mikkelsen and Keiding, 2002).

It was also noticed that the flocs produced by the combined treatment required 15 minutes of growth to reach their final size, compared to 8 minutes for coagulation only.

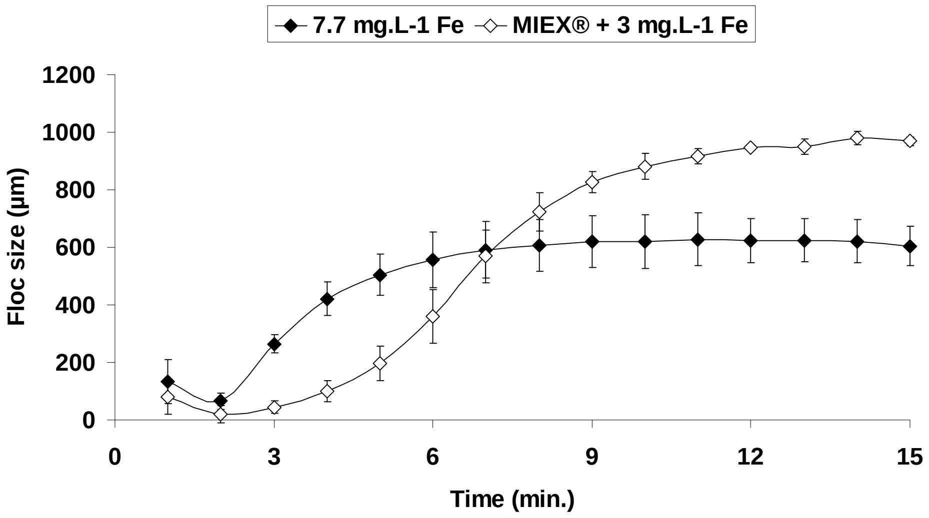


Figure 4.71 Floc growth for 7.7 mg.L^{-1} Fe and magnetic resin + 3.0 mg.L^{-1} Fe.

The floc settling velocity also confirmed that combined treatment enhanced floc settling rates in high SUVA waters. When standardising the floc size to 500 µm and 1000 µm, settling velocities of 750 and 1070 µm.s^{-1} were calculated for coagulation alone (Figure 4.72). In comparison, increased settling velocities of 1080 and 1550 µm.s^{-1} were calculated for standardised floc sizes of 500 µm and 1000 µm respectively from combined treatment. A calculation of the 95 % confidence interval showed that for coagulation the confidence limits for 500 µm and 1000 µm sized flocs ranged from 550 to 1020 and from 780 to 1470 µm.s^{-1} respectively. For combined treatment the confidence limits for 500 µm and 1000 µm ranged from 750 to 1600 and from 780 to 1470 µm.s^{-1} respectively. An overlap of the data was therefore seen, but combined treatment produced on average a faster settling floc, which was as previously done thought to be related to changes in the effective density of the flocs (Section 4.4.2). But again there was no difference between the d_f value (1.52) for both systems, which also showed here no direct correlation between fractal dimensions and settling properties. In a visual comparison flocs from combined treatment were also seen in this case to be of a more compact structure than those from coagulation, which allows them to settle faster (Yukselen and Gregory, 2004) (Appendix 6).

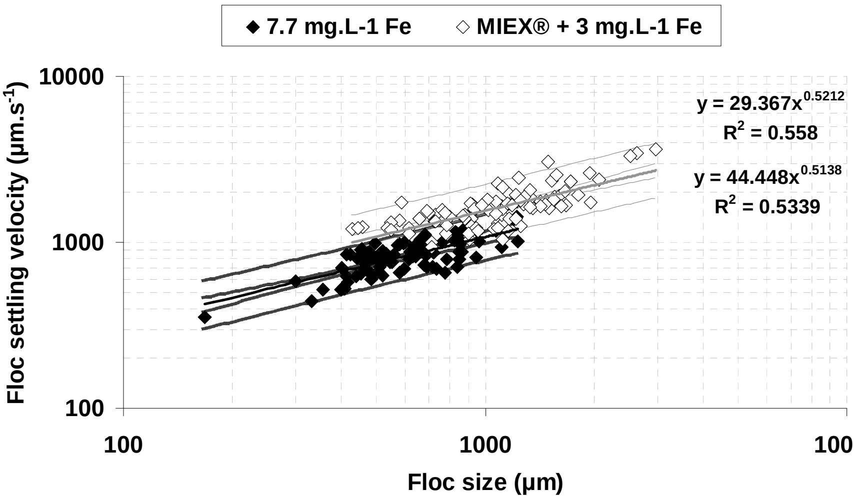


Figure 4.72 Floc settling velocity for 7.7 mg.L^{-1} Fe and magnetic resin + 3.0 mg.L^{-1} Fe.

A comparison of the DOC:Fe ratio gave values of 1.58:1 and 1.22:1 for combined treatment and coagulation alone, indicating again that larger floc sizes after combined treatment cannot be related to a higher level of inorganic material in the floc matrix (Bache *et al*., 1999). Considering that HPSEC profiles (Figure 4.68) had shown that NOM of the highest MW was barely removed by magnetic resin, the improved floc properties in terms of size and settling, were again related to the previously described bridging and compaction effect of large molecules inside the floc matrix (Section 4.4.2).

From the third test method for floc strength evaluation based on exposing flocs to different levels of shear it was also observed in this case that flocs from combined treatment were more sensitive to stress (Figure 4.73). This was because the steeper gradients were again obtained for combined treatment by constructing floc strength plots. To illustrate, floc strength gradients of -1.12 and -0.58 were obtained for combined treatment and coagulation respectively. Nonetheless the fairness of this test is also questioned here, because of the natural tendency of large flocs to break and hence generate a larger gradient (Argaman & Kaufman, 1970; Thomas *et al*., 1999).

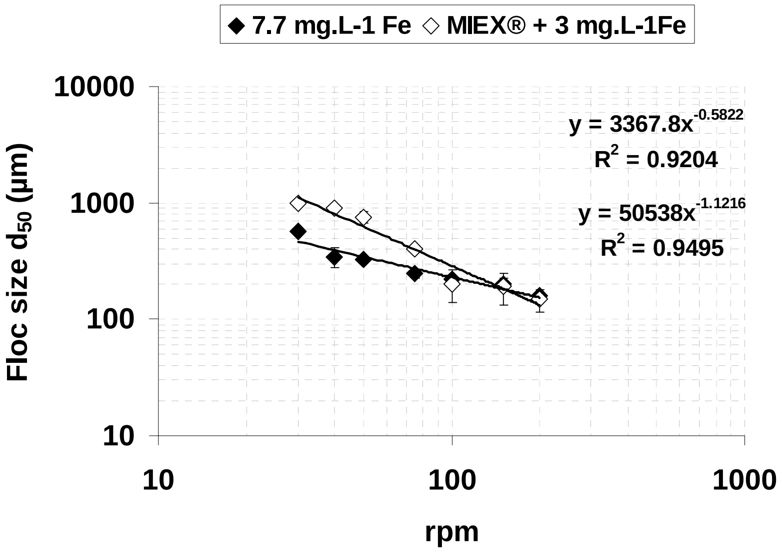


Figure 4.73 Floc strength profiles (d_{50}) for coagulation alone and combined treatment.

Although there is no strong correlation between turbidity and particle number (Beard and Tanaka, 1977), it was assumed that the lower post DAF turbidity for combined treatment indicated a lower particle count. As coagulation alone had shown to have a lower pre DAF turbidity in the flocculators this would mean that the particles had been less efficiently removed and resulted in a higher post DAF turbidity.

An analysis of the volumetric floc size distribution from both compared systems showed that coagulation was more effected by increased shear rates in terms of breakdown to small particles sizes (Figure 4.74). At low shear conditions (30 rpm) at which floc growth measurements were undertaken showed that 20 % and 8 % of flocs from coagulation and combined treatment respectively were <300 µm. When increasing the shear rate to 40 rpm, a significant increase in particles <300 µm for coagulation was observed (40 %), whilst no increase of that size class was seen for combined treatment flocs. When increasing the rpm to a maximum of 200 the difference in number of flocs <300 µm rose to similar values for coagulation (87 %) and combined treatment (92 %) respectively. However when comparing the percentage of very small flocs <50 µm at 200 rpm it was observed that 10 % of particles were below this size for coagulation alone, while it was only 4 % for combined treatment. Although those numbers do not indicate how many flocs of this reduced size existed, they indicated at least that coagulation alone flocs were more prone to breaking down to smaller sizes. This made flocs from coagulation alone more difficult to remove during flotation. This was because work on flocs has shown that floc rise rates during flotation are related to particle size with smaller flocs having much lower rise velocities than large flocs. This results from smaller particles having a lower probability of contact between bubble and floc than larger particles (Boller and Blaser, 1998; Ljunggreen *et al*., 2004).

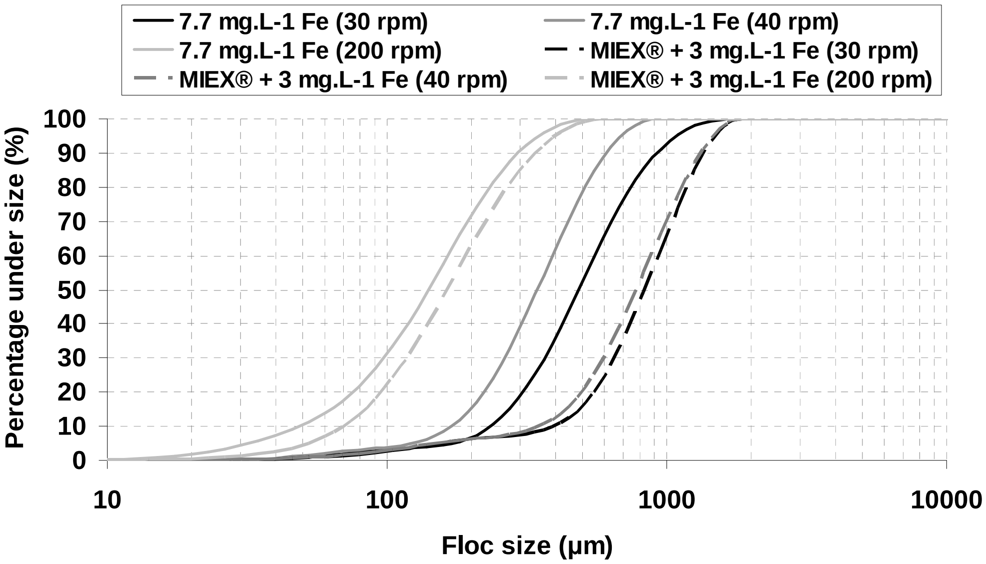


Figure 4.74 Comparison of volumetric floc size distribution after different periods of increased shear with and without magnetic resin pre-treatment.

However the translation of shear rates in the bench-scale jar tester to those likely to occur in DAF is not simple. While being difficult to model due to the complex flow and shear patterns, the average shear rates in DAF have been estimated to be between 1000 to 7600 s^{-1} (Masschelein, 1992; Fukushi *et al*., 1995). The average velocity gradients in the jar tester apparatus have been calculated as 175 s^{-1} (Section 3.7.2). However other modelling work has shown that in a zone around the blade and wall of the jar tester, the average velocity gradient can be of 554 s^{-1} (Bouyer *et al*., 2001). Furthermore, modelling using computational flow dynamics (CFD) has identified in a jar tester regions with an average velocity gradient around 2000 s^{-1} (Korpijarvi *et al*., 2000). It was therefore likely that some of the shear rates experienced by a floc in a jar tester at high rpm may approach those experienced in a DAF, making comparisons possible.

From the above data based on volumetric floc size distribution (Figure 4.74) it was seen, as deducted from the floc growth test and settling velocity, that combined treatment enhances floc strength and thereby is also beneficial for solid-liquid separation by DAF. This was because flocs from combined treatment were able to maintain a larger particle size distribution, reducing the turbidity load going onto the filter and giving rise to longer filter run times.

Considering that volumetric floc size distribution had been the tool allowing making the observation that combined treatment was less effected by increased shear rates in terms of breakdown to small particles sizes, it would be suggested here to make it a standard investigation method for floc strength.

4.5.5 THMFP of treated water

The investigation of the impact of the different treatment systems on the THMFP showed that magnetic resin treatment alone reduced the overall THMFP of 424 ± 4 $\mu g.L^{-1}$ in the raw water to 164 ± 18 $\mu g.L^{-1}$ (Table 4.6). Coagulation alone reduced the overall raw water THMFP to a similar level of 170 ± 20 $\mu g.L^{-1}$. Combined treatment was however able to reduce the overall THMFP for the water from the pilot plant to the highest extent. The overall THMFP values were of 110 ± 43, 105 ± 33 and 110 ± 42 $\mu g.L^{-1}$ after combined treatment using a 50, 60 and 70 % coagulant dose reduction.

This highest level of overall THMFP reduction by combined treatment was in accordance with Fearing *et al.*, (2004). In that study the overall raw water THMFP of 685 $\mu g.L^{-1}$ (SUVA: 4.5 $L.m^{-1}.mg^{-1}$ DOC) was reduced to 34 $\mu g.L^{-1}$ by combined treatment. However in contrary to our work, it was seen by Fearing *et al.*, (2004), that magnetic resin treatment resulted in a much higher overall THMFP (225 $\mu g.L^{-1}$) than coagulation alone (62.5 $\mu g.L^{-1}$). In that study this observation was related to the higher SUVA level after magnetic resin (4.6 $L.m^{-1}.mg^{-1}$ DOC) than after coagulation (1.0 $L.m^{-1}.mg^{-1}$ DOC) and combined treatment (0.5 $L.m^{-1}.mg^{-1}$ DOC). This was because aromatic NOM had been described to form more THMs than non-aromatic NOM (Krasner *et al.*, 1996; Kitis *et al.*, 2001). Indeed specific reactivity values of 59.6, 59.2, 22.3 and 11.7 $\mu g.mg^{-1}$ C were calculated for raw water, magnetic resin treatment, coagulation and combined treatment for Fearing *et al.*, (2004).

Table 4.6 THMFP of Albert water and of the investigated treatment systems.

	DOC ($mg.L^{-1}$)	SUVA ($L.m^{-1}.mg^{-1}$ DOC)	THMFP ($\mu g.L^{-1}$)	THMFP ($\mu g.mg^{-1}$ C)
Raw water	7.3	5.5	424 ± 4	44 ± 4
Magnetic resin treated water	3.7	5.8	164 ± 18	58 ± 12
7.7 $mg.L^{-1}$ Fe	1.4	2	170 ± 20	85 ± 14
Magnetic resin + 3.8 $mg.L^{-1}$ Fe	0.9	1.4	110 ± 43	122 ±48
Magnetic resin + 3.0 $mg.L^{-1}$ Fe	1.2	1.3	105 ± 33	92 ± 27
Magnetic resin + 2.3 $mg.L^{-1}$ Fe	1.1	1.7	110 ± 42	92 ± 38

In contrary to the results of Fearing *et al*., (2004) an increase of the specific reactivity of DOC with a decrease of SUVA was observed for the work on the Cranfield pilot plant. For the raw water (SUVA: 5.5 $L.m^{-1}.mg^{-1}$ DOC) and magnetic resin treated water (SUVA: 5.8 $L.m^{-1}.mg^{-1}$ DOC), specific reactivity values of 44 ± 4 and 58 ± 12 $\mu g.mg^{-1}$C respectively were calculated. While for coagulation (SUVA: 2 $L.m^{-1}.mg^{-1}$ DOC) and combined treatment with 50 % Fe reduction (SUVA: 1.4 $L.m^{-1}.mg^{-1}$ DOC) specific reactivity values of 85 ± 14 and 122 ± 48 $\mu g.mg^{-1}$ C respectively were calculated. Combined treatment with 60 (SUVA: 1.3 $L.m^{-1}.mg^{-1}$ DOC) and 70 % Fe reduction (SUVA: 1.7 $L.m^{-1}.mg^{-1}$ DOC) had both specific reactivity values of 92 ± 27 and 92 ± 38 $\mu g.mg^{-1}$ C respectively.

Luong *et al*., (1982) hypothesised that during chlorination humic substances, which have a high MW and SUVA level, consume a part of the chlorine for the “activation” of their structure through oxidation reactions to produce active sites followed by substitution reactions with chlorine. Therefore exposing isolated lower MW NOM to the same chlorine dose may provide a higher driving force for organo-chlorine formation since less chlorine is required for the partial molecule oxidation and resulting in a high specific reactivity of NOM of low SUVA and MW. Goslan *et al*., (2002) also showed this trend when chlorinating four different MW fractions isolated by ultrafiltration from raw water. Here material of low SUVA and low MW had a higher specific reactivity. The MW cut-offs of 1-0.5 kDa (SUVA: 2.5 $L.m^{-1}.mg^{-1}$ DOC) and <0.5 kDa (SUVA: 2.0 $L.m^{-1}.mg^{-1}$ DOC) had a specific reactivity of 144.7 and 154.2 $\mu g.mg^{-1}$ C respectively while the MW cut-offs >3 kDa (SUVA: 5.2 $L.m^{-1}.mg^{-1}$ DOC) and 3-1 kDa (SUVA: 3.7 $L.m^{-1}.mg^{-1}$ DOC) had a specific reactivity of 19 and 49.6 $\mu g.mg^{-1}$ C respectively.

From the above findings on the high specific reactivity of NOM of low SUVA and MW it was concluded that the observed comparable overall THMFP values after magnetic resin treatment and coagulation alone were related to different levels of specific reactivity of the residual organic material. To illustrate, after magnetic resin treatment more DOC, of higher SUVA and MW, but lower specific reactivity was seen to be left in the water. While less DOC of lower SUVA and MW, but higher specific reactivity was left after coagulation alone in the water.

Considering that the lowest level of residual DOC, and low MW NOM but highest specific reactivity was seen after combined treatment, it was concluded that the lowest overall THMFP observed in these samples was only due to the highest DOC removal in these samples, especially in the low MW area. As magnetic resin had previously been shown to efficiently remove low MW material (Section 4.2.6.1), a connection between combined treatment and lowest residual DOC and overall THMFP in this high SUVA source was anticipated. This was especially because in a comparative study by Drikas *et al*., (2003) on a low SUVA water with one peak, indicating a MW of 1-2 kDa for NOM, the application of magnetic resin resulted in the lowest residual overall THMFP. Similar specific reactivity values of 37.8, 37 and 33.6 $\mu g.mg^{-1}$ C were measured for the raw water, coagulation alone and magnetic resin treatment in that study. Therefore the highest reduction of the overall raw water THMFP, by magnetic resin when compared to coagulation was related to the lower residual DOC in the former sample (Magnetic resin: 1.4 $mg.L^{-1}$, coagulation alone: 2.1 $mg.L^{-1}$), showing the advantage of magnetic resin to reduce the THMFP by removing low MW NOM fractions recalcitrant to coagulation.

In summary it was seen in this section, that combined treatment improved the DOC and overall THMFP reduction when compared to coagulation alone. The lower overall THMFP was thereby inferred to result from the improved DOC reduction, especially of low MW organic molecules with a high specific reactivity.

Turbidity after DAF was also seen to be lower after combined treatment than after coagulation and was related to higher floc strength in the former system. This is because floc strength characterisation inferred that flocs from combined treatment would be able to withstand higher shear in the DAF process than flocs from coagulation alone. This insured that combined treatment flocs maintained a larger particle size distribution, increasing their probability of contact with air bubbles and successfully float from the system. This would reduce the solids load going onto the sand filter and give rise to longer filter run times. Post sand filter turbidity was seen to be the same for coagulation only and combined treatment using 50 and 60 % coagulant dose reduction. Combined treatment using a 70 % coagulant dose reduction gave rise to slightly higher and more unstable post sand filter turbidities. This was related to insufficient removal of charged NOM in this treatment system, identified by the most negative zeta potential and inferred to result in a mechanism of repulsion with the negatively charged sand. This observation shows that adequate coagulant dosing is crucial to maintain robust treatment.

4.6 Magnetic resin regenerant solution

4.6.1 Aim

The aim of the research reported in this section was to gain greater insight into the characteristics of NOM removed by magnetic resin. Regenerant solutions produced by the regeneration of magnetic resins used in different WTWs with brine were analysed since it was hypothesised that the regenerant would only contain the NOM removed during treatment. The regenerant was also compared to raw and coagulated water samples from the same sources.

4.6.2 Comparison of raw water and magnetic resin regenerant

4.6.2.1 DOC and SUVA values

To allow direct comparison of the NOM contained in both, the regenerant and raw water from Albert, Wanneroo, Aireys Inlet and Kluizen (7.0, 11.0, 9.8 and 13.1 mg.L^{-1} DOC respectively) the regenerant solutions were adjusted to similar levels (Figure 4.75).

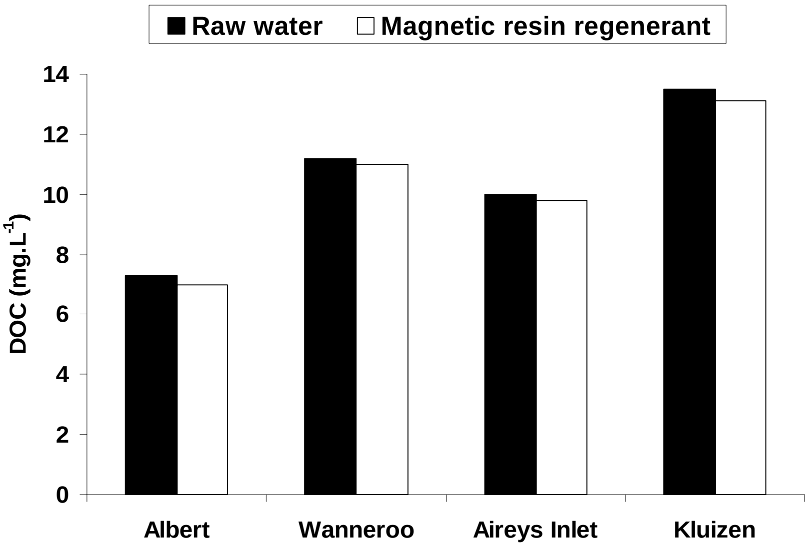


Figure 4.75 DOC level in raw water and diluted magnetic resin regenerant solutions for Albert, Wanneroo, Aireys and Kluizen water.

Even though the DOC levels were matched the NOM contained in all samples was clearly different in terms of SUVA, MW and hydrophobicity. The raw waters of Wanneroo, Aireys Inlet and Kluizen had SUVA values of 4.5, 2.0 and 1.9 L.m^{-1}.mg^{-1}

DOC respectively compared to higher SUVA values of 5.7, 3.6 and 3.0 $L.m^{-1}.mg^{-1}$ DOC respectively for the NOM in the regenerant solutions indicating the tendency of the magnetic resin to preferably remove material with higher UV_{254} absorbance. This was in agreement with the findings presented for the continuous magnetic resin tests (Section 4.2), where a preferential removal of material of a high UV_{254} absorbance by magnetic resin was shown. The regenerant collected from Albert water though showed a different trend where the SUVA values of 5.6 and 4.5 $L.m^{-1}.mg^{-1}$ DOC for the raw water and the regenerant solution respectively, indicated a higher concentration of material with a lower UV_{254} absorbance in the latter.

The main difference in the Albert regenerant sample to all the others is that it was collected over a period of 8 weeks (beginning of April 2006 to beginning of June 2006) whilst the raw water was collected one specific day in June 2006. In comparison the regenerant solutions from the 3 other sources had been collected over a period of 2 to 8 days during which the raw water samples were collected. This extended collection period for Albert means that the regenerant is not representative of the collected raw water sample.

4.6.2.2 Fractionation

XAD fractionation of Albert raw water and regenerant showed that although the total level of hydrophobic NOM had barely changed (77 and 74 % in the raw water and regenerant respectively), significant differences were observed in the balance between HAF and FAF (Figure 4.76). Albert raw water contained 27 and 50 % of HAF and FAF respectively, whilst the regenerant solution contained 6 and 68 % of HAF and FAF respectively. These large differences were related to Albert regenerant not being representative of the raw water, because XAD fractionation of the raw water and regenerant solution from Wanneroo, Aireys Inlet and Kluizen showed only minor differences in terms of hydrophobicity. The raw waters contained 64, 58 and 49 % of hydrophobic NOM (HAF and FAF) respectively, whilst their regenerant solutions contained 63, 62 and 57 % of hydrophobic NOM (HAF and FAF) respectively. Little change was observed for all fractions for Wanneroo and Kluizen. For Aireys Inlet there was some variation in both the HPIA and HPINA levels indicating increased removal of hydrophilic acids (HPIA) by the magnetic resin in this water.

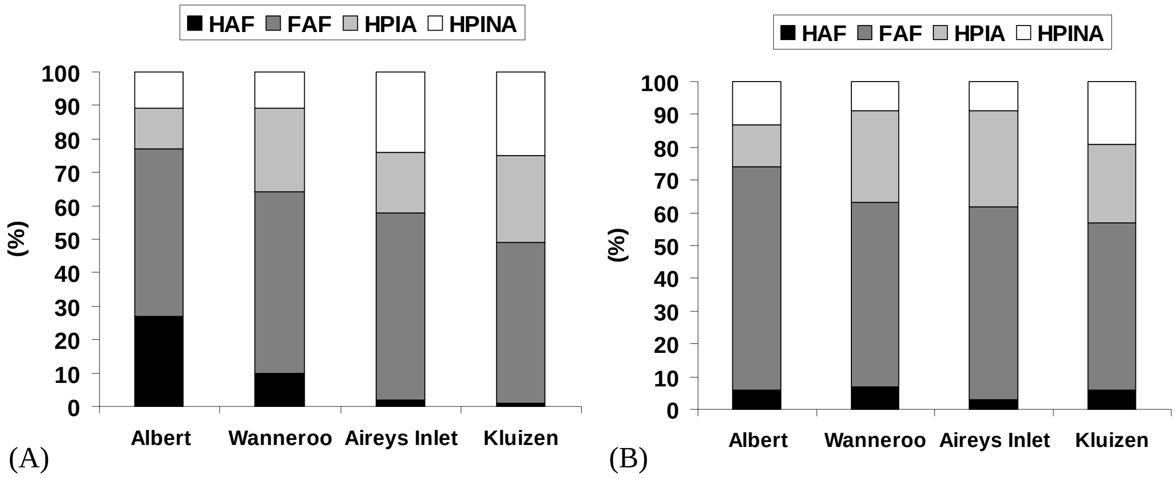


Figure 4.76 Fractionation of Albert, Wanneroo, Aireys Inlet and Kluizen water (A) Raw water, (B) Magnetic resin regenerant.

The data confirmed that material captured by the magnetic resin fits into the HAF, FAF and HPIA bands but also showed that the resin has the ability to remove NOM characterised by the XAD fractionation method as HPINA. This agrees with previous studies on river waters that reported HPINA removal by magnetic resin (Boyer and Singer, 2005; Kim *et al.*, 2005; Zhang *et al.*, 2006) but it does not correlate to this work (Section 4.2.6.1) which showed the inability of magnetic resin to successfully remove model hydrophilic neutral molecules (<5 % DOC). However the previous research (Boyer and Singer, 2005; Kim *et al.*, 2005; Zhang *et al.*, 2006) did not provide any charge density investigation of the removed HPINA, which could have helped elucidating the nature of the removal process.

4.6.2.3 Charge density

The charge density of the regenerant solutions was also significantly higher than in the raw waters indicating that the resin was selectively removing highly charged organic matter, as indicated by (Croué *et al.*, 1999) for other anion exchange resins.

Albert, Wanneroo, Aireys Inlet and Kluizen raw water had a charge density of 4.2, 2.6, 3.4 and 3.8 meq.g^{-1} DOC respectively, which increased to 13.4, 5, 8.4 and 8.5 meq.g^{-1} respectively in the regenerant (Figure 4.77).

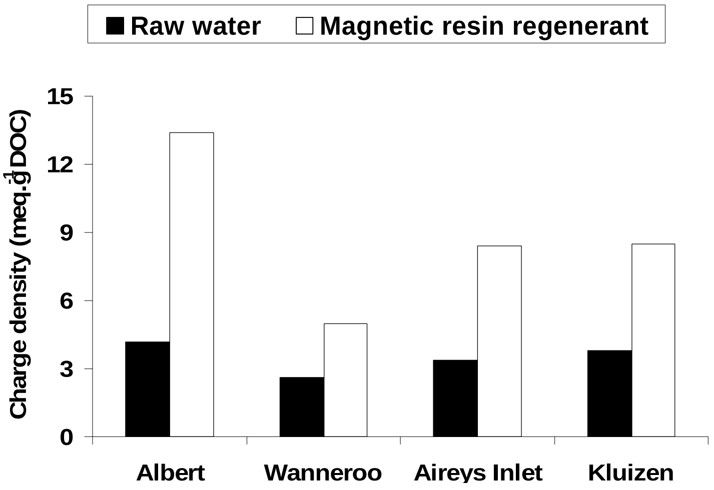


Figure 4.77 Charge density of raw water and magnetic resin regenerant solutions.

Given that the preferential removal of charged material by the magnetic resin was observed and that HPINA is usually described as being charge neutral (Edzwald, 1993; Kam and Gregory, 2003; Sharp *et al.*, 2006a), the presence of any charge density allowing its removal by anion exchange was investigated. The other potential mechanism for DOC removal of neutral compounds by anion exchange resins is surface adsorption (such as Van der Waals forces) which was shown previously to be a minor removal route for anion exchange resins (Symons *et al.*, 1995). Charge density measurements on the fractions from the regenerant solutions showed values of 5.4 to 17, 5.5 to 15 and 1 to 5.5 meq.g^{-1} DOC for HAF, FAF and HPIA respectively (Figure 4.78).

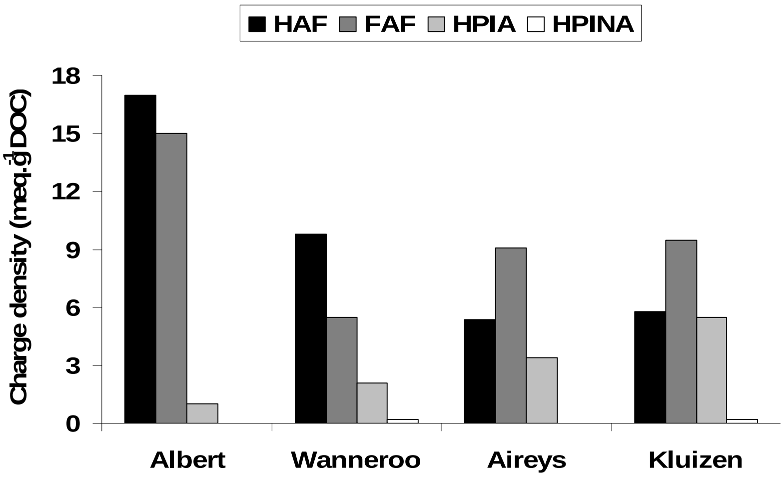


Figure 4.78 Charge density of magnetic resin regenerant fractions for Albert, Wanneroo, Aireys Inlet and Kluizen raw water.

A charge density of 0.2 meq.g^{-1} DOC was measured for HPINA taken from Wanneroo and Kluizen regenerants, whilst no charge was detected for both the Albert and Aireys Inlet regenerant. The fact that charge density was measurable for some of the HPINA fractions, which was in agreement with Croué *et al*., (1999), also indicated that this type of NOM may be removed by anion exchange. Investigation of the removal of hydrophilic neutral model compounds (D-mannose, D-xylose and PEG) showed no efficient removal by anion exchange (<5 % DOC) (Section 4.2.6.1). This indicated that removal of NOM defined as HPINA in the raw water was most likely the result of compounds of this fraction that contain a small amount of charge. However, it should be noted that a certain level of carry-over of charged material such as HPIA during the fractionation process could not be totally excluded (Section 3.5.3). The same mechanism of carry-over could have occurred for the previous studies which had claimed that HPINA was removed by magnetic resin, but had not measured the charge density of the removed NOM (Boyer and Singer, 2005; Kim *et al*., 2005; Zhang *et al*., 2006).

4.6.2.4 HPSEC profiles

The HPSEC profiles show differing profiles for the raw waters and the regenerant solutions. For all four raw waters the HPSEC profiles had several peaks eluting between 5.8 and 11 minutes indicative of NOM with a MW range >5 kDa to 0.5 kDa (Figures 4.79).

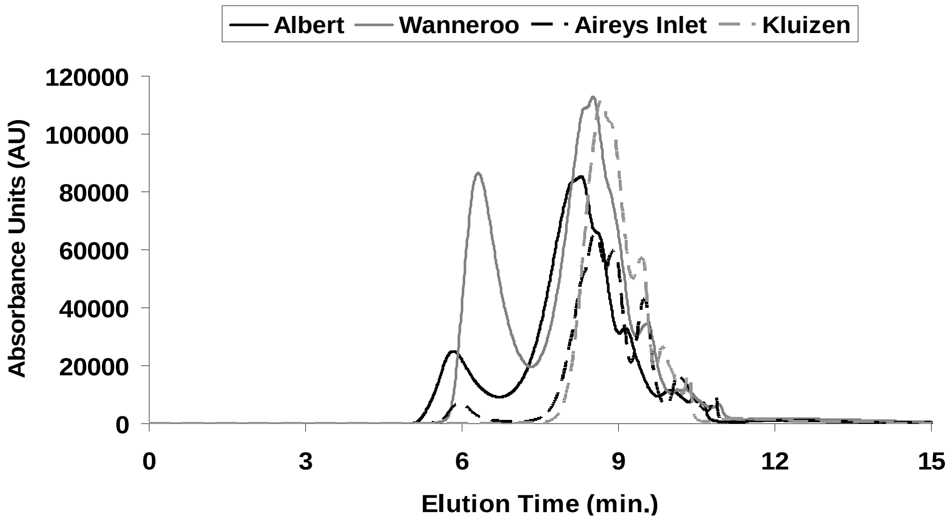


Figure 4.79 Raw water HPSEC profiles for Albert, Wanneroo, Aireys Inlet and Kluizen water.

The HPSEC profiles of all regenerant samples though showed remarkably similar profiles (Figure 4.80), where material was detected between 6.8 to 7 minutes elution time and quickly dropped towards 10.5 to 11.5 minutes elution time. This indicates the highest removal by magnetic resin of UV_{254}-absorbing material between 5 and 2 kDa and was in accordance with the HPSEC profiles in section 4.2, which had shown the best removal of NOM by magnetic resin in that range.

Also it should be noted that when comparing the major peaks (eluted between 8.3 and 8.8 minutes) in the raw waters and regenerant solutions there are differences in the peak heights. For Wanneroo, Aireys Inlet and Kluizen the peaks in the regenerant sample were increased by 200, 170 and 120 % respectively when compared to the raw waters. This indicates preferential removal of highly UV_{254} absorbing material by magnetic resin. This preferential removal of strongly UV_{254} absorbing material by magnetic resin in raw waters could be confirmed by the removal data under Section 4.2 in this thesis, as well as by all previous research, which had shown up to 30 % more UV_{254} absorbance removal than DOC reduction by magnetic resin (Hamm and Bourke, 2001; Boyer and Singer, 2006; Shorrock and Drage, 2006; Wert *et al.*, 2006).

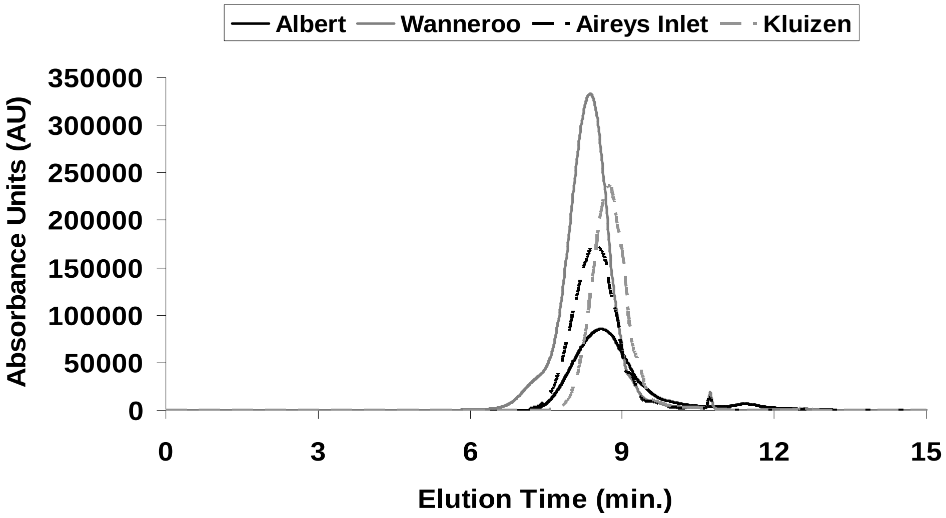


Figure 4.80 Magnetic resin regenerant HPSEC profiles for Albert, Wanneroo, Aireys Inlet and Kluizen raw water.

4.6.3 Coagulation of raw water and magnetic resin regenerant

The raw water coagulation conditions (dose and pH) were identified in preliminary optimisation tests. The results are summarised here for the comparison to the removal accomplished by the regenerant solution: Albert - 7.7 mg.L^{-1} Fe (pH 4.2); Wanneroo - 12 mg.L^{-1} Fe (pH 5.0); Aireys Inlet - 8 mg.L^{-1} Fe (pH 4.5); Kluizen -12 mg.L^{-1} Fe (pH 4.5).

4.6.3.1 DOC and SUVA values of coagulated waters

The raw waters and regenerant solutions showed different trends in terms of DOC and SUVA level reduction for all the sources. For Albert similar DOC reduction levels of 78 and 80 % were measured in the raw water and the regenerant solution respectively (Figure 4.81). For Wanneroo, the DOC removal for the raw water was 85 %, compared to 78 % in the regenerant solution. While for Aireys Inlet and Kluizen the DOC removal was slightly higher for the regenerant solutions (75 and 90 %) than for the raw water (70 and 75 %).

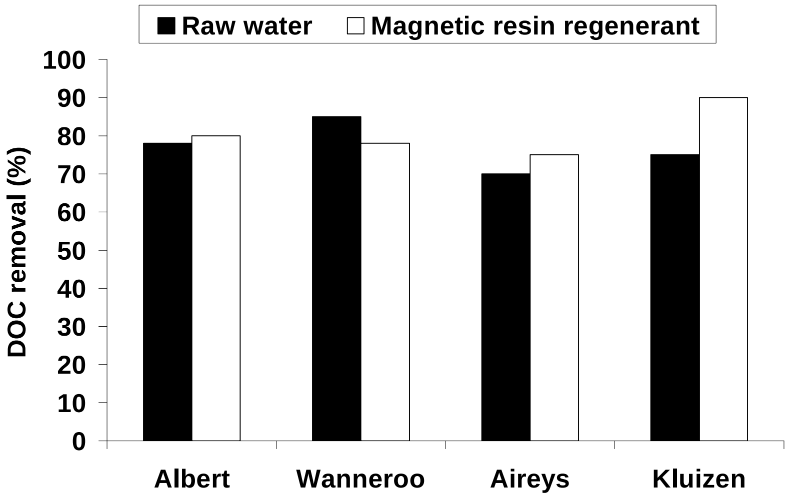


Figure 4.81 DOC removal in raw water and diluted magnetic resin regenerant solutions for Albert, Wanneroo, Aireys and Kluizen water after coagulation.

The zeta potential results showed that the coagulated regenerant solutions had negative zeta potential values greater than their respective raw waters. For Albert, Wanneroo, Aireys Inlet and Kluizen a zeta potential of 3.3 ± 0.5 mV, 4.3 ± 0.3 mV, 4.6 ± 0.4 mV and -4.3 ± 1.1 mV respectively was measured in the raw water (Table 4.7). While values of -2.8 ± 0.5 mV, -23.4 ± 3.6 mV, -8.4 ± 1.9 mV and -11.2 ± 3 mV were measured for the coagulated regenerant solutions of Albert, Wanneroo, Aireys Inlet and Kluizen.

Table 4.7 Zeta potential values for Albert, Wanneroo, Aireys Inlet and Kluizen raw water and regenerant solution.

	Raw water	Regenerant
Albert	3.3 ± 0.5 mV	-2.8 ± 0.5 mV
Wanneroo	4.3 ± 0.3 mV	-23.4 ± 3.6 mV
Aireys Inlet	4.6 ± 0.4 mV	-8.4 ± 1.9 mV
Kluizen	-4.3 ± 1.1 mV	-11.2 ± 3 mV

All raw waters were observed to lie within the range of +5 to -10 mV described to provide optimum DOC removal (Parsons *et al*., 2004; Sharp *et al*., 2004). However, among the regenerant solutions only Albert and Aireys Inlet fell in this band. Kluizen regenerant had a zeta potential of -11.2 ± 3 mV, which was just over the lower limit of -10 mV, while the value of -23.4 ± 3.6 mV for Wanneroo was a long way outside the boundary indicating optimal removal. This suggested that the applied coagulant dose, which had been optimised on the raw water, had not been sufficient to totally destabilise and neutralise the NOM suspension in Wanneroo regenerant (Duan and Gregory, 2003). Considering that the used coagulant dose (12 mg.L^{-1} Fe) had been optimised on Wanneroo raw water, with a charge density of 3.4 meq.g^{-1} DOC, while the regenerant had a charge density of 5 meq.g^{-1} DOC, a lower DOC reduction in the latter solution is likely because of incomplete charge neutralisation. However, it was surprising that in Wanneroo regenerant, which had the lowest charge density of all regenerant solutions (5 meq.g^{-1} DOC), the DOC removal was less efficient. To illustrate, a comparative ratio of the DOC (mg.L^{-1}) in the water to the added Fe dose (mg.L^{-1}) gave a value of 0.92:1 for Wanneroo regenerant and of 1.22:1 for Aireys regenerant, which was of similar character in terms of hydrophobicity than Wanneroo regenerant. Despite the higher DOC: Fe ratio in Aireys Inlet regenerant and a much higher charge density (8.4 meq.g^{-1} DOC), the DOC had been more successfully neutralised in this solution as seen from the zeta potential value (-8.4 ± 1.9 mV).

An investigation of the SUVA levels showed a similar trend to the DOC after coagulation. For Albert values of 65 and 60 % reduction in the raw water and regenerant solution respectively showed a slightly higher reduction for the coagulation of the raw water. While for Aireys Inlet and Kluizen the SUVA reduction was greater for the regenerant solution with 50 and 45 % reduction respectively compared to 45 and 10 % reduction respectively in the raw water. The SUVA value for Wanneroo was reduced by 95 % in the raw water, whilst in the regenerant solution showed a reduction by 65 %.

When increasing the coagulant dose for Wanneroo brine after optimisation to 22 mg.L^{-1} Fe, the zeta potential decreased to -2.9 ± 0.2 mV which was well within the optimal removal range. Although the DOC and SUVA were removed by 95 and 90 %

respectively, this still does not explain why such an increased coagulant dose was required in the regenerant sample with the lowest charge density.

4.6.3.2 Fractionation of coagulated waters

XAD fractionation showed that the residual NOM after coagulation had similar fractional character for treatment of both the raw waters and regenerant solutions. It should be noticed here that for Wanneroo the sample coagulated with 22 mg.L^{-1} Fe was used to insure optimal DOC reduction. For HAF which was readily removed by hydrolysing metal salts (Edzwald and Tobiason, 1999) a removal of 100 % was observed for all samples (Figure 4.82).

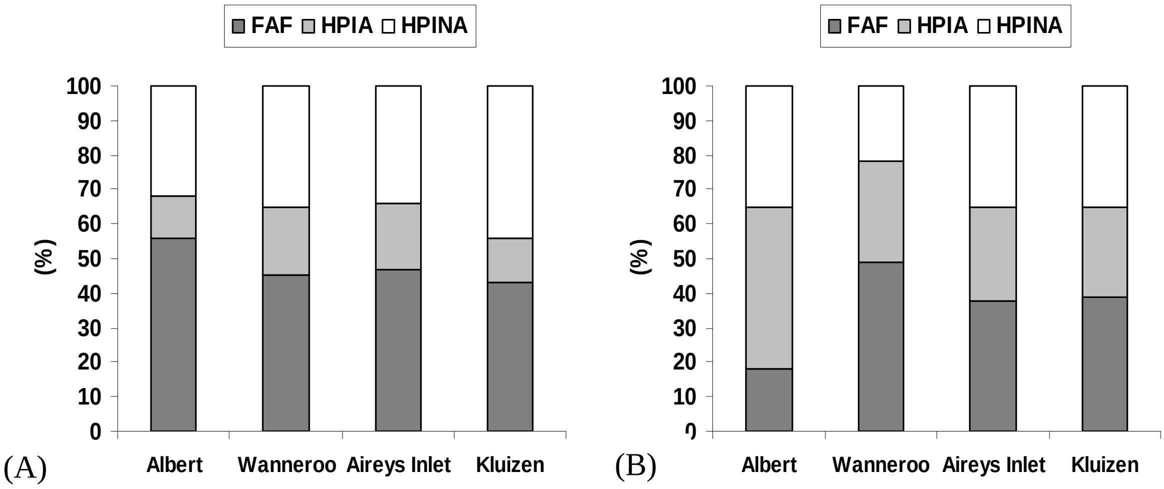


Figure 4.82 Fractionation after coagulation (A) Raw water, (B) Magnetic resin regenerant.

Fulvic acid, which has been shown to be less readily removed by coagulation than HAF HAF (Randtke, 1988), was present at similar levels of between 43-47 % in all the coagulated raw waters and 38-49 % in all the coagulated regenerant solutions. The only exception was the source of Albert where FAF made up 56 % of the residual NOM in the raw water and 18 % of the regenerant solution.

The same trend of similar levels was seen for the HPINA which made up 32-44 % and 22-35 % in the coagulated raw waters and regenerant solutions respectively. HPIA however was the only fraction which increased for all regenerant solutions in comparison to the raw waters. For Wanneroo, Aireys Inlet and Kluizen the raw waters and regenerant solutions contained 13 to 20 % and 26 to 29 % HPIA, while for Albert this fraction had increased from 12 % in the raw water to 47 % in the regenerant solution after coagulation. This trend can be explained by the proven good removal efficiency of using magnetic resin for removal of hydrophilic acids (Section 4.2.6.1). This agrees with other studies that have shown good removal of this fraction by anion exchange resins (Bolto *et al*., 2004).

From this data it was observed that the residual NOM after coagulation of raw water and regenerant contained a similar fraction distribution with a tendency for increased levels of HPIA in the regenerant. Considering that this NOM was present in the regenerant but had not been removable by coagulation, it can be concluded that magnetic resin was able to remove a fraction of NOM recalcitrant to coagulation and would be the reason for the previously observed enhanced DOC reduction by combined treatment.

4.6.3.3 HPSEC profiles of coagulated waters

The main area of residual UV_{254} absorbing material after coagulation was seen to lie between 9 and 11 minutes elution time (approximately 3.5 to 0.5 kDa) for all of the raw waters and regenerant solutions (Figure 4.83, Figure 4.84, Figure 4.85, Figure 4.86). This observation was in accordance with the data on raw water coagulation, previously presented in this thesis (Section 4.3), as well as with Sharp *et al*., (2006c) who observed the MW of NOM recalcitrant to coagulation to be in the sub 3 kDa range.

The similarity in residual MW, fractional composition and the observation that coagulation is not able to totally remove NOM from regenerant solution showed that magnetic resin offers some advantage in removal of low MW material that cannot be removed and would explain the better removal of low MW material by combined treatment, observed in most analysed source waters.

For Wanneroo, however a new peak eluting at 5.8 minutes and indicating material of an approximate MW >5 kDa was seen to form after coagulation of the regenerant solution (Figure 4.84). Optimisation of the coagulant dose (22 $mg.L^{-1}$ Fe) reduced this peak by

40 %, but was not able to totally remove it. The formation of a new peak after coagulation has not been observed on any of the other regenerants and must be related to the specific characteristics of Wanneroo water.

Wanneroo water taken which is a borehole water from aquifers contains iron which was partially removed by oxidation at the WTW (Section 3.1.5) resulting in a residual level of 1-4 mg.L^{-1} before magnetic resin treatment (Cadee *et al*., 2004). This iron is present as ferrous iron (Fe^{2+}) due to the anaerobic conditions in these waters and would be coated by NOM through mechanisms such as complexation (Liang and McCarthy, 1995). Beside hindering the oxidation of ferrous iron to ferric iron (Fe^{3+}) during water treatment (Sung and Morgan, 1980), complexation with NOM would also allow the indirect removal of ferrous iron by magnetic resin and introduce it into the regenerant solution.

Similar mechanisms have been reported for silica, where hydroxide groups on the silica surface interact by hydrogen bonding with the carbonyl oxygen in the carboxylic functional groups of NOM (Buleva and Petkanchin, 1999). This increased the silica zeta potential by 10 % and thus making it more negative (Dixon and Kolarik, 1990). Lowering the pH from 8 to 3.5 was reported to double the amount of NOM coating the silica and thereby also the negativity of the zeta potential (Liang and McCarthy, 1995; Petrovic *et al*., 1999).

Such a coating mechanism by NOM on ferrous iron could also explain the formation of large aggregates after coagulation of Wanneroo regenerant, especially as the pH was dropped from 7.2 to 5. This could also explain the observed increase in zeta potential. Those formed colloids have been reported to be < 0.1 µm (Liang and McCarthy, 1995). This size of particle would not be retained by filtration prior to HPSEC. The fact that the higher coagulant dose had been able to increase the zeta potential to -2.9 mV, but not to completely avoid the formation of the observed peak, was related to the observation that the DOC removal had only been increased from 78 to 95 %. Therefore there was still NOM left in the water which could interact with ferrous iron rather than being removed by coagulation. However this mechanism would need further experimentation before it could be proven.

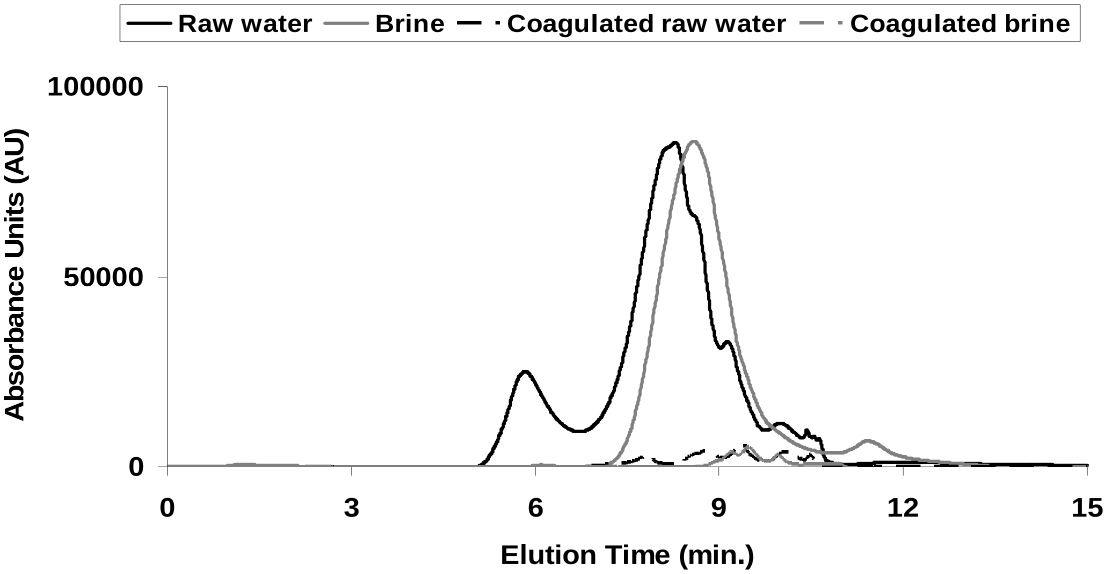


Figure 4.83 HPSEC Profiles after coagulation of Albert raw water and magnetic resin regenerant.

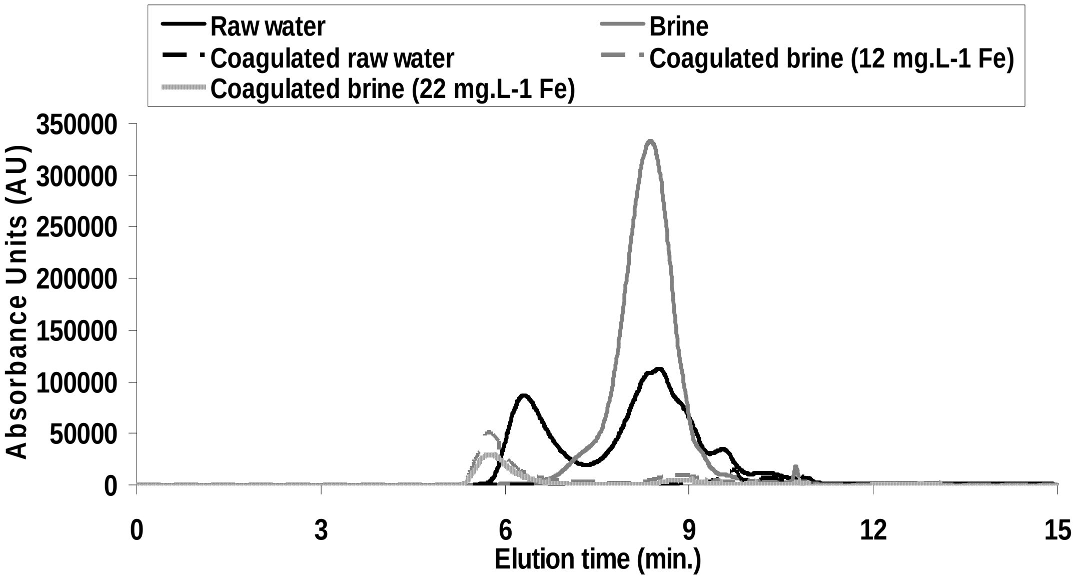


Figure 4.84 HPSEC Profiles after coagulation of Wanneroo raw water and magnetic resin regenerant.

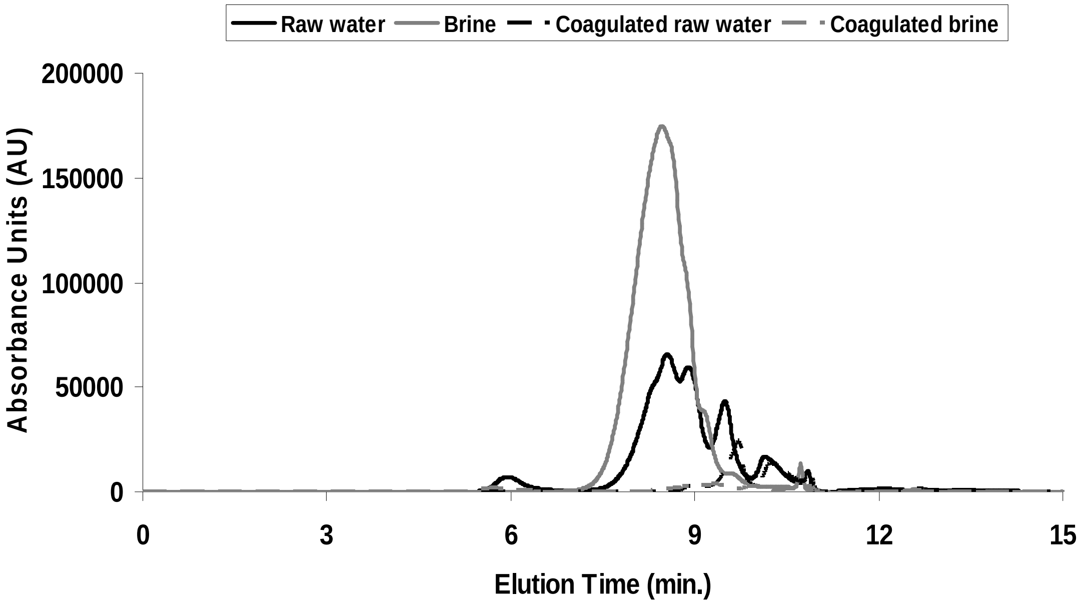


Figure 4.85 HPSEC Profiles after coagulation of Aireys Inlet raw water and magnetic resin regenerant.

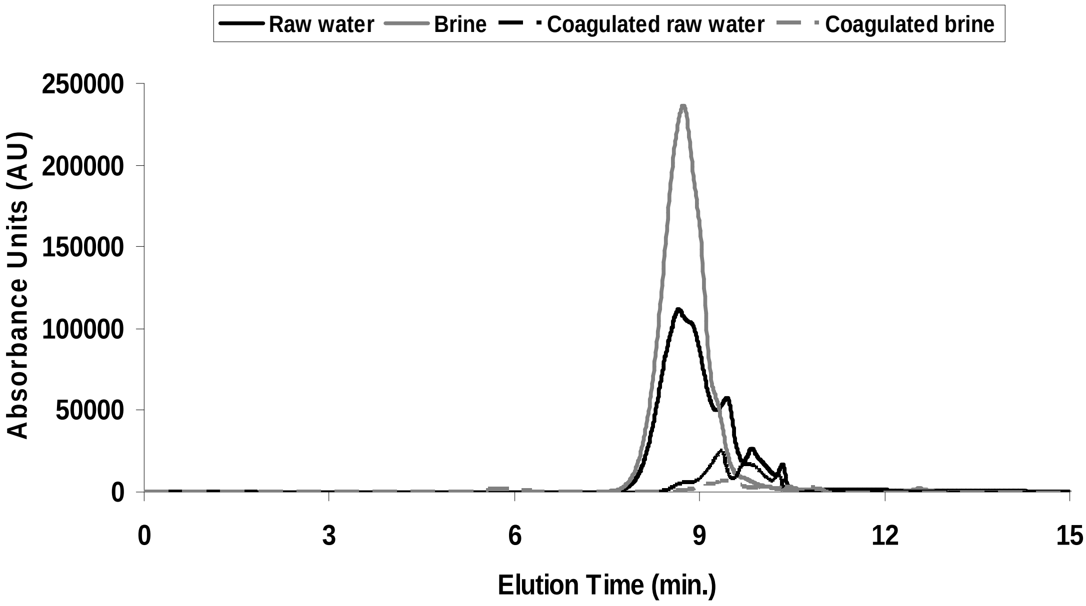


Figure 4.86 HPSEC Profiles after coagulation of Kluizen raw water and magnetic resin regenerant.

In summary, it was seen in this section that investigation of the regenerant samples is able to confirm the preferential removal by magnetic resin of mid to low MW, high UV_{254} absorbing organic material with a high charge density and that its hydrophobicity did not affect removal. The HPINA was also detected in the regenerant which suggests that magnetic resin could also reduce this fraction often reported to be recalcitrant to coagulation. However it must be noted that the work on charge neutral model compounds showed that these were not removed by magnetic resin. The results show some charge density in the HPINA fraction, suggesting an overlap between this fraction and material from other fractions. However the secondary removal path of surface adsorption could not be totally excluded.

Furthermore it was observed that after coagulation raw waters and regenerant solutions contained NOM fraction of similar character in terms of hydrophobicity and MW. This showed that magnetic resin was able to remove a fraction of NOM recalcitrant to coagulation which would explain the enhanced removal of DOC and low MW NOM in most analysed raw waters.

5. Overall discussion

The aim of this thesis was to identify the characteristics of NOM preferentially removed by magnetic resin to help assessing its efficiency for the treatment of different types of source waters. The impact of the magnetic resin process on downstream coagulation and chlorination was investigated as well to assess any potential impact on water quality. The work undertaken during this thesis allowed to achieve all these objectives and to obtain a deeper scientific insight into the mechanisms involved in NOM removal by magnetic resin and its implications for the water industry.

Continuous bench-scale tests on source waters as well as the investigation of regenerant solutions abstracted from full-scale and pilot-scale plants identified NOM preferentially removed by magnetic resin, as being of high charge density, mid to low MW (5 to 2 kDa) and high UV_{254} absorbance, without being influenced by its hydrophobicity.

The increased charge density of NOM in the regenerant solutions (5 to 13.4 $meq.g^{-1}$ DOC) when compared to the respective raw waters (2.6-4.2 $meq.g^{-1}$ DOC) was in accordance with the general concept of anion exchange resins having a preference for anions of higher valency (Dronnet *et al*., 1998; Bae *et al*., 2002). As a consequence, the NOM of increased charge density concentrates in the resin regenerant. From this trend of preferential removal of highly charged species, it can nonetheless not be deducted that magnetic resin will be more effective for the treatment of a source containing NOM of a higher charge density, than for a source containing NOM of comparatively lower charge density. This is because the charge density varies among the myriad of different organic molecules contained in different natural sources (Edzwald, 1993; Scott *et al*., 2001; Sharp *et al*., 2006a; Park *et al*., 2006) leading to the obvious conclusion that the high charge density of NOM removed by magnetic resin has to be seen in context to the other organic material present. Comparative treatment of two sources of different charge density (0.3-6.5 $meq.g^{-1}$ DOC) with a single resin dose allowed similar DOC removal (65-71 %), confirming the above statement. Therefore it is of general conception in this work, that the charge density of NOM removed by magnetic resin can not be quantified as a specific value that would indicate whether a source is well suited for magnetic resin treatment.

Comparative tests on charge neutral compounds did not show any significant level of DOC reduction (<5 %) and anion exchange was clearly seen to be the main removal path on magnetic resin. This inefficiency to remove charge neutral compounds was however in contradiction to results from the literature showing magnetic resin able to remove 36-91.6 % of NOM defined as hydrophilic neutral non-acids (Boyer and Singer, 2005; Kim *et al*., 2005; Zhang *et al*., 2006) as well as to the observed presence of these compounds in the analysed magnetic resin regenerant. Charge density measurements allowed confirming the presence of charge in some of these fractions, which was in accordance with Croué *et al*., (1999) but in contradiction with Sharp *et al*., (2006c). The presence of dissociated functional groups would however define this NOM as being of acidic character (Fettig *et al*., 1999) and would be in contradiction with its definition as being a non-acid. A clear statement about the removal mechanisms of hydrophilic non-acids by magnetic resin could therefore not be made. This was especially because all studies had defined the HPINA fraction through XAD-fractionation, a method which cannot exclude carry-over from one fraction into the other (Leenheer, 1981), potentially leading to charge measurable in the hydrophilic non-acids fraction. Considering however that Symons *et al*., (1995), observed uncharged, low MW NOM to be removed onto anion exchange resin, without any increase of the exchange ion (chlorine) in the solution, a secondary path for NOM removal onto magnetic resin could not be excluded.

The MW of NOM was also observed in this thesis as governing the treatability of water by magnetic resin. However this was not relating from an inability of magnetic resin to remove a specific MW fraction from the range detectable by HPSEC.

The observed high removal of strongly UV_{254} absorbing NOM of 5 to 2 kDa was related to the high charge density present in this fraction as seen from the regenerant solutions, without excluding the removal of higher or lower MW NOM. Bench-scale tests on raw waters, model compounds and the coagulation of brine solutions indeed showed that magnetic resin was able to remove low MW, hydrophilic NOM in the sub 2 kDa range, described as being mostly recalcitrant to coagulation (Sharp *et al*., 2006c). This good removability of hydrophilic, low MW NOM allowed magnetic resin to proliferate itself as alternative treatment method for the raw water source of Draycote dominated by this material, when considering that a DOC removal rate similar to that obtained by coagulation alone had been possible (60-65 %). Drikas *et al*., (2003) showed that magnetic resin was able to enhance DOC reduction in full-scale by 20 % when comparing it to coagulation alone in a source dominated by sub 2 kDa NOM and demonstrating that magnetic resin can be more efficient for the treatment for different water sources than coagulation alone.

Magnetic resin also removed high MW NOM (>5 kDa), with HPSEC showing a reduction of this material up to 95 %, after a single use of magnetic resin. However under continuous use of magnetic resin in bench-scale in order to simulate conditions similar to those experienced in large scale, the removal level of this peak quickly decreased in parallel to the overall DOC remaining in the water.

Increasing the contact time from 10 to 20 minutes, which was within the parameters indicated for magnetic resin use, did not enhance DOC removal. This indicated that the NOM attached onto the external surface of the resin beads had not been able to efficiently diffuse towards the pores and free exchange sites on the surface to allow additional NOM being removed, a mechanism already described by Gönder *et al.*, (2006). Furthermore it was expected that the small pore sizes (9.7 nm) in magnetic resin (Dahlke, 2002), in comparison to other anion exchange resins (20-7000 nm) (Symons *et al*., 1995; Bolto *et al*., 2004) additionally slowed down the intraparticular diffusion, of NOM reported to contain molecules of the size ranging from 2 to 50 nm (Cornel *et al.*, 1986; Thurman and Malcolm, 1986). From this it was concluded that although magnetic resin had a high water content (83 %), allowing rapid intraparticular diffusion (Symons *et al.*, 1995; Bolto *et al.*, 2004), the small pore size on the surface did not allow to efficiently take advantage of this property of the resin.

A result of this was physical surface blockage by the large molecules, a mechanism known to result in decreasing removal levels on anion exchange resins (Gottlieb *et al.*, 1996; Lee *et al*., 1997; Hebb *et al*., 2003). Considering that while the removal of high MW NOM (>5 kDa) quickly decreased, NOM of lower MW (<5 kDa) was still removed to higher degrees, a secondary mechanism controlling the removal process was suspected. Most likely this is a mechanism of steric repulsion, arising from residual functional groups on the large molecules and repelling further approaching high MW NOM, while allowing smaller organic molecules to exchange on residual free exchange sites. This explanation was in accordance with the conclusions given by Karanfil *et al*., (1996) and Avena and Koopal (1999) who had observed a mechanism of selective removal of low MW NOM onto preloaded GAC and precipitate. An increase in magnetic resin was logically seen to allow the removal of more NOM by providing a larger accessible external exchange surface. However this still did not allow magnetic resin to compete in terms of DOC removal efficiency with coagulation in waters dominated by high MW NOM.

A combination of magnetic resin treatment followed by subsequent coagulation with reduced Fe doses by 60 to 80 %, showed in bench and pilot-scale to increase the DOC removal by up to 15 % as well as to lower the level of low MW NOM (sub 3 kDa). These beneficial impacts of combined treatment were in accordance with Fearing *et al*., (2004) and Jefferson *et al*., (2004). The effect of reduced levels of low MW NOM was related to the observed ability of magnetic resin to remove this material. A further advantage arising from combined treatment was a lower residual overall THMFP, arising from the enhanced removal of the low MW NOM, which develops a high specific reactivity in the presence of chlorine (Luong *et al*., 1982; Goslan *et al*., 2002).

Furthermore, combined treatment has positively affected floc formation in high SUVA waters generating a floc type more resistant to shear and therefore resulting in less smaller particles under conditions of increased stress, that are difficult to separate out of the water. The general conception is that increased inorganic contents increase the floc strength in NOM-Fe flocs (Bache *et al*., 1999). This statement cannot be fully supported in this thesis, considering that flocs from combined treatment contained a higher NOM level, making the nature of NOM contained within the floc matrix appear as the most probable factor affecting floc properties. This was because a positive impact on floc properties by magnetic resin was only seen in the investigated high SUVA sources. Here magnetic resin pre-treatment had shifted the balance between the different NOM fractions in favour of high MW NOM as observed from the HPSEC, while no such effect was seen in low SUVA waters dominated by a NOM of lower MW. The increase of higher MW NOM inside the floc was expected to result in a greater number of binding points becoming available within the floc structure, as well as an increase in bridging potential and the capacity to form flocs by electrostatic patch mechanisms, giving rise to a more compact structure (Ray and Hogg, 1987; Gregory and Li, 1991; Bolto, 1995; Gregory, 1996; Aguilar *et al*., 2003). Although this mechanism remained an assumption, it was clearly observed in comparative work on model compounds that the character of organic material highly affects the floc formation process either by its presence or by interactions with other, different constituents. To illustrate, the presence of tannic acid and L-glutamic acid resulted in the formation of flocs of 1943 and 885 µm, indicating that former flocs were stronger, because they were able to grow to a larger size (Parker *et al*., 1972; Matsuo and Unno, 1981; Muehle, 1993; Spicer and Pratinsis, 1996; Mikkelsen and Keiding, 2002).

Increased UV_{254} absorbance as the third factor characterising NOM removed by magnetic resin was in accordance with the literature, describing the UV_{254} absorbance to be removed up to 30 % more than DOC (Boyer and Singer, 2005; Kim *et al*., 2005; Wert *et al*., 2005). However the presence of UV_{254} absorbance was not regarded crucial for NOM removal by magnetic resin, because low MW, non-UV_{254} absorbing material was well removed by magnetic resin in this study. Furthermore a potential hydrophobic bonding between the aromatic structures inside the NOM molecules and the resin structure was not expected. This is because this mechanism is known to take place on hydrophobic resin (Gustafson and Lirio, 1968), excluding magnetic resin which is of hydrophilic structure. The strong presence of UV_{254} absorbance in the material removed by magnetic resin in source waters was therefore thought only to relate to the good removal of highly aromatic NOM because of its high charge density (Ussiri and Johnson, 2004), without excluding good removal of charged non-UV_{254} absorbing material.

This knowledge about the characteristics of NOM preferentially removed by magnetic resin and its impact on downstream processes generated in this thesis allowed to define a considerable range of advantages for water utilities considering the implementation of magnetic resin.

The presented continuous magnetic resin bench-scale test method is able to more appropriately reflect the DOC removal by the resin that can be expected in large scale application than the widely used single resin application test. This is because the latter test does not take a reduced DOC removal efficiency due to a pre-loaded surface into account, and can result in false expectations regarding the efficiency of magnetic resin used in large scale. The continuous bench-scale test is therefore a valuable method for water utilities to predict the efficiency of magnetic resin, without requiring expensive pilot-plant studies.

In general it was seen from this thesis and the comparative literature that the implementation of magnetic resin as pre-treatment allows the use of reduced coagulant doses for all water sources, due to a reduction of the NOM load. Furthermore in river waters dominated by low MW and hydrophilic NOM, magnetic resin was seen either to be able to compete or even allow more DOC removal than coagulation alone, as seen in the literature. Therefore it can be suggested that water utilities treating this water type could consider replacing the plants based on coagulation by magnetic resin plants and totally eliminate their coagulant costs.

Beside large chemical cost savings the implementation of magnetic resin as pre-treatment to coagulation was seen in this thesis to bring another range of beneficial effects for water utilities treating high SUVA. The observed reduced overall THMFP after combined treatment in high SUVA waters, due to the ability of magnetic resin to enhance the removal of low MW material, could help water utilities stay in compliance with the THM regulations. Given the increased solid-liquid separation after combined treatment in high SUVA waters due to enhanced floc properties, magnetic resin could be a useful tool for water utilities to reduce the turbidity load going onto the sand filters and insure longer filter run times and less frequent backwashing.

Considering the large coagulant dose savings through combined treatment (60 to 80 %), it was also expected that the volume of sludge produced would be significantly reduced allowing further cost savings for the water utilities. Following the guideline for sludge production estimation given by Parsons and Jefferson (2006), it was calculated that a 60 % coagulant reduction after magnetic resin treatment during the undertaken pilot plant test on Albert water could allow reducing the sludge volume by 45 % (19.8 $mg.L^{-1}$) when compared to coagulation alone (37.4 $mg.L^{-1}$).

Sludge production estimate guideline (Parsons and Jefferson, 2006).

Sludge solids= 2 * turbidity (NTU)
+ 0.2 * colour removed (HU)
+ 1.9 * iron precipitated ($mg.L^{-1}$ Fe)

Notes:

- Quality of Albert raw water and coagulant dose: 1.7 NTU, 75 HU, 7.7 $mg.L^{-1}$ Fe.
- Quality of magnetic resin pre-treated water and coagulant dose: 1.3 NTU, 48 HU, 4 $mg.L^{-1}$ Fe.

In response to the observed necessity of combined treatment to allow increased DOC removal in high SUVA sources, different alterations in the design of magnetic resin are suggested to render it more efficient as a single treatment option in presence of high MW NOM. A first potential alteration would be to design magnetic resin with larger pore sizes to enhance pore diffusion. However this would inflict longer regeneration times to allow NOM to diffuse out of the pores (Slunjski *et al*., 1999), which would increase the inventory of necessary resin to allow a continuous process. Thereby this option relies too strongly on intra-particle NOM diffusion is likely to be a less efficient way to enhance magnetic resin. Another option would be to reduce the momentary average bead diameter of 165 ± 55 μm (Section 4.1). This would increase the external surface to volume ratio of the resin and provide a more effective sink for high MW NOM, without having to increase the resin dose and subsequently the process costs. Considering that Cornelissen *et al*., (2008) confirmed an increase in DOC removal with decreasing bead diameters after comparison of different resin types, this redesign option was thought to be the most promising.

Furthermore it was observed in this thesis that magnetic resin could be contaminated by suspended material such as macroscopic algae during solid-liquid separation by settling. No impact on the treatment efficiency by algae or other suspended material such as silt has until now been reported in any previous study on full-scale or pilot-scale magnetic resin plants. However it could be questioned whether a continuous solid build-up could affect the process; such as by interfering with the resin dosing, releasing turbidity into the treated water or potentially becoming a nutrient source for bacteria, leading to a biofilm formation on the resin beads, previously seen to affect NOM adsorption on other exchange resins (Flemming, 1987). Considering however that frequent regenerations steps with NaCl concentrations of 12 to 20 w% were reported to be lethal even for halophilic bacteria by exposing them rapidly to different salt concentrations which leads to hyposaline shock, a biofilm formation on magnetic resin was thought of low probability (Korber *et al.*, 1996; Franzetti *et al.*, 2001; Smith *et al.*, 2002). This would also allow implementing magnetic resin as a treatment for sewage water given that Zhang *et al.*, (2006) reported a 60 % TOC reduction in a synthetic wastewater. Nonetheless the addition of a further treatment step, such as membrane filtration, to avoid a solid build-up and allow efficient treatment of highly turbid waters could have to be considered to keep magnetic resin an attractive option for DOC reduction in a large range of water types, despite potential additional costs.

Until now the magnetic resin process has shown to be competitive with other additional treatment processes used to enhance water quality. At the Green Valley WTW (California, USA) which treats 3820 $m^3.d^{-1}$ of water, the costs arising from implementing a magnetic resin pre-treatment plant were compared to GAC contactors (Nestlerode *et al.*, 2006b). GAC had been chosen as comparative treatment option as it was believed to be the only treatment option beside magnetic resin to allow Green Valley WTW to meet the regulations of the second stage DBP rule in the USA (Drinking Water Quality Program, 2005). Considering that GAC had been reported to increase DOC removal by up to 15 % when used as post-treatment to coagulation (Snoeyink and Chen, 1985), it was accepted for cost comparison in this thesis. Implementation of biologically activated carbon (BAC), allowing DOC reduction by biodegradation beside adsorption as occuring on GAC, could have been another option in the case of Green Valley WTW. However it is questionable whether direct installation of BAC would have been of any advantage when compared to GAC. Firstly this is because a microbial film develops over time in every GAC contactor (Sketchell *et al.*, 1995). Secondly because a biofilm around the GAC granules can hinder the transfer of DOC which implies, that the adsorption process would be restricted by the biofilm. DOC reduction by biofilm would therefore probably just overlap with adsorption, rather than allowing an increased level of removal (Urfer *et al.*, 1997; Liang and Chiang, 2007).

At Green Valley WTW magnetic resin was seen to be more economical than GAC, even when the used regenerant solution was tankered off for disposal. The magnetic resin plant which was implemented as pre-treatment to coagulation had been estimated to bring capital costs of £ 400,000 to 500,000 and operational and maintenance costs (O&M costs) of £ 28,000 per year (Table 5.1). The compared GAC contactors designed as post-treatment to coagulation were on the other hand seen to have higher capital and O&M costs of £ 450,000 to 745,000 and £ 40,000 to 280,000 respectively.

Table 5.1 Cost comparison for magnetic resin plant and GAC contactors (Adapted from Nestlerode *et al.*, 2006b).

Process	Capital costs (£)	O&M costs (£/year)
Magnetic resin plant	£ 400,000 to 500,000	£ 28,000
GAC contactors	£ 450,000 to 745,000	£ 40,000 to 280,000

Notes:

- The O&M costs for the magnetic resin plants were based on the following assumptions: 57 $kW.h^{-1}$ per 1000 m^3 at £ 0.06 per $kW.h^{-1}$, salt consumption of 180 kg per 1000 m^3 at £ 25 per ton, magnetic resin loss of 12 L per 1000 m^{-3}, disposal of 200 m^3 of regenerant solution per year at £ 0.03 per L.
- The GAC contactor capital and O & M costs were based on USEPA numbers and the following assumptions: TTHM target of 60 $\mu g.L^{-1}$, contact time of 10 to 20 minutes, GAC replacement interval ranging from 2 to 6 months.

Furthermore it is suggested that the costs for the regenerant brine disposal will be reduced by savings made through a reduction of the chemical costs as well as through potentially lower sludge volumes requiring disposal by landfill. This was because Nestlerode *et al.*, (2006b) reported a 30 % coagulant dose reduction after implementation of magnetic resin treatment at Green Valley WTW. While no such advantage can be seen to arise from GAC that it is designed to be used as post-treatment and thereby not affecting the coagulation process.

In summary magnetic resin was seen in this thesis as a valuable alternative or additional treatment method that could allow tackling some of the most urgent problems in the water industry, such as increased THM formation due to NOM recalcitrant to traditional treatment methods, high turbidity load onto filters due to poor floc quality, as well as increased chemical and waste disposal costs. However it was also observed that further research has to be done in terms of optimisation of the magnetic resin design, to potentially allow a cost-effective implementation of the process in a wider range of sources.

6. Conclusions

This project allowed identifying the characteristics of NOM preferentially removed by magnetic resin, as well as broadening the knowledge about the mechanisms influencing the efficiency of magnetic resin to remove NOM from different water types. Furthermore bench-scale as well as pilot-scale investigation have demonstrated that magnetic resin has beneficial effects on downstream treatment in terms of coagulant dose reduction, floc growth and strength, solid-liquid separation, DOC reduction as well as reduced THMFP. The conclusions from this work are the following:

- The novel continuous bench-scale test method for magnetic resin used in this thesis has shown to be more effective in simulating the NOM removal trend in large scale application. Therefore this method should be implemented in future studies rather than the widespread use of a single magnetic resin application that does not consider the impact of resin re-use on its removal efficiency.

- Given that charge neutral organic model compounds could not be removed and that magnetic resin regenerant was characterised by NOM of high charge density, the presence of dissociated functional groups was regarded as the main path for NOM onto magnetic resin. However a secondary path for NOM removal onto magnetic resin could not be excluded by the work undertaken in this thesis.

- Although magnetic resin was seen to preferentially remove highly charged organic material in the 5 to 2 kDa area, HPSEC of treated raw waters showed that the removal of NOM of higher or lower MW by magnetic resin was not excluded. Comparative coagulation of raw waters and magnetic resin regenerant evidenced that magnetic resin was able to remove NOM smaller than 2 kDa, recalcitrant to coagulation. This ability of magnetic resin to remove low MW NOM, allowed the process to compete with coagulation for the treatment of natural waters dominated by this fraction and even to be more efficient for the removal of hydrophilic acids. High MW NOM, nominally characterised here as >5 kDa, could also be removed by magnetic resin. However this material has the potential to rapidly surface block magnetic resin and hinder the attachment of further high MW NOM. Subsequent coagulation with Fe doses reduced by up to 80 %, remains therefore necessary to efficiently reduce the DOC level in these sources. This combined treatment however allowed to increase the total DOC removal in high SUVA waters (up to 10 %) as well as showing an increased removal of NOM smaller than 2 kDa.

- The observed effective removal of low MW, non-UV_{254} absorbing, hydrophilic acids onto magnetic resin, disqualified high UV_{254} absorbance as characteristic necessary to NOM for being removed by magnetic resin. The increased UV_{254} absorbance measured for NOM contained in the magnetic resin brine regenerant, could therefore only be related to the high charge density of aromatic organic material in natural sources, making it a good candidate for anion exchange.

- Given the ability of magnetic resin to increase the DOC removal by removing low MW NOM that has a high reactivity in the presence of chlorine, combined treatment was seen to reduce the THMFP to the highest extent in high SUVA water. Thereby magnetic resin treatment before coagulation was seen to be a powerful tool to reduce the THM level and could help water utilities meet legislative standards.

- The necessity of combined treatment to efficiently remove NOM from high SUVA waters dominated by high MW NOM resulted in enhanced floc properties in terms of size, settling velocity and stress resistance. Considering that stronger flocs remain larger under conditions of elevated shear, they are more probable to attach to bubbles during clarification by DAF. In pilot-scale this ability of combined treatment flocs to remain larger gave lower residual turbidities after DAF and thereby less solids going onto the sand filter, expected to give rise to longer filter run times. Magnetic resin was thereby seen to be an efficient pre-treatment method to allow increased solid-liquid separation in high SUVA sources.

- Increased floc properties after magnetic resin pre-treatment were only seen in waters dominated by high MW NOM where magnetic resin had reduced the level of lower MW NOM. The beneficial impact of combined treatment was related to a higher level of high MW NOM being incorporated into the coagulant floc, enhancing its strength by potential bridging and compaction mechanisms. The nature of NOM incorporated into the floc matrix was the most important factor rather than its concentration. Comparative tests on different model compounds allowed confirming this statement. However, beside the nature of a specific compound the presence of several compounds could alter the floc properties in a different manner. This observation confirms the beneficial impact magnetic resin can have on flocs by removing a specific NOM fraction.

- Although combined treatment did not increase NOM reduction in all investigated waters when compared to coagulation, it nonetheless enabled to reduce the coagulant dose by up to 80 %. This reduction in coagulant dose was in result of magnetic resin reducing the NOM load in the raw waters, which would otherwise have required higher coagulant doses for effective removal. Magnetic resin is thereby able to allow water utilities make large chemical costs savings, a benefit not observed for other additional treatment methods for DOC reduction, such as GAC, used as a post-treatment to coagulation.

- An increase of magnetic resin contact time from 10 to 20 minutes during the continuous bench-scale tests did not lead to any increase in DOC reduction despite the possibility for most NOM from a high SUVA water to diffuse into the pores of magnetic resin during a 24 hour flow interruption test. It was concluded that the small pores of 9.7 nm median diameter on magnetic resin did not allow any rapid intraparticular diffusion of the large NOM molecules. A design change of the magnetic resin bead was therefore suggested. Furthermore, considering that a simple increase in resin dose had increased the removal of high MW NOM, a bead size reduction allowing a higher external surface area to volume would allow increased NOM removal without increasing the required resin concentration and would be the most proficient redesign alternative.

7. Further work

This work has shown that beside charge density the molecular weight of NOM can affect its removal by magnetic resin and that the reduction of specific MW fractions can positively affect downstream treatment processes such as solid-liquid separation and filtration. However further research is needed in this area and should focus on the following issues:

1. The analysis of the effectiveness of magnetic resin to remove NOM of different MW in this thesis was based on the elution of UV_{254} absorbing compounds from the HPLC. However this method does not take the non-UV_{254} absorbing compounds into account that could also block up the resin. As well it does not allow monitoring potential interactions between different molecules that were seen to affect their removability. Therefore a DOC detector on the HPLC would give a more complete MW distribution of the sample analysed.

2. The proposed bridging mechanism of high MW material in coagulant flocs should be further investigated. However an analytical grade organic model compound should be chosen in contrary to the technical grade humic acid used in this study. As a naturally occuring high MW organic model compound could not be found, a synthetic organic compound with similar properties could be used.

3. Alternative mechanisms that could enhance the floc properties should be investigated beside bridging effects by high MW compounds given that smaller compounds such as tannic acid and L-glutamic acid were also seen to increase the resistance of flocs to shear and their settling velocity.

4. Comparative tests between magnetic resin under its current design and a version with smaller resin beads should be undertaken to elaborate whether a redesign based on a higher suface to volume area could enhance the removal of high MW.

5. Further tests into the area of intramolecular interactions should be undertaken to gain more understanding of these mechanisms thought to influence the removability of NOM as well as to influence the properties of flocs.

6. Given that a secondary removal path beside anion exchange for NOM removal onto magnetic resin could not be excluded, further work is necessary. A test monitoring the leaching of chlorine off magnetic resin in presence of different charged and uncharged model compounds as presented by Symons *et al*., (1995), could help ellucidating the existence of alternative removal mechanisms.

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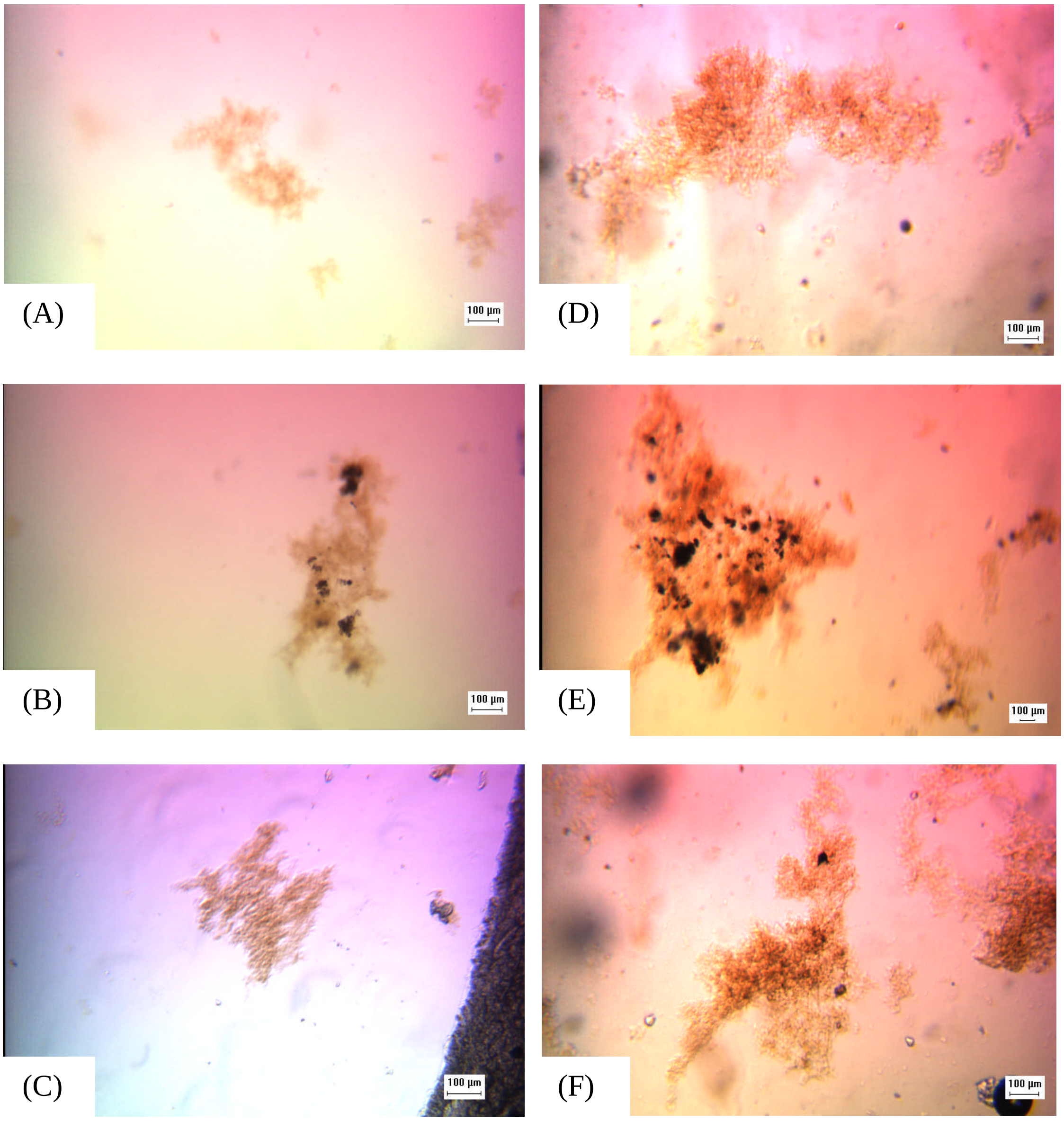
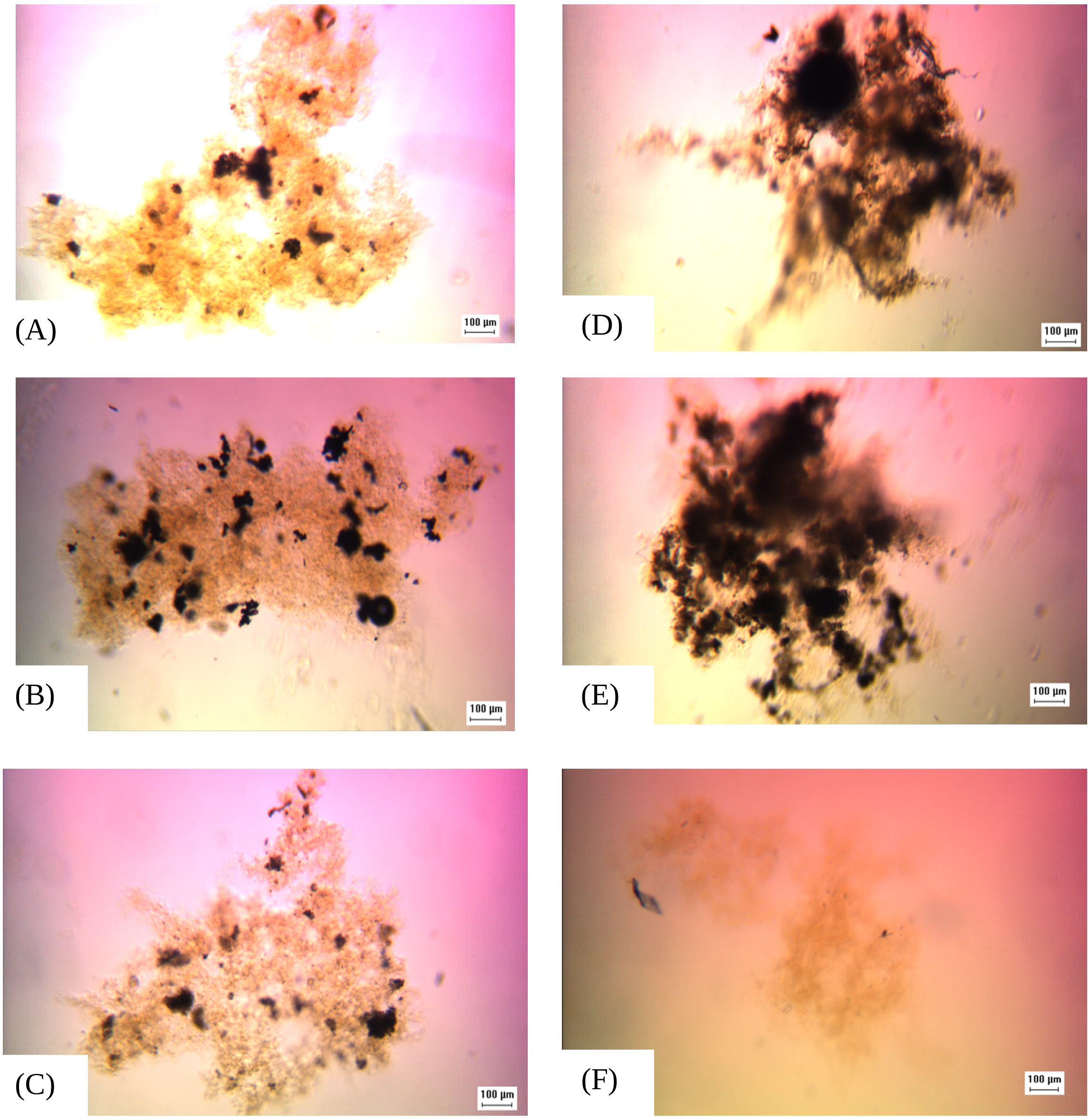
Appendix 1



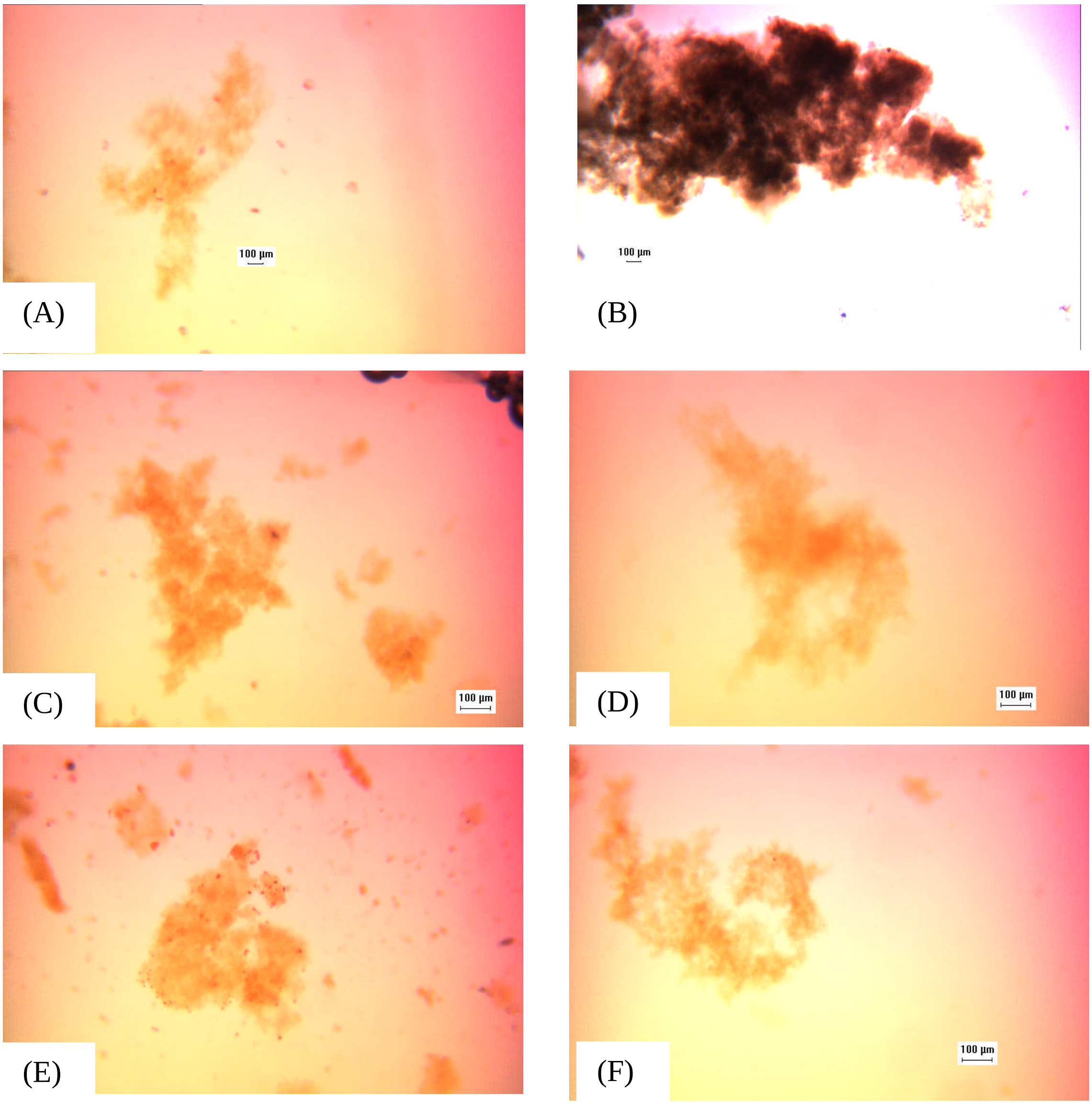
Microscopic floc pictures: Penwhirn: (A) Coagulation, (B) Combined treatment (Unfiltered), (C) Combined treatment (Filtered); Albert: (D) Coagulation, (E) Combined treatment (Unfiltered), (F) Combined treatment (Filtered).

Appendix 2



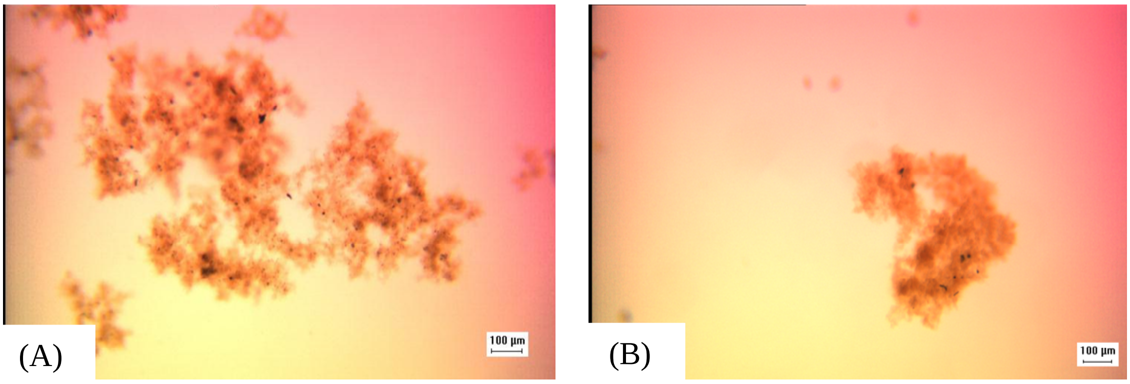
Microscopic floc pictures: Draycote: (A) Coagulation, (B) Combined treatment (Unfiltered), (C) Combined treatment (Filtered); Barcombe: (D) Coagulation, (E) Combined treatment (Unfiltered), (F) Combined treatment (Filtered).

Appendix 3



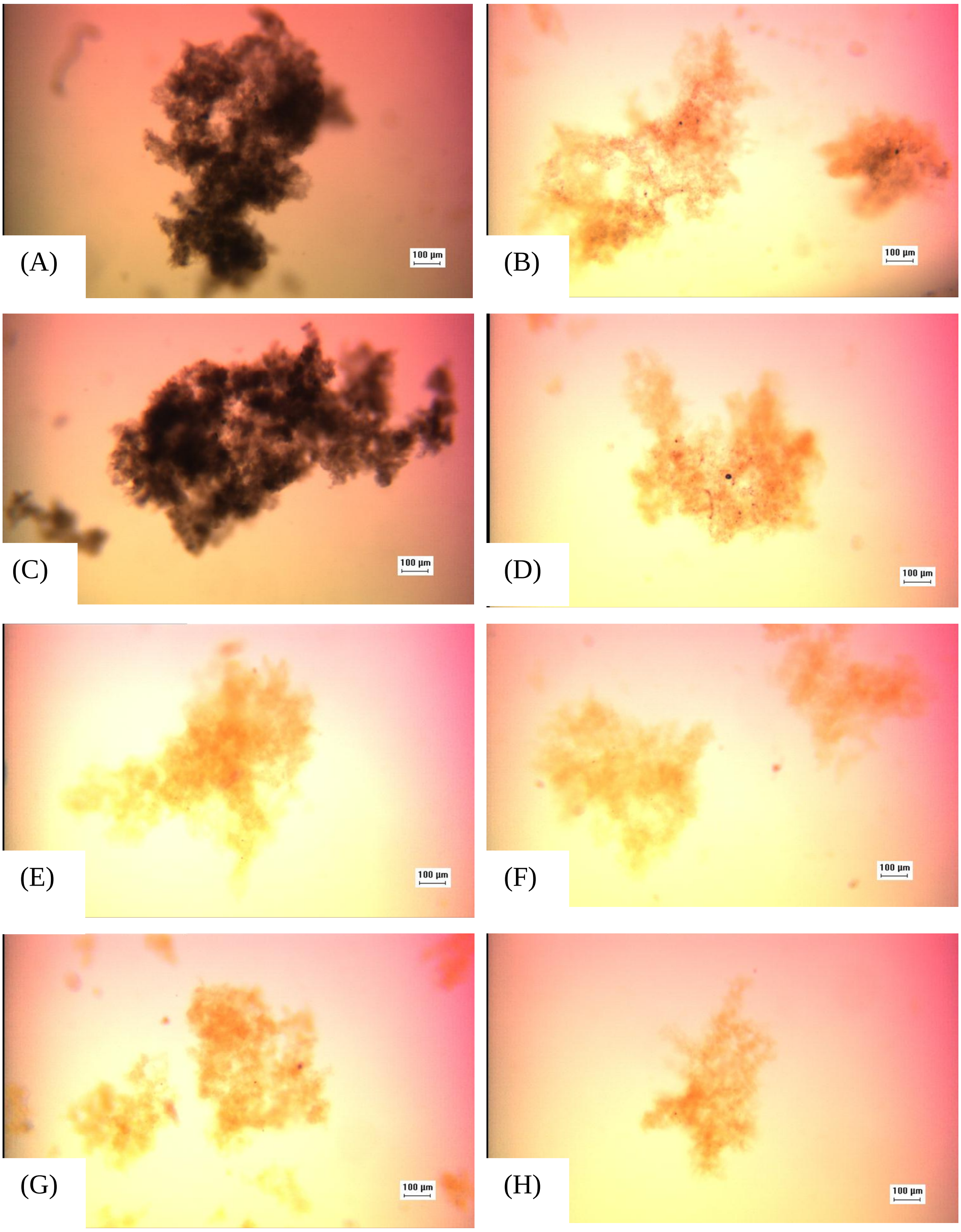
Microscopic floc pictures: (A) Precipitate, (B) Tannic acid (C) Resorcinol (Filtered), (D) L-glutamic acid, (E) D-mannose, (F) D-xylose.

Appendix 4



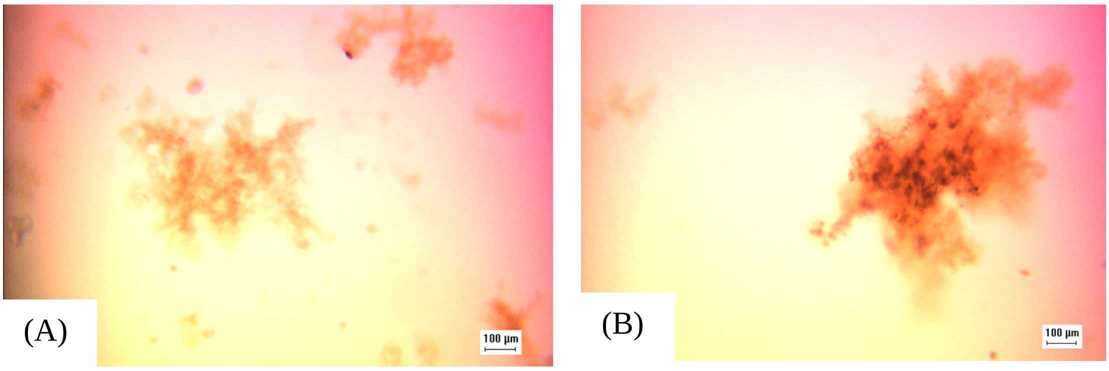
Microscopic floc pictures: Humic acid: (I) Coagulation, (J) Combined treatment.

Appendix 5



Microscopic floc pictures: Tannic acid and L-glutamic acid: (A) Coagulation, (B) Combined treatment; Tannic acid and D-mannose: (C) Coagulation, (D) Combined treatment; Resorcinol and L-glutamic acid: (E) Coagulation, (F) Combined treatment; Resorcinol and D-mannose: (G) Coagulation, (H) Combined treatment;

Appendix 6



Microscopic floc pictures for investigated treatment systems from Albert WTW: (A) Coagulation, (B) Combined treatment.