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Process Options for the Treatment of Humic Rich
Waters

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Abstract

Seasonal periods of high rainfall have led to difficulties in removing sufficient natural organic matter (NOM) to meet trihalomethane (THM) standards, and hence better or alternative treatments are required. Typically bulk water parameters such as dissolved organic carbon (DOC) and UV absorbance at 254nm (UV_{254}) are used to optimise treatment processes. Here the isolated fraction character and molecular weight (MW) distribution was used in conjunction with bulk water parameters to tailor process options for the treatment of humic rich waters. Three options for the removal of NOM were proposed. A staged coagulation based on the optimisation of isolated fractions. The results showed that although no significant reduction in DOC or UV_{254} was observed filter breakthrough was significantly reduced. Secondly a novel magnetic ion exchange process (MIEX[®]) for the removal of NOM was evaluated. The results showed that a combination of MIEX[®] and ferric reduced the THM formation potential (THMFP) by more than 50% and lower MW compounds that are known to be untreated by conventional coagulation were reduced. This option was also shown to be the most robust option for the treatment of waters with differing quality caused by seasonal changes and different catchments. Finally the addition of a range of adsorbents including carbons, hydroxides and clays to both the raw water and the isolated low MW fractions showed that an increase in DOC and UV_{254} removal was achievable. This was proposed as a post coagulation option during times of high organic loading. All processes provide viable options for the treatment of humic rich waters during times when current processes are being challenged and having difficulty meeting THM standards.

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Abbreviations and Notation

AA	Activated alumina	
AC	Activated carbon	
ACE	Acetate carbon equivalents	
AMW	Apparent molecular weight	(Daltons)
BAC	Biologically activated carbon	
BAF	Biologically activated filter	
BV	Bed volume	
COD	Chemical oxygen demand	
CSIRO	Commonwealth Scientific and Industrial Research Organisation	
DAF	Dissolved air flotation	
DBP	Disinfection by-product	($\mu\text{g L}^{-1}$)
DI	Deionised	
DOC	Dissolved organic carbon	(mg L^{-1})
DWI	Drinking Water Inspectorate	
FAB-MS	Fast atom bombardment mass spectrometry	
FAF	Fulvic acid fraction	
FI	Flocculation index	
GAC	Granular activated carbon	
HAA	Haloacetic acid	($\mu\text{g L}^{-1}$)
HAC	High activity carbon	
HAF	Humic acid fraction	
HPI-A	Hydrophilic acid	
HPI-NA	Hydrophilic non-acid	
HPLC	High performance liquid chromatography	
HPO-A	Hydrophobic acid	
HPSEC	High performance size exclusion chromatography	
IC	Inorganic carbon	(mg L^{-1})
IEX	Ion exchange	
IOCS	Iron oxide coated sand	
K_f	Freundlich number	(mg DOC g^{-1}) ¹⁻ⁿ
MAC	Medium activity carbon	

MF	Microfiltration	
MIEX [®]	Magnetic ion exchange	
MW	Molecular weight	(Daltons)
MWCO	Molecular weight cut-off	
NF	Nanofiltration	
NMR	Nuclear magnetic resonance	
NPOC	Non-purgeable organic carbon	(mg L ⁻¹)
NOM	Natural organic matter	(mg L ⁻¹)
PAC	Powdered activated carbon	
PACl	Polyaluminium chloride	
PDA	Photometric dispersion analyser	
PDADMAC	Polydiallyldimethylammonium chloride	
PTFE	Polytetrafluoroethylene	
Py-GC-MS	Pyrolysis gas chromatography mass spectroscopy	
Q _e	Normalised adsorbent mass	(mg DOC g ⁻¹)
RE	Relative efficiency	
RO	Reverse osmosis	
SHA	Slightly hydrophobic acid	
SUVA	Specific ultraviolet absorbance	(L.mg ⁻¹ m ⁻¹)
t	time	(seconds, minutes)
TC	Total carbon	(mg L ⁻¹)
THM	Trihalomethane	(µg L ⁻¹)
THMFP	Trihalomethane formation potential	(µg mg ⁻¹ C)
TOC	Total organic carbon	(mg L ⁻¹)
USEPA	United States Environmental Protection Agency	
UF	Ultrafiltration	
UV	Ultraviolet	(m ⁻¹)
VHA	Very hydrophobic acid	
ZP	Zeta potential	(mV)

1 Introduction

1.1 Background

Most water sources throughout the world contain natural organic matter (NOM), and it is best described as a complex mixture of organic compounds. NOM itself is considered harmless, however legislation requires that disinfection is applied to drinking water in order that the water remains fit for human consumption when it reaches the tap. It is the conversion of NOM into disinfection by-products (DBPs) when chlorine is used that can cause problems (Krasner *et al.*, 1989). These by-products are varied and can include the trihalomethanes (THMs) and haloacetic acids (HAAs) first identified in 1974 (Rook, 1974). These two groups of DBPs in particular have led to concern by the regulators such as the United States Environmental Protection Agency (USEPA) and the World Health Organisation (WHO) as many have been shown to cause cancer in animals (Singer, 1999; Rodriguez *et al.*, 2000). Legislation has tightened to control the amount of DBPs allowed in drinking water and currently the UK allows an upper limit of $100 \mu\text{g L}^{-1}$ for total THMs (chloroform, dichlorobromomethane, dibromochloromethane and bromoform) based on a spot sample, whilst US regulations allows a maximum of $80 \mu\text{g L}^{-1}$. The US has also imposed a limit on the total of five HAAs (monochloro-, dichloro-, trichloro-, monobromo- and dibromo-acetic acids) of $60 \mu\text{g L}^{-1}$ (Drinking Water Inspectorate UK, 1998; USEPA, 1998).

The treatment of water for potable use has traditionally focussed on the removal of either colour or turbidity. Where the main treatment processes used for their reduction is coagulation by metal salts, membrane filtration, ion exchange/adsorption and

biodegradation. The processes are typically optimised by using parameters such as the overall removal of turbidity, dissolved organic carbon (DOC) or ultraviolet absorbance at 254 nm (UV_{254}). A summary of process options used to remove DOC and typical removals reported are shown in Table 1.1.

Table 1.1 Conventional process options and performance for DOC removal

Method	DOC Removal, (%)	Reference	Disadvantages
Coagulation	10 - 60	Croué <i>et al.</i> , 1993; Owen <i>et al.</i> , 1993; Dennett <i>et al.</i> , 1995; Edzwald, 1993; Crozes <i>et al.</i> , 1995; Volk <i>et al.</i> , 2000; Bolto <i>et al.</i> , 2002b; Matilainen <i>et al.</i> , 2002; Wang <i>et al.</i> , 2002	High coagulant doses and sludge production. Removal efficiencies related to water source.
Ion Exchange/ Adsorption	60 - 80	Fu and Symons, 1990; Owen <i>et al.</i> , 1993; Newcombe <i>et al.</i> , 1997; Summers and Roberts, 1998	Expensive. Extra waste streams.
Membranes	80 - 100	Jacangelo <i>et al.</i> , 1995; Amy and Cho, 1999; Fu <i>et al.</i> , 1994; Lin <i>et al.</i> , 1999; Judd and Hillis, 2001; Pikkarainen <i>et al.</i> , 2004	Expensive. Still requires pre-treatment to prevent membrane fouling.
Ozonation /Biodegradation	27 - 75	Goel <i>et al.</i> , 1995; Graham, 1999	Variable removal efficiencies.

The disadvantages of using bulk water quality parameters for the optimisation of conventional treatment are that many waters may appear similar by DOC or UV_{254} , but the character of the organic material within the water may be different in terms of molecular weight (MW) and reactivity. Consequently different treatment issues may exist. Recently MW distribution or isolation of aquatic organic matter has been used to study the character and treatability of the different organic molecules or MW ranges in

NOM (Matilainen *et al.*, 2002). This has shown considerable benefits in the treatment of NOM in that the removal efficiency of the MW distribution by each treatment process at a WTW can be compared. In contrast with the research presented in this thesis, previous studies have focussed on individual waters at one particular time and either bulk or isolated fractions but rarely both. In this thesis one source water was studied over a three year period and here bulk water parameters as well as MW distribution and reactive fraction removal was assessed. The four isolated fractions obtained using the method developed by Malcolm and MacCarthy (1992) and Aiken (1992) are hydrophobic acid (HPO-A), consisting of humic and fulvic acid fractions, HAF and FAF respectively, a hydrophilic acid fraction (HPI-A) and a hydrophilic non-acid fraction (HPI-NA). Published data (Goslan *et al.*, 2002) has shown that the FAF and HPI-NA are particularly reactive with chlorine during certain times of the year usually following heavy rainfall and can challenge a WTWs ability to comply with the current UK THM standard.

1.2 Motivation for work

The work described in this thesis focussed on Albert water treatment works (WTW) which is a three-stage plant ($33000 \text{ m}^3 \text{ d}^{-1} - 55000 \text{ m}^3 \text{ d}^{-1}$) on the western side of Halifax, England. The raw water treated is typical of many other waters that are sourced from an upland catchment and is therefore representative for many of the treatment issues faced in the north of the UK. The source water quality has been shown to vary significantly from season to season and during November and December the raw water DOC and colour increases substantially and the THM formation potential (THMFP) of the raw water can almost double (Table 1.2). This has led to increased difficulties in the treatment of these types of water causing the WTW to exceed the

current THM regulations. There has also been a reduction in the performance of the filtration process following coagulation. This has been attributed to high levels of NOM in the source water leading to the formation of weak flocs which break up on the filters, leading to breakthrough.

Table 1.2 Raw water quality (Albert WTW)

Parameter	Units	Water Quality (Jun-Jul)	Water Quality (Nov-Dec)
DOC	mg L ⁻¹	7.12-8.36	10.9-12.1
Colour	Hazen	59-80	88-105
UV ₂₅₄	m ⁻¹	39.5-40.6	58.7
pH	-	6.3-6.6	6.4-6.8
Turbidity	NTU	2.7-3.2	3.3-4.1
THMFP	µg L ⁻¹	~470	~900

Similarly during the past decade an overall increase in the colour from year to year has been observed. This in turn has led to an increase in coagulant demand and hence increased costs (Figure 1.1).

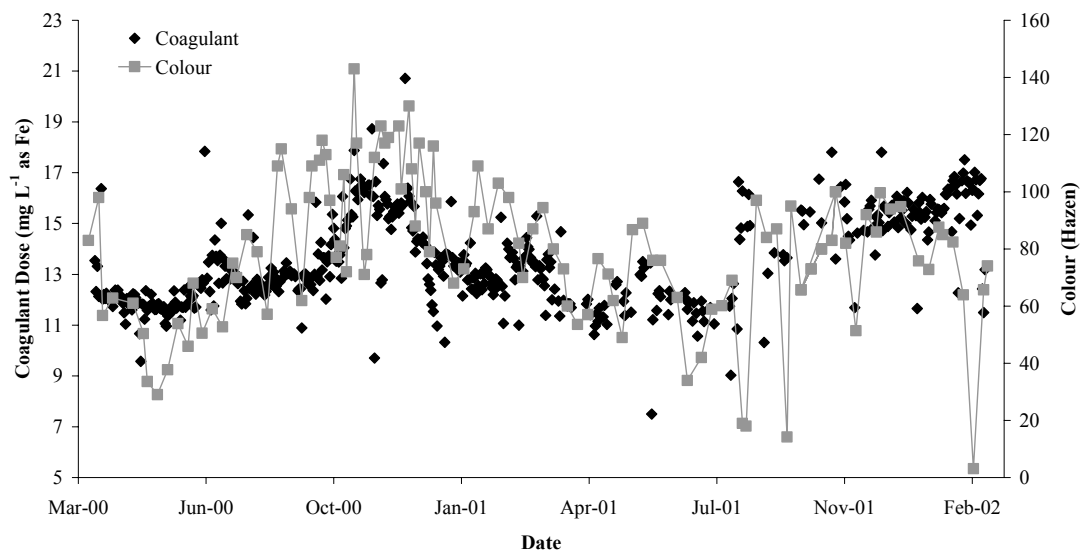


Figure 1.1 Variation in colour and coagulant dose (Albert 03/00-03/02)

As well as seasonal and annual increases in the amount of NOM in the raw water, the distribution of the four isolated fractions changes significantly. It has been shown that the amount of FAF and HPI-NA fractions varied from 25 to 60% and 10 to 35% respectively during 2000. These fractions were also shown to have a significant THMFP during the times when their concentration is at a maximum ($186.5 \mu\text{g mg}^{-1} \text{C}$ and $85.4 \mu\text{g mg}^{-1} \text{C}$ for FAF and HPI-NA respectively) (Goslan *et al.*, 2002). The HPI-NA as well as being highly reactive with regards to the formation of THMs is also considered to be the most recalcitrant to removal by conventional treatment processes (i.e. coagulation). Here by targeting the treatment processes studied for the removal of the FAF and HPI-NA fractions, a customised treatment process can be adopted for the removal of these fractions and so reduce the THMFP of the treated water from Albert WTW.

1.3 Scope of study

Elevated levels of DOC lead to a number of water treatment challenges including:

- how to meet THM standards; and
- the break up of weak flocs.

The main aim of this study was to propose possible treatment processes and if possible with low capital cost and short to medium term solutions. This will be achieved by the optimisation of the current processes and investigating alternative chemical processes. In addition could it be possible to tailor the existing processes to remove the more reactive material by looking at either the individual isolated fractions and MW ranges. Initially the isolation and fractionation of the raw and filtered waters from Albert WTW

were carried out in conjunction with an EngD research project (Goslan, 2003) and then this project focussed on the treatment options by:

- targeting the THMFP forming material;
- reducing the overall DOC load; and
- meeting new THM standards.

1.4 Thesis plan and publications

A review of the literature was carried out (Chapter 2) in order that NOM character could be related to treatment options. This has been presented as a poster at the American Water Works Association Water Quality Technology Conference, 11-15 November, 2002. Nashville, TN, USA (Goslan, E.H., Fearing, D.A., Banks, J., Wilson, D., Hillis, P., Campbell, A.T. and Parsons, S.A. Assessing Seasonal Variations in the Disinfection By-Product Precursor Profile of a Reservoir Water and later published: Goslan, E.H., Fearing, D.A., Banks, J., Wilson, D., Hillis, P., Campbell, A.T., and Parsons, S.A. (2002) Seasonal Variations in the Disinfection By-Product Precursor Profile of a Reservoir Water. *Journal of Water Supply: Research and Technology – AQUA*, **51** (8), 475-482. This paper showed that by fractionating the water into HAF, FAF, HPI-A and HPI-NA more information on reactivity could be gained than bulk water analysis alone. The literature review also identified which treatment methods would be best suited for the removal of NOM from humic rich waters (Chapter 2). Initially the effect of coagulation on the four isolated fractions was determined and consequently an optimised two-stage coagulation process was developed and the findings published: Fearing, D.A., Goslan, E.H., Banks, J., Wilson, D., Hillis, P., Campbell, A.T., and Parsons, S.A. (in press) Staged Coagulation for the Treatment of Refractory Organics. *Journal of Environmental Engineering-ASCE*. The paper discussed how although no

significant removal of NOM was observed the filter run times were increased and turbidity breakthrough reduced. Secondly a novel ion exchange process developed specifically for the removal of NOM was investigated on a number of waters, the four isolated fractions and the effect on the MW distribution and the results of the initial tests published: Fearing, D.A., Banks, J., Guyetand, S., Monfort Eroles, C., Jefferson, B., Wilson, D., Hillis, P., Campbell, A.T., and Parsons, S.A. (in press) Combination of Ferric and MIEX[®] for the Treatment of Humic Rich Water. *Water Research*. The results of the research showed how the low MW compounds that are thought to be responsible for high THM levels in treated water were reduced as was the overall DOC and THMFP of the finished water. This meant that even during times of high organic loading the process would be able to treat the water effectively. Adsorbents offer a possible post coagulation option and here the addition of a ‘disposable’ adsorbent (β -FeOOH or activated carbon (AC)) improved removal of the more recalcitrant NOM compounds. The results of these were submitted for publication to Water Research (Fearing D.A., Murray C.A., Guyetand S., Banks J., Wilson D., Hillis P.H., Campbell A.T. and Parsons S.A. (submitted) Comparison of Adsorbents for the Treatment of Humic Rich Waters. *Water Research*. Finally a review of the proposed treatment processes were compared and the results presented at NOM Research: Innovations and Applications for Drinking Water Treatment, 2-5 March, 2004. Victor Harbor, SA, Australia. Fearing D A., Banks J., Wilson D., Hillis P.H., Campbell A.T. and Parsons S.A. NOM Control Options: The Next Generation.

All the published results and further treatment results are reported and discussed in the Results and Discussion (Chapter 5).

Finally any conclusions made from the research were discussed (Chapter 6) and suggestions for further work made in Chapter 7.

2 Literature Review

2.1 Natural organic matter

Natural organic matter is ubiquitous in water sources throughout the world and can be described as a heterogeneous mixture of organic compounds of varying colour, structure and reactivity. NOM although harmless itself reacts with chlorine to form disinfection by-products (Krasner *et al.*, 1989). These by-products are mostly in the form of trihalomethanes, haloacetic acids and many other halogenated compounds and were identified as early as 1974 (Rook, 1974). In the UK THMs are of major concern as the current legislation allows $100 \mu\text{g L}^{-1}$ of total THMs to be present in the supplied water (Drinking Water Inspectorate UK, 1998). Furthermore US legislation for THMs and the five HAAs is currently set at $80 \mu\text{g L}^{-1}$ and $60 \mu\text{g L}^{-1}$ respectively (USEPA, 1998). NOM can cause problems such as bacterial regrowth in the distribution system (Croué *et al.*, 1999), cause irreversible fouling on membranes (Carroll *et al.*, 2000; Fan *et al.*, 2002), competes with target compounds for the active sites on activated carbon and blocking pores preventing adsorption (Morran *et al.*, 1996) and can effect the coagulation process with regards to floc strength and size, making downstream clarification processes less efficient (Jarvis *et al.*, 2004).

This review focuses on the current bulk characterisation techniques used for describing NOM and the bulk water removal processes used. This is in order that removal strategies for the treatment of NOM and in particular isolated fractions of NOM can be assessed and evaluated.

2.2 Composition of NOM

NOM in water is usually a result of living or decaying vegetation (Goel *et al.*, 1995) and consists of both hydrophobic and hydrophilic components. Each of these components can be further separated into acids, bases and neutrals (see Section 2.2.1), each with different chemical characters (Table 2.1).

Table 2.1 Natural organic matter composition (Adapted from Edzwald, 1993)

Fraction	Chemical Groups
Hydrophobic	
Acids	Humic and fulvic acids, aromatic acids, phenols and tannins
Bases	Proteins and aromatic amines
Neutrals	Hydrocarbons, high MW aldehydes, ethers and furans
Hydrophilic	
Acids	Hydroxy acids and sugars
Bases	Amino acids, purines and pyrimidines
Neutrals	Polysaccharides, low MW alcohols, aldehydes and ketones

The largest fraction of NOM in water is generally hydrophobic acids making up approximately 50% of the DOC (Thurman, 1985; Owen *et al.*, 1993) and these can be described as the aquatic acids or humic substances comprising of humic acids, fulvic acids. Hydrophobic acids have high MWs, 500-10,000 Daltons (Da) (Thurman, 1985) and have a varied and poorly defined character (Speitel *et al.*, 1999). The colour of humic substances changes with an increase in MW and carbon content along with a decrease in oxygen content (Figure 2.1). Seasons also play a major part in the DOC distribution of a raw water and it has been reported that for Albert raw water the hydrophobic material distribution can range from 65% to 80%. It can also be seen that in particular the FAF and the HPI-NA can vary significantly, 25 to 60% and 10 to 35% respectively (Figure 2.2, Goslan *et al.*, 2002).

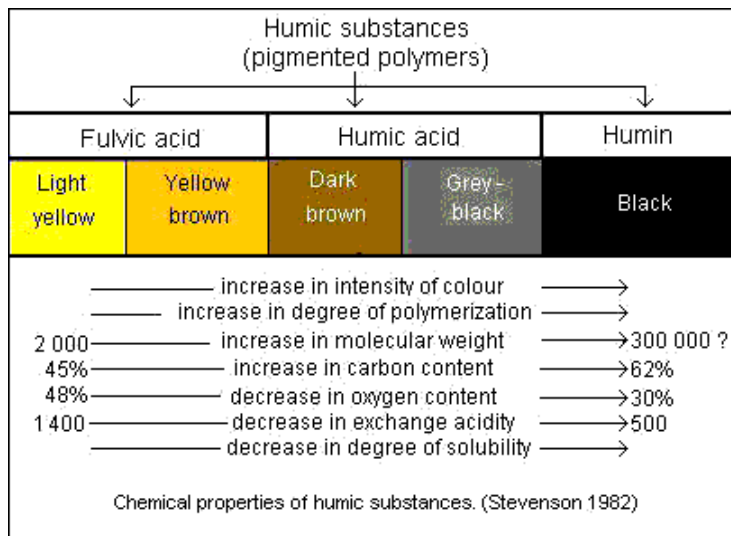


Figure 2.1 Effect of chemical properties of humic substances on colour (Stevenson, 1982)

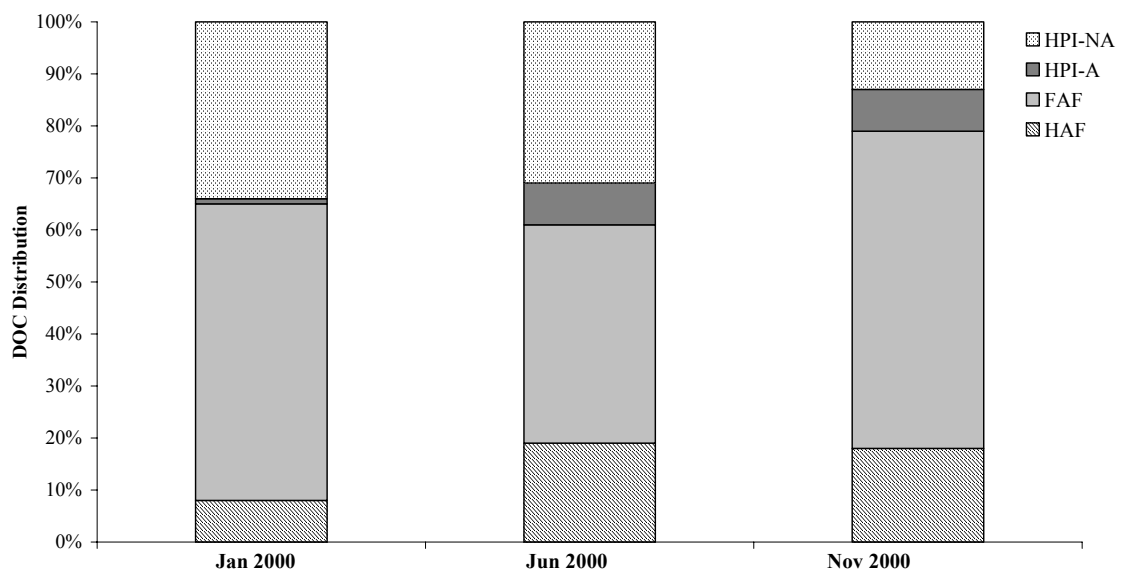


Figure 2.2 DOC distribution of the Albert WTW raw water at three different times (Source; adapted from Goslan *et al.*, 2002)

2.2.1 NOM fractionation

Isolation of aquatic NOM is widely used to study the character, reactivity and treatability of the different fractions that are inherent in NOM. From this information optimisation of current treatment processes and evaluations of novel techniques could be tested in order that removal strategies could be tailored for the individual fractions that are responsible for THM compliance problems during certain times of the year. Generally the initial stage of fractionation is the removal of colloidal matter by filtration through 0.45 μm pore filters followed by the concentration and fractionation of the resultant dissolved matter. The dissolved matter can be isolated by a number of options including molecular charge or size (Figure 2.3).

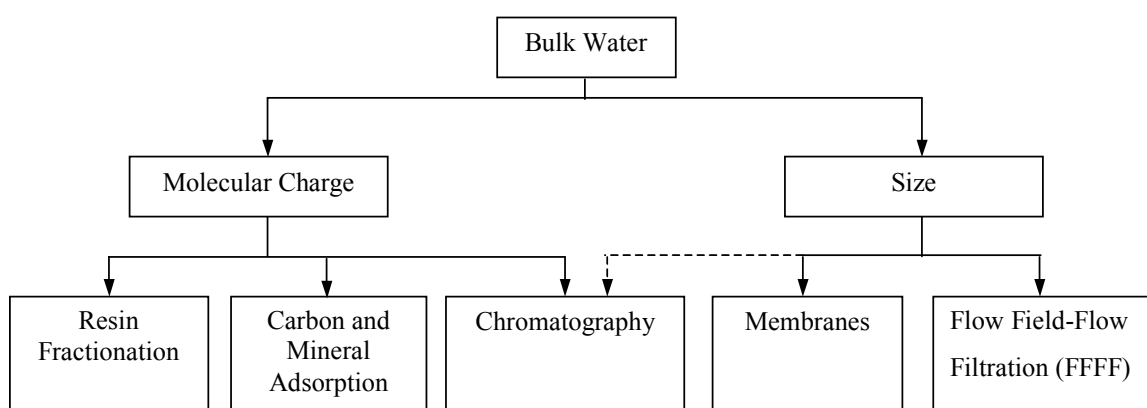


Figure 2.3 Options for fractionation of NOM

Thurman and Malcolm, (1981) developed a method for the resin fractionation of NOM using a two column adsorption technique. The columns contained XAD-8 and XAD-4 Amberlite non-functional macroporous resins and the method allows for the isolation and separation of both the hydrophobic and hydrophilic portions of the water. The following are the four fractions that can be obtained by using this method: HPO-A

fraction consisting of HAF and FAF, HPI-A and HPI-NA that passes through the both columns. The remainder of the DOC is made up from the hydrophobic neutrals and hydrophilic neutrals that are not eluted from the XAD-8 column. The remaining methods have been discussed in detail elsewhere as they are outside the scope of this review (Goslan, 2003).

2.2.2 *NOM structure*

Little is known about the individual organics found in NOM although the structure of humic and fulvic acids has been studied and is very complex (Figures 2.4 and 2.5). A simplification of their structure can be made in that they can both be regarded as polymers with an aromatic ring representing the monomer and they both contain acidic functional groups such as carboxylic acids $-\text{COOH}$ (Owen *et al.*, 1993). From these representations it can be seen that humic acid contains more carboxylic acid groups per mole of material. The charge density of the hydrophobic fractions has previously been reported as between 5-10 meq g^{-1} (Tipping, 1993) and more recently studies have shown the values to be between 4.2 and 6.8 meq g^{-1} (Sharp *et al.*, 2004).

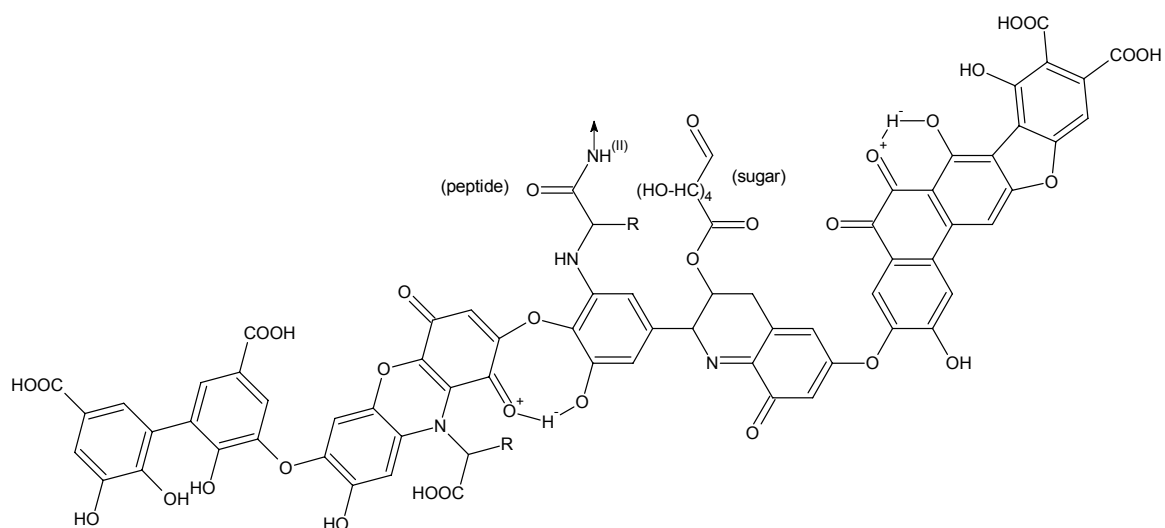


Figure 2.4 Suggested structure of humic acid (Stevenson, 1982)

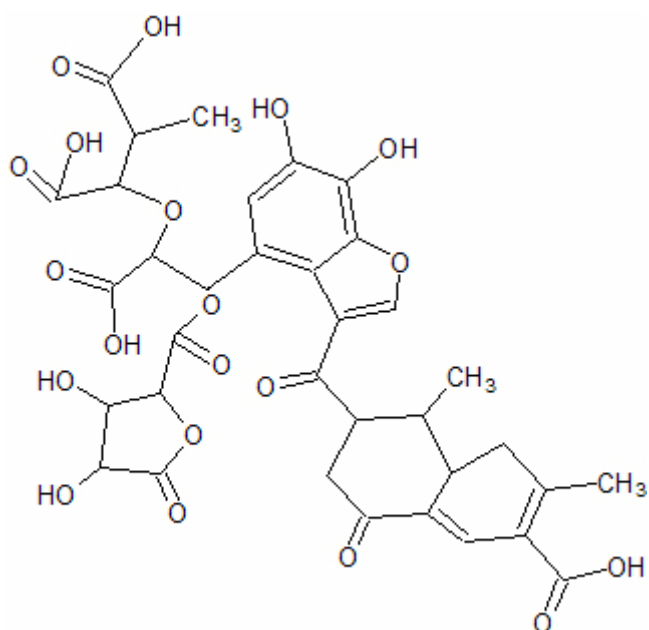


Figure 2.5 Suggested structure of fulvic acid (Source: adapted from Kubicki and Apitz, 1999)

2.3 Reactions with chlorine

NOM reacts with chlorine to produce the THM chloroform (CHCl_3) and if there is bromine in the water source then mono-, di- and tri brominated THMs along with a mixture of chlorinated and brominated acetic acid species will also be produced. A general equation for the reaction of NOM with chlorine is shown in equation 2.1 (Singer, 1999). The distribution of the THMs formed is dependent on the bromide concentration, pH and temperature where the formation of THMs is increased with increasing pH and temperature, making the problem of controlling THM precursors more important in the summer months.



The reactivity of the isolated fractions in terms of THM and HAA formation varies considerably from water to water as well as season to season (Goslan *et al.*, 2002). The HAF is generally reported to be the main cause of natural colour (Speitel *et al.*, 1999) and THMFP. For example Krasner *et al.*, (1996) showed that the HPO-A fraction produced $51 \mu\text{g THM mg}^{-1} \text{DOC}$ when compared to $21 \mu\text{g THM mg}^{-1} \text{DOC}$ for the hydrophilic acid fraction. Croué *et al.*, (1993) also reported reactivity of the fractions but gave an individual value for the humic and fulvic acid fractions of 46 and $27 \mu\text{g THM mg}^{-1} \text{DOC}$ respectively, and a reactivity for the hydrophilic fraction of $27 \mu\text{g THM mg}^{-1} \text{DOC}$. Contrary to this Goslan *et al.* (2002) reported the seasonal variation in the reactivity of the fractions. It was shown that generally the FAF was the most reactive fraction with a maximum value of $187 \mu\text{g THM mg}^{-1} \text{DOC}$ reported in the autumn compared to $119 \mu\text{g THM mg}^{-1} \text{DOC}$ for the HAF. A summary of the data reported is shown in Table 2.2.

Table 2.2 Seasonal variations in fraction reactivity (Goslan *et al.*, 2002)

Fraction	Reactivity ($\mu\text{g THM mg}^{-1}\text{ DOC}$)		
	January	June	November
HAF	32	64	119
FAF	41	27	187
HPI-A	18	37	171
HPI-NA	9	2	85

Whilst the relative reactivity of the hydrophobic fraction is typically higher than the hydrophilic fraction, there are a number of examples where this relationship doesn't always fit. For example Owen *et al.*, (1993) showed that hydrophilic material is the main cause for concern with regards to its THMFP. It was reported that 65% of the TOC and 56% of the THMFP from the Colorado river was contributed by hydrophilic compounds and that these fractions were exerting the largest chlorine demand when compared to the hydrophobic material ($2.4 \text{ mg Cl}_2 \text{ mg}^{-1}$ hydrophilic vs. $0.32 \text{ mg Cl}_2 \text{ mg}^{-1}$ hydrophobic), which consequently meant a higher concentration of THMs. A summary of reactivities from different authors is presented in Table 2.3.

Table 2.3 Summary of isolated fraction reactivities

Fraction	Reactivity		Reference
	$\mu\text{gTHM mg}^{-1}\text{C}$	$\mu\text{gHAA mg}^{-1}\text{C}$	
Hydrophobic Acid	3	3	Marhaba and Pipada, 2000
	73	-	Croué <i>et al.</i> , 1993
	55	84*	Croué <i>et al.</i> , 1999a
	36	-	Galapate <i>et al.</i> , 1999
	51	-	Krasner, 1996
	171	-	Goslan <i>et al.</i> , 2002
	38	-	
	12.8	-	
	13.8	-	Bolto <i>et al.</i> , 1999
Hydrophilic Acid	916	5	Marhaba and Pipada, 2000
	27	-	Croué <i>et al.</i> , 1993
	36	58*	Croué <i>et al.</i> , 1999
	8.6	-	Galapate <i>et al.</i> , 1999
	21	-	Krasner, 1996
	171	-	Goslan <i>et al.</i> , 2002
	37	-	
	11.4	-	Bolto <i>et al.</i> , 1999
21.9	-		
Neutral	1	<1	Marhaba and Pipada, 2000
	23	48*	Croué <i>et al.</i> , 1999
	12	-	Krasner <i>et al.</i> , 1996

*- di- and tri-chloroacetic acid only

2.4 Bulk water NOM properties

NOM character is often described by reference to the non-specific parameters of a water source. This is partly because of its ease of measurement without complex or off-line instruments. For instance the ability of humic substances to absorb UV_{254} , due to their aromatic or conjugated character is widely used to give an indication of the amount of humic substances in a water source (Dennett *et al.*, 1995).

Previous research has shown there is not a very strong correlation between raw water DOC and the potential to form THMs, consequently, other parameters in combination

with DOC can be used to give a more accurate prediction of the amount of THMs formed by a particular portion of the NOM (Speitel *et al.*, 1999). An example of this is the specific UV absorbance (SUVA, $\text{m}^{-1}\cdot\text{L mg}^{-1}$), which is the ratio of UV absorbance at 254 nm in m^{-1} to DOC concentration in mg L^{-1} . SUVA gives a relative indication of the hydrophobic content in water and give reasonable predictions of THMFP (Krasner, 1996).

A number of relationships between water quality and NOM character and reactivity are often noted in the literature. These include:

- the higher the DOC the higher the UV_{254} ; and
- the higher the UV_{254} the higher the colour.

Here data from a number of literature and water sources were analysed to test these relationships. There was a good correlation between DOC and UV_{254} where as expected, the data showed (R^2 value of 0.88) that the higher the DOC the higher the UV_{254} (Figure 2.6).

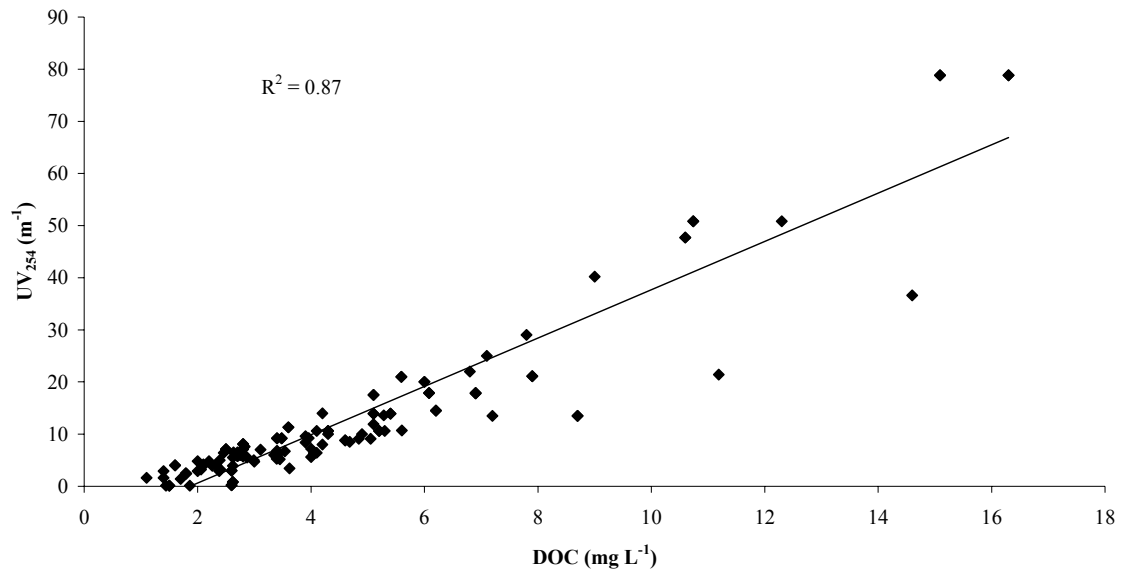


Figure 2.6 Relationship between UV₂₅₄ and DOC for a range of raw waters (Croué *et al.*, 1993; Owen *et al.*, 1993; Edzwald, 1993; Chow *et al.*, 1999; Volk *et al.*, 2000; Bell-Ajy *et al.*, 2000; Singer and Bilyk, 2002)

The relationship between DOC and THMFP is known to be poor but by using SUVA a clearer correlation, (R^2 value of 0.55) between organic character and reactivity with chlorine can be seen (Figure 2.7).

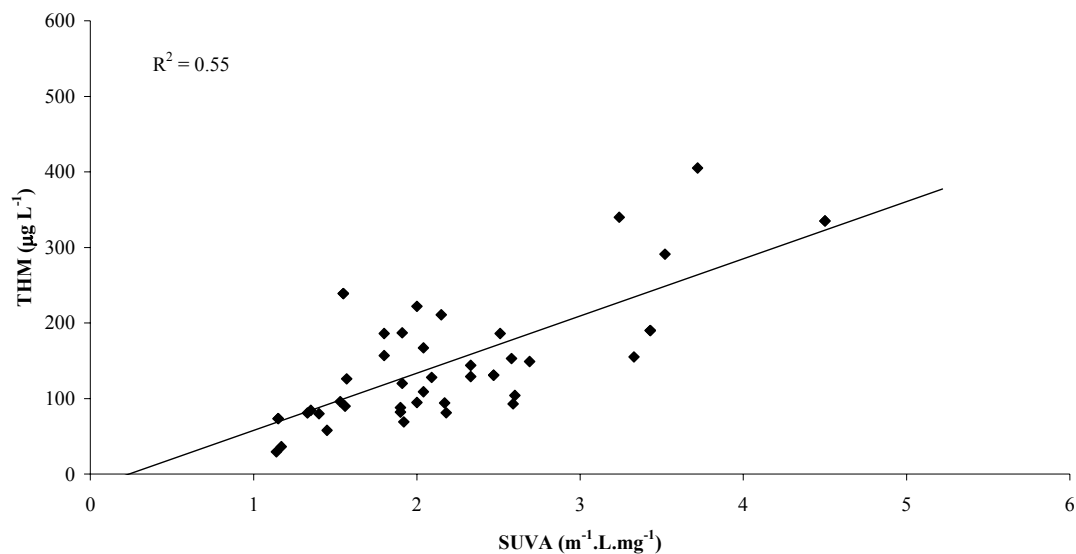


Figure 2.7 Relationship between THM and SUVA for a range of raw waters (Croué *et al.*, 1993; Owen *et al.*, 1993; Singer and Bilyk, 2002)

SUVA can also be used to describe the composition of the water in terms of hydrophobicity and hydrophilicity (Table 2.4).

Table 2.4 Nature of water using SUVA as a guide

SUVA	Composition
>4	High hydrophobicity, high MW, aquatic humics
2-4	Mixture of hydrophobics and hydrophilics
>2	Low hydrophobicity, low MW, non-humics

Source; adapted from Edzwald and Tobiasson, 1999

It has been considered that the fraction of the NOM that is hydrophobic (humic) in nature i.e. SUVA >4 is the most important when reducing THMs (Thurman, 1985). More recent research has shown that hydrophilic (non-humic) substances i.e. SUVA <2 also play a major role in the formation of THMs (Owen *et al.*, 1993). The non-humic fraction may also be accountable for the majority of the biodegradable organic carbon, this fraction has a propensity to be utilised by bacteria as a source of carbon, which in

turn promotes regrowth and coliform occurrences in distribution systems (Volk *et al.*, 2000).

SUVA has also been shown to correlate well with the aromatic content of NOM (Singer, 1999-Figure 2.8) indicating that the more aromatic the compound the more hydrophobic the NOM will be. The crosses indicate other isolated fractions.

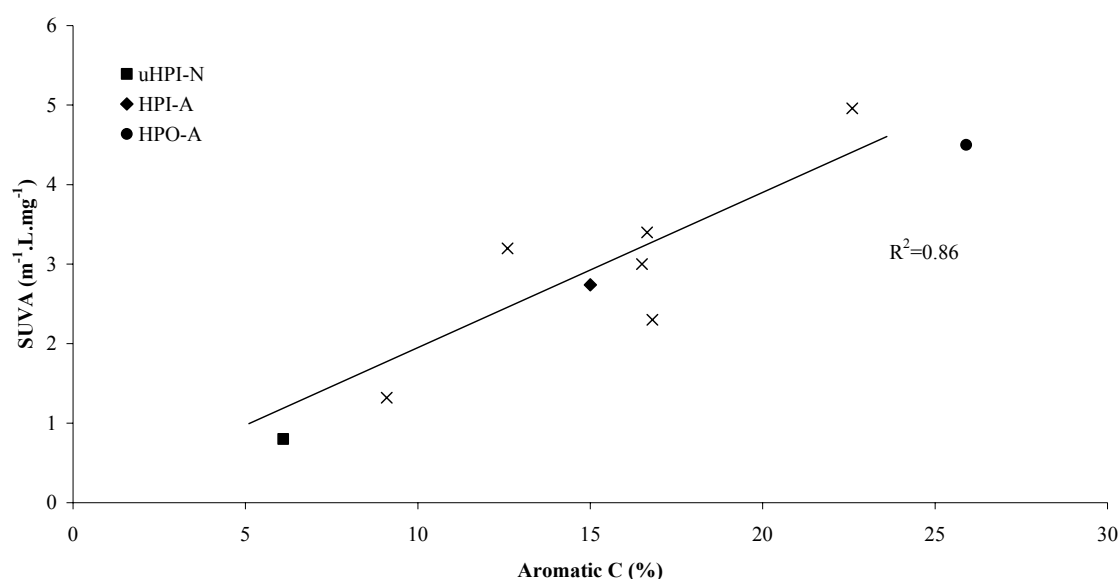


Figure 2.8 Relationship between SUVA and aromatic carbon for several NOM isolates (Singer, 1999)

Characterisation of the molecular size of humic substances can be achieved by employing size exclusion chromatography (HPSEC). The technique is based on molecules of differing sizes permeating at different speeds on to a porous matrix. The small molecules permeate the matrix to a larger degree than the larger compounds and are therefore retained longer. Larger molecules are consequently eluted first from the column (Hongve *et al.*, 1996). Popular column packings are silica based e.g. TSK gels and Protein-pak (Peuravouri and Pihlaja, 1997; Zhou *et al.*, 2000). HPSEC has been

widely used to profile the MWs of aquatic organics (Pelekani *et al.*, 1999). A monitoring program of the treatment of a Finnish water treatment works (WTW) with inlet raw water characteristics of 5.5 mg L^{-1} DOC showed the effectiveness of each process for the removal of specific MW ranges (Matilainen *et al.*, 2002). A chromatogram of the UV_{254} response vs. time for the raw and treated water is shown in Figure 2.9.

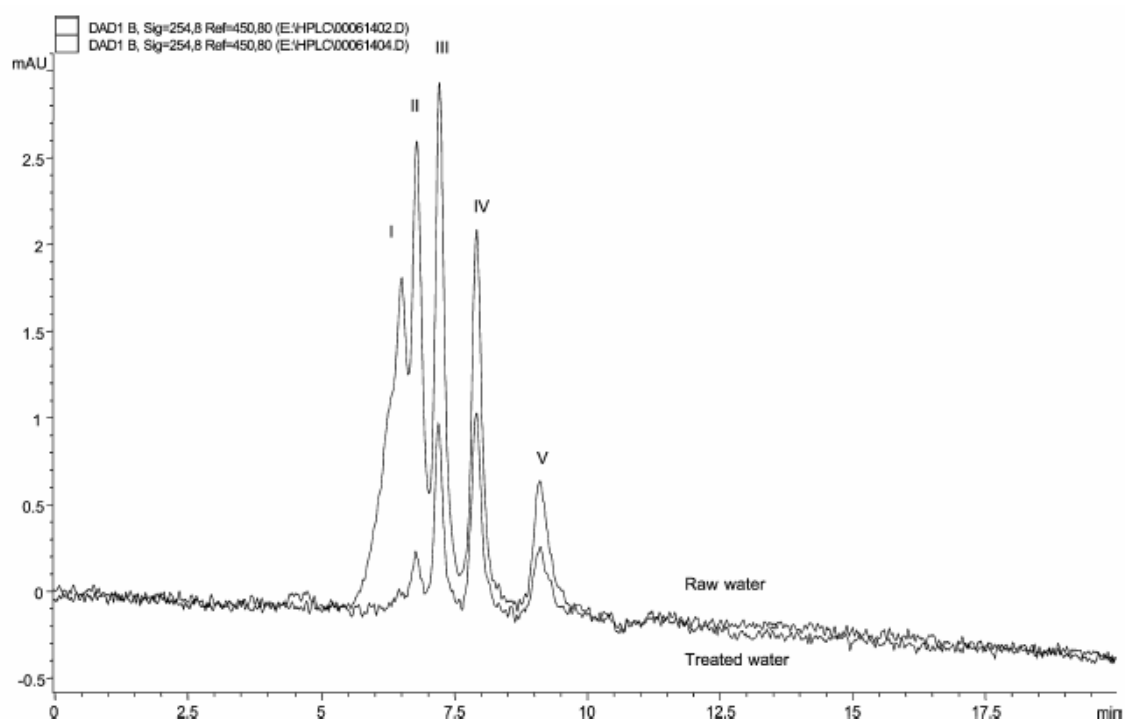


Figure 2.9 HPSEC chromatogram for raw and treated water for Rusko WTW (Finland) (Source; Matilainen *et al.*, 2002)

They showed that the high MW peaks (I and II) are removed almost completely by the treatment process and the lower MW peaks (III, IV and V) are less well removed. The effectiveness of each treatment process within the WTW on the 5 defined peaks showed that the coagulation stage was responsible for the reduction in the high MW material and had a relatively small effect on the low MW material. The activated carbon stage

was shown to be the most effective for the removal of the lower MW compounds (Figure 2.10).

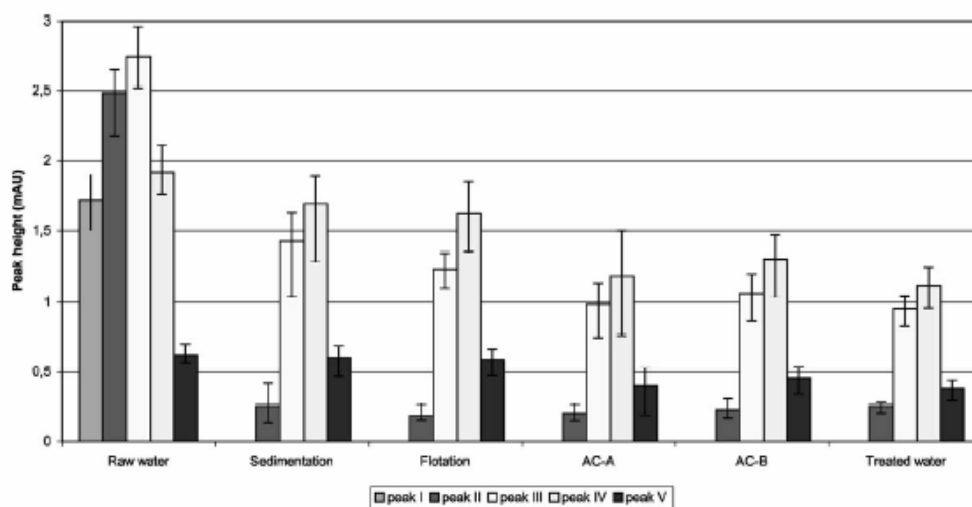


Figure 2.10 Effectiveness of individual treatment processes on the removal of different MW range materials by HPSEC (Source; Matilainen *et al.*, 2002)

Other characterisation techniques include pyrolysis gas chromatography mass spectrometry (Py-GC-MS), fast atom bombardment mass spectrometry (FAB-MS) fluorescence and both liquid and solid state nuclear magnetic resonance (NMR).

2.5 Process options for removing NOM

It is clear that to control THM and HAA formation we must reduce the concentration of precursors and hence reduce the overall DOC. There are a number of proven technologies for the removal of NOM (especially the more reactive fractions) used in the water treatment industry. These include physical, chemical and biological processes and are each capable of different DOC removal performance, Table 2.5. Each of these processes will be considered individually in the following sections.

Table 2.5 Examples of DOC removal efficiencies for commonly used water treatment processes

Method	Further Information	DOC Removal, (%)	Reference
Membranes		80 - 100	Jacangelo <i>et al.</i> , 1995; Amy and Cho, 1999; Fu <i>et al.</i> , 1994 and Lin <i>et al.</i> , 1999
Coagulation	Aluminium Sulphate	10 - 40	Croué <i>et al.</i> , 1993; Owen <i>et al.</i> , 1993; Dennett <i>et al.</i> , 1995; Edzwald, 1993; Crozes <i>et al.</i> , 1995 and Volk <i>et al.</i> , 2000
	Ferric Chloride	40 - 60	Dennett <i>et al.</i> , 1995; Crozes <i>et al.</i> , 1995 and Volk <i>et al.</i> , 2000
	PACl	20 - 40	Volk <i>et al.</i> , 2000
Ion Exchange/ Adsorption	IEX	80	Fu and Symons, 1990
	GAC	60 - 80	Owen <i>et al.</i> , 1993
Ozonation /Biodegradation	O ₃	27	Goel <i>et al.</i> , 1995
	Biodegradation	50	Goel <i>et al.</i> , 1995
	O ₃ + Biodegradation	75	Goel <i>et al.</i> , 1995

PACl = Polyaluminium Chloride; IEX = Ion Exchange; GAC = Granular Activated Carbon; O₃ = Ozone

2.5.1 Coagulation

2.5.1.1 Introduction

The treatment of surface water is traditionally focussed on the removal of turbidity, recently however, water treatment facilities have started to optimise their works for the removal of natural organic matter (Chow *et al.*, 2000). As natural organic matter is almost always anionic at the pH of natural water (Sharp *et al.*, 2004), it has a strong affinity to cationic additives such as metal coagulants and cationic polyelectrolytes, consequently coagulation is regarded as a vital unit process when treating a water source for the removal of organic matter (Volk *et al.*, 2000; Lind, 1995). The definition of coagulation as a process varies but three definitions include:

- ‘A process for combining small particles into larger aggregates’ (Amirtharajah and O’Melia, 1990);
- ‘Coagulation involves the addition of chemicals into a water to produce chemical species that act to destabilize contaminants and improve their removal’ (Dennett *et al.*, 1995); and
- ‘Coagulation is a process for combining colloid materials and small particles into larger aggregates and for adsorbing dissolved organic matter on to these aggregates, thereby facilitating their removal in subsequent sedimentation/flotation and filtration stages’ (Jiang and Graham, 1998).

Whilst there are several mechanisms proposed for coagulation with metal salts it is likely that a combination of two (i) charge neutralisation by complexation with the metal species and (ii) adsorption onto hydroxide species are observed during the coagulation of NOM. (Gregor *et al.*, 1997; Bell-Ajy *et al.*, 2000; Cheng *et al.*, 1995; Dennet *et al.*, 1995). Iron and aluminium salts are primarily used as they promote the formation of strong aggregates that are resistant to shear, important in effective coagulation (Gregory, 1989).

Detailed descriptions of the mechanisms involved are reviewed elsewhere (Dennet *et al.*, 1995; Amirtharajah and O’Melia, 1990) and it is generally accepted that the pH of the system determines which of the two mechanisms is dominant (Cheng *et al.*, 1995; Dennet *et al.*, 1995; Krasner and Amy, 1995).

The type of coagulant employed at a water treatment works varies greatly, but generally metal salts, such as iron (Dennett *et al.*, 1995; Wahlroos, 1991; Sinsabaugh *et al.*, 1986)

and aluminium (Lind, 1995; Billica and Gertig, 2000; Gregor *et al.*, 1997; Marhaba and Pipada, 2000; Chow *et al.*, 1999) are favoured. Recently the use of cationic polyelectrolytes with high charge densities have been reported as being effective for the reduction of NOM (Kam and Gregory, 2001; Bolto *et al.*, 1999).

2.5.1.2 Coagulation conditions

Performance of any coagulation process is dependant on:

- coagulant choice;
- pH;
- coagulant dose; and
- mixing time.

The choice of whether to use iron or aluminium salts as coagulants is dependent on the water type and its effectiveness in treating the individual water. Here published data from 72 waters using either iron or aluminium based coagulants was analysed to identify any trends linking character to performance. There was no overall trend linking coagulant type to DOC removal efficiency although the results did show that on average the use of iron tends to produce higher removal efficiencies than would be expected if aluminium were used, (Figure 2.11).

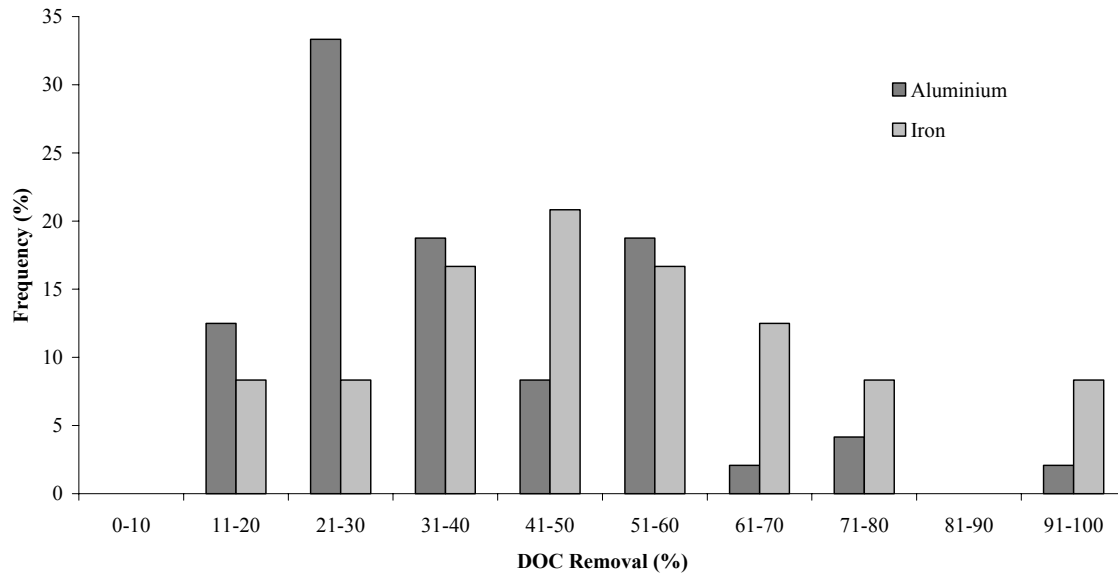


Figure 2.11 Comparison of percentage DOC removal by aluminium and iron based coagulants (Croué *et al.*, 1993; Owen *et al.*, 1993; Dennett *et al.*, 1995; Edzwald, 1993; Crozes *et al.*, 1995; Volk *et al.*, 2000)

Crozes *et al.* (1995) suggested several theories as to why iron may be a more effective coagulant than aluminium:

- ferric chloride presents approximately two times more active positive charges per dry weight of coagulant than aluminium sulphate (alum);
- ferric chloride solution is more acidic than alum solution and the alkalinity consumed during coagulation is twice as much for ferric chloride; therefore, for a smaller coagulant dosage the pH will be lower (Equation 2.2).

$$\text{Amount of Coagulant (mg L}^{-1}\text{)} \times \frac{\text{Alkalinity "as CaCO}_3\text{" (g mol}^{-1}\text{)}}{\text{MW of Coagulant (g mol}^{-1}\text{)}} = \text{Alkalinity Required (mg L}^{-1}\text{)} \quad (2.2)$$

For example 9.26 mg L⁻¹ and 4.5 mg L⁻¹ of alkalinity will be consumed for a 10 mg L⁻¹ dose of ferric chloride and alum respectively; and

- finally, it has been reported that the specific surface area of aluminium and ferric hydroxide flocs are similar, however due to there being a higher concentration of active metal in iron (III) chloride solution and the higher MW of iron, similar doses of iron produce approximately 2.8 times more metal hydroxide than for a similar dose of aluminium. This results in the surface area available for adsorption being considerably higher than that if aluminium was used.

A number of individual studies have been carried out where both iron and aluminium based coagulants are compared (Lind, 1995; Volk *et al.*, 2000). Lind (1995) compared 36 water treatment works utilising a variety of aluminium and iron based coagulants. This demonstrated that aluminium coagulants provided considerably greater DOC removal when compared to iron coagulants. However, Volk *et al.* (2000) showed that for some water sources iron is a more effective coagulant than aluminium. No clear conclusions could be gained as to what conditions made each more suitable.

Jiang and Graham (1998) studied the effect of partially pre-hydrolysing aluminium and iron coagulants on the formation of polymeric species. This had the advantage of the treatment plant being able to operate over a wider range of conditions such as pH and water temperature. This is useful as in some parts of the world there is a significant variation in the temperature from season to season. The results of this study showed that for a natural water source DOC, a 28% increase in removal of the humic fraction (DOC of 2.8 mg L^{-1}) was observed when polyferric sulphate was compared to ferric sulphate although little improvement was observed for the non-humic fraction when either the conventional or the hydrolysed coagulant was used.

Gregory and Dupont (2001) also compared conventional and pre-hydrolysed coagulants, in this study the rate of growth of the floc and the floc size formed from alum and three commercial polyaluminium chloride (PACl) products were compared. The residual turbidity obtained from the three PACls was lower in all cases than the alum with reductions from ~7 to 2 NTU observed. Dynamic monitoring of the coagulants showed that the PACls were also faster to form flocs and produce a floc size almost double that of alum in terms of flocculation index.

A key parameter in optimising coagulant performance is pH. Amirtharajah and O'Melia (1990) reported that the conditions for optimum removal of DOC using aluminium or iron based coagulants were at acidic pHs (pH 4.5–5.5 using iron and 5–6 for aluminium). This was explained as at lower pHs the humic substances become more protonated and the coagulating species becomes more positively charged, which in turn makes adsorption more favourable (Crozes *et al.*, 1995). Chadik and Amy (1983) reported that lowering the pH from 8.5 to 6.0 for iron coagulation of Biscayne Aquifer water led to a reduction in the amount of metal coagulant required and an increase in DOC and THM removal compared to coagulation at ambient conditions.

Whilst there is no overall relationship between coagulant type and removal efficiency a comparison of DOC vs. dose for 57 different water sources shows a relationship between initial DOC and coagulant dose. Where as expected the greater the initial DOC of the raw water the greater the amount of coagulant required for optimum removal (Bell-Ajy *et al.*, 2000; Singer and Bilyk, 2000; Volk *et al.*, 2000; Croue *et al.*, 1993; Owen *et al.*, 1993; Crozes *et al.*, 1995).(Figure 2.12).

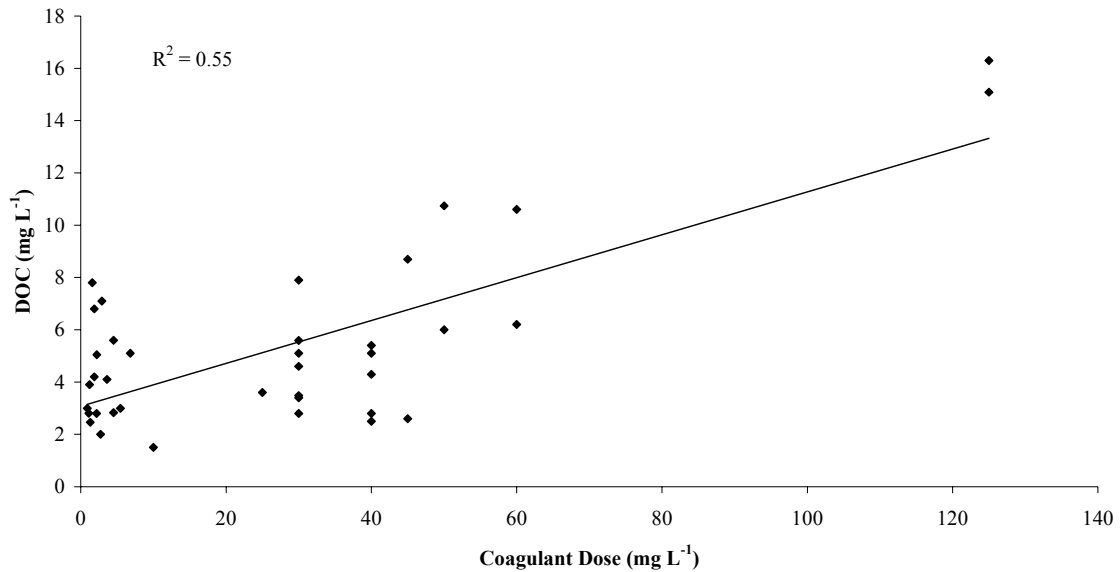


Figure 2.12 Effect of DOC vs. coagulant dose for a range of 57 waters (Bell-Ajy *et al.*, 2000; Singer and Bilyk, 2000; Volk *et al.*, 2000; Croue *et al.*, 1993; Owen *et al.*, 1993; Crozes *et al.*, 1995)

Where removal of DOC is of prime concern the United States Environmental Protection Agency (USEPA) have acknowledged enhanced coagulation or granular activated carbon as the best available technology for the reduction of disinfection by-products (Volk *et al.*, 2000; Cheng *et al.*, 2000). Enhanced coagulation is described as the treatment strategy with the single objective of removing total organic carbon (TOC), rather than colour and turbidity, in order that DBP consents in the US can be achieved (Edzwald and Tobiasson, 1999; Volk *et al.*, 2000; Crozes *et al.*, 1995; Krasner and Amy, 1995). The requirements used by the US EPA to decide whether enhanced coagulation is to be employed at a water treatment works (step 1) are shown in Table 2.6. If the source water has a TOC concentration of 2 mg L^{-1} or less the water treatment works does not have to practice enhanced coagulation. For influent TOC levels greater than 2 mg L^{-1} the TOC removal required decreases with increasing alkalinity. In the event of the removal criteria not being technically feasible an alternative TOC performance

criteria must be determined (step 2). This can be achieved by using jar tests and/or pilot studies under differing pH conditions depending on the alkalinity of the water. The step 2 TOC removal alternative is established by determining the coagulant dosage required when an additional dose (10 mg L^{-1} for alum or 9.1 mg L^{-1} for ferric chloride) results in a TOC removal of less than 0.3 mg L^{-1} or the settled water has a SUVA of less than $2 \text{ m}^1 \text{ L.mg}^{-1}$ (Edzwald and Tobiason, 1999; Volk *et al.*, 2000).

Table 2.6 Enhanced coagulation: required TOC percent removals (Edzwald and Tobiason, 1999; Crozes *et al.*, 1995)

Raw water TOC, mg L^{-1}	Raw Water Alkalinity, mg L^{-1} "as CaCO_3 "		
	<60	60 - 120	>120
>2 - 4	35	25	10
>4 - 8	45	35	25
>8	50	40	30

A few problems have been highlighted with the use of enhanced coagulation (Edzwald and Tobiason, 1999):

1. Step 2 does not allow for coagulants such as PACl, which may be an effective coagulant at neutral pHs;
2. TOC measurements are required when determining enhanced coagulation and it is DOC not TOC that is shown to be of major interest in the removal of NOM, as filtration will remove any particulate matter in a source water;
3. Overdosing of coagulant may lead to higher purchasing costs and greater sludge production;
4. There may also be a problem with poor downstream solid-liquid separation and residual aluminium when coagulation with aluminium based coagulants at low pH is employed;

5. Assumes water with $SUVA < 2$ will not have THM problems; and
6. Under enhanced coagulation conditions optimum turbidity removal may not be achieved (Crozes *et al.*, 1995).

An alternative to enhanced coagulation is multiple stage coagulation (Chow *et al.*, 1999; Wahlroos, 1991; Carlson and Gregory, 2000; Billica and Gertig, 2000). This can be further split into sequential and independently optimised multiple stage coagulation.

Chow *et al.* (1999) investigated the removal of DOC from three raw waters using alum as the coagulant. A series of jar tests controlled at pH 6 were performed and dosed repeatedly with the same alum dose five times. The results showed DOC removal for a water with an initial TOC of 9 mg L^{-1} increased from 50% to 60% after the second dose. Subsequent alum doses showed no additional removal. The data though did show an increased removal of UV absorbing compounds after each dose, although this was only significant for the high TOC, high SUVA water tested and was correlated with an increased removal of high MW organics.

Alternatively, a number of researchers have looked at two-stage coagulation where each stage is optimised independently. Wahlroos (1991) used two-stage coagulation with iron coagulants to improve organics removal (measured as chemical oxygen demand-COD) from 50 to 90% using an initial dose at pH 4.8-5 followed by a secondary dose at a pH of 8.0. Carlson and Gregory (2000) reported similar experiments on snow melt water using sequential coagulation. They reported that the first stage was conducted at a pH of 4.8–5.1 intended for the removal of humic substances and the second stage was at pH 8.0–8.5 and was intended for particulate removal. They identified that current

treatment efficiency was reduced at elevated TOC levels this was thought to be due to NOM restabilising the alum flocs. Two-stage coagulation was shown to improve the treatability of the source water especially when it contained high levels of humic material. Billica and Gertig (2000) following on from the work by Carlson and Gregory looked at the impact of this sequential coagulation on filter performance. They reported that when using single stage coagulation with alum during periods of elevated TOC, breakthrough of particles would be observed after 5 hours and would rise from 5 counts ml^{-1} to 40 counts ml^{-1} after 9 hours. With two-stage coagulation no particle breakthrough was observed.

2.5.1.3 *Effect of bulk water character on removal*

The character of organic material in terms of hydrophobicity, hydrophilicity and MW greatly affects its removal with metal coagulants (Chow *et al.*, 2000). Whilst few studies have been undertaken on fractionated organic material a number have reported the SUVA value. Generally as SUVA increase so does the SUVA removal (Figure 2.14).

Water sources with a SUVA value between 3 and 4 can be regarded as a mixture of hydrophobic and hydrophilic material. The removal of DOC in this range is generally difficult to predict as is observed by the scatter in removal efficiencies (Figure 2.13A). If we consider those waters strictly hydrophilic or hydrophobic the difference in removal efficiencies can clearly be observed (Figure 2.14). The data described in Figure 2.14 shows that when a water is hydrophobic in nature ($\text{SUVA} > 4$) 50% removal of DOC will normally be achieved. If the water is hydrophilic in nature ($\text{SUVA} > 2.5$) much lower removal efficiencies will be achieved. This can be related back to Figure

2.11 where the water sources that only achieve 11-20% DOC removal all have SUVA values less than 3 and the sources that realise greater than 70% removal tend to have SUVA values of $4.5 \text{ m}^{-1} \cdot \text{L} \cdot \text{mg}^{-1}$ or above.

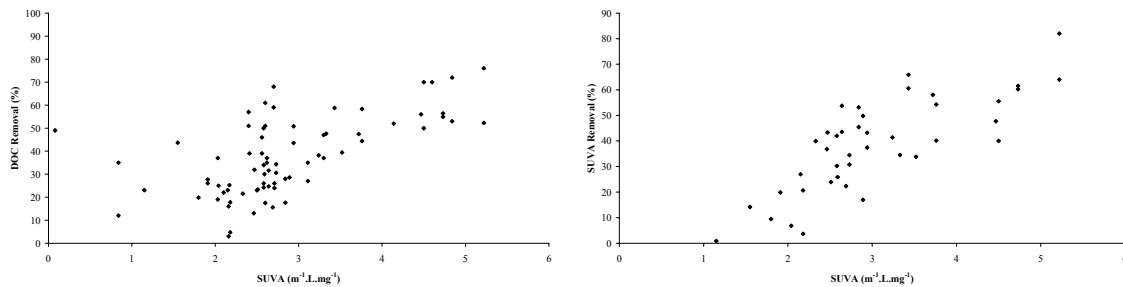


Figure 2.13 Relationship between SUVA and (A) DOC removal and (B) SUVA removal for a range of raw water sources (Bell-Ajy *et al.*, 2000; Singer and Bilyk, 2000; Volk *et al.*, 2000; Croue *et al.*, 1993; Owen *et al.*, 1993; Crozes *et al.*, 1995; Chow *et al.*, 1999; Edzwald, 1993)

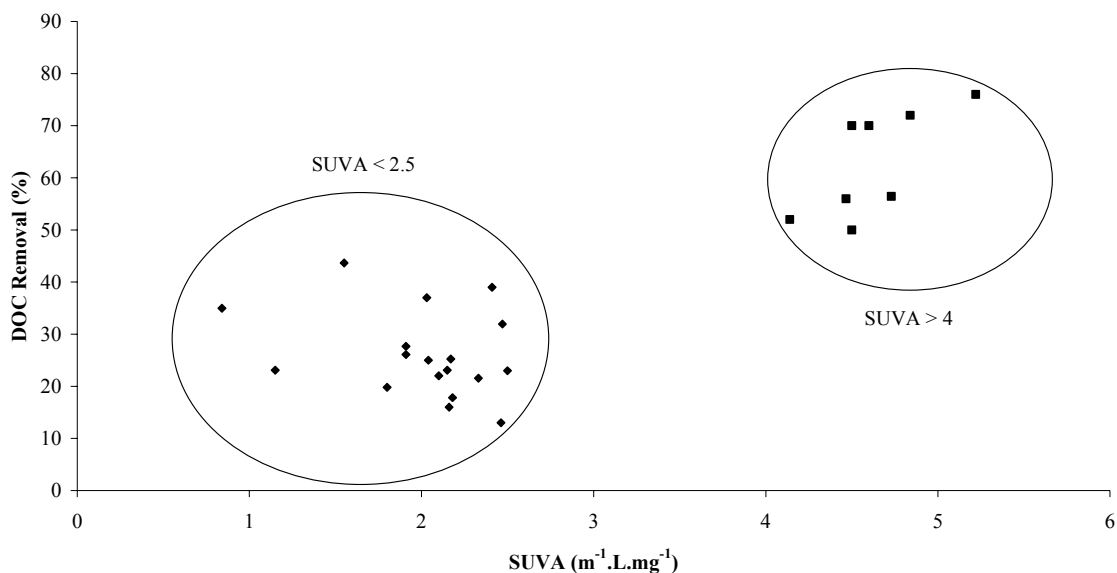


Figure 2.14 Relationship between SUVA and DOC removal focussing on hydrophobic and hydrophilic water sources. (Croué *et al.*, 1993; Owen *et al.*, 1993; Edzwald, 1993; Crozes *et al.*, 1995; Chow *et al.*, 1999; Volk *et al.*, 2000; Bell-Ajy *et al.*, 2000)

2.5.1.4 Effect of fraction character on removal

Studies on the removal of individual fractions are less well documented. Croué *et al.* (1993) showed that although high removals of both DOC and THMFP were achieved by coagulation of the humic acid fraction of the organic matter (87%), lower removals were achieved for both the fulvic and hydrophilic acid fractions (55 and 52% respectively) (Table 2.7). This is expected as in this case the humic acid fraction is more reactive, in terms of forming THMs ($46 \mu\text{g mg C}^{-1}$ for humic acid compared to $27 \mu\text{g mg C}^{-1}$ for both fulvic and hydrophilic acid) (Croué *et al.*, 1993) and is more readily removed due to its lower charge density and therefore lower doses of coagulant will be required to coagulate equal mass concentrations of humic acid compared to fulvic acids (Kavanaugh, 1978). Marhaba and Pipada (2000) reported similar findings where higher DOC removal efficiencies were achieved on hydrophobic i.e. humic plus fulvic fractions (68%) than on the hydrophilic acid fractions (51%). Bolto *et al.* (2001) reported on the removal of four isolated fractions by coagulation with alum concluding that the easiest fraction to treat was the very hydrophobic fraction (69% UV removal). Contrary to this Chow *et al.* (2000) reported that the easiest fraction to remove by alum coagulation was the hydrophilic charged fraction (~95%) followed by the very hydrophobic fractions (~65%). This is explained by the relatively high SUVA of this fraction compared to the other isolated fractions and hence higher DOC removal (see 2.5.1.3).

Another common finding in all the coagulation studies reviewed is that the neutral fractions are the most recalcitrant to removal with coagulation. Marhaba and Pipada (2000) found that only 44% and 52% DOC removal was seen for hydrophilic and hydrophobic neutrals respectively, compared to a 68% and 71% reduction in the

hydrophobic acid and base fraction respectively. Similarly Chow *et al.* (2000) observed a 40% DOC reduction for the neutral fractions compared to a 60% reduction for both the very and slightly hydrophobic acids. Bolto *et al.* (2001) observed a 30% removal of UV absorbers for the neutral fraction.

Comparison of the removal of fractions by different authors is difficult unless exactly the same method of fractionation is used. For example Peuravouri *et al.* (2001) compared the fractions obtained using DAX-8 and XAD-8 resins. Although there is very little difference in the major elemental composition of the two fractions obtained, ¹³C NMR spectroscopy of the fractions showed that the isolate collected from the DAX-8 had a greater content of aliphatics than that collected from the XAD-8. The results that are considered to be comparable in terms of fractionation procedure used are inconclusive in terms of DOC removal indicating that the nature of the fractions are site and probably season specific and cannot be used to predict the efficiency of coagulation on removal of DOC (Table 2.7).

As well as fractions, a number of researchers have looked at removal of MW ranges of NOM. Jiang and Graham (1998) studied the effect of pre-polymerised coagulants on isolated fractions. The advantage of pre-polymerising coagulants is that the coagulating species formed under normal coagulation can be deteriorated by changes in the water temperature and raw water characteristics. Pre-polymerising ensures that optimal coagulant species are preformed. They showed that the fractions with the highest MWs (> 3000 Da) were easily removed by both standard and pre-polymerised coagulants (80-90%), however the fractions with lower MWs (3000-1000 Da) were considerably better removed by pre-polymerised coagulants with up to a 24% increase compared to

conventional coagulants in terms of DOC removal. The fractions with lower MWs were more recalcitrant to removal by both types of coagulant. Although slightly higher removal efficiencies (40%) were observed with the pre-polymerised coagulants on the fractions with a MW of 500-1000 Da compared to ~20% for conventional coagulants due to the greater cationic charge on the pre-polymerised coagulant compared to the conventional coagulants.

Changes in the molecular size distribution of a water during treatment by coagulation by means of HPSEC have been reported (Vuorio *et al.*, 1998). The results showed that for the 8 distinct molecular size fractions complete removal of the first fraction (i.e. the fraction with the largest molecular size) is achieved and that the second and third fractions were removed by 92 and 85% respectively. The fourth largest fraction was removed by approximately 50% whilst the remaining four low MW fractions experienced very low removal. Similarly Vartianien *et al.* (1987) looked at 19 water works that employed alum coagulation and showed that for the first 6 fractions considered previously the removals were 100, 89 and 81% for fractions one, two and three respectively whilst only 66, 40 and 33% reductions were experienced for fractions 4, 5 and 6 respectively. The molecular size range of fractions one to three is approximately 5000-10000 Da whereas fractions 4 to 6 had an approximate MW distribution of <5000 Da. Similarly Matilainen *et al.* (2002) showed that for raw water (5.5 mg L⁻¹ DOC) 5 distinct peaks are observed by HPSEC. The absolute peak heights for these peaks were monitored throughout the treatment process. It was found that following alum coagulation that peaks 1 and 2 (high MW) were almost completely removed (100 and 93% respectively), however peaks 3 to 5 (medium and low MW) achieved lower reductions (55, 15 and 6% respectively).

Table 2.7 Comparison of reactivity and removal of NOM fractions

Fraction	AKA	Reactivity	DOC (mg L ⁻¹)	Removal (%)	Reference
HPO-A	-	3 µg TTHM mg ⁻¹ C	1.2	68 (DOC)	Marhaba and Pipada, 2000
HAF	HPO-A	46 µg CHCl ₃ mg ⁻¹ C	5.0	87 (DOC)	Croué <i>et al.</i> , 1993
FAF		27 µg CHCl ₃ mg ⁻¹ C	4.9	55 (DOC)	
HPI-A	-	27 µg CHCl ₃ mg ⁻¹ C	4.3	52 (DOC)	Chow <i>et al.</i> , 2000
HPO-A	VHA	~55 ACE mg ⁻¹ C	2.4	60 (DOC)	
HPI-A	SHA	~50 ACE mg ⁻¹ C	1.2	65 (DOC)	Bolto <i>et al.</i> , 1999
HPO-A	VHA	12.8 µg THM mg ⁻¹ C	1.7	71 (UV ₂₅₄)	
		13.8 µg THM mg ⁻¹ C	4	91 (UV ₂₅₄)	
HPI-A	SHA	11.4 µg THM mg ⁻¹ C	0.9	65 (UV ₂₅₄)	
		21.9 µg THM mg ⁻¹ C	0.5	88 (UV ₂₅₄)	

(ACE – acetate carbon equivalents)

2.5.1.5 Polymers

Recently there has been interest in the use of organic polymers as a primary coagulant for DOC removal (Bolto *et al.*, 1999; Bolto *et al.*, 2001; Edwards *et al.*, 1994; Kam and Gregory, 2001). Polymers potentially have a number of benefits over conventional metal salts such as:

- less pH dependent;
- no residual metal ions;
- no reduction in alkalinity;
- longer filter runs; and
- lower sludge volume (Bolto *et al.*, 1999).

Kam and Gregory (2001) investigated the effect of a range of high MW cationic copolymers of acrylamide and dimethyl aminoethyl acrylate and a lower MW poly diallyl dimethylammonium chloride (polyDADMAC) on a commercial and an aquatic humic acid. They concluded that maximum removal of DOC occurred for polymers of high charge density (85% removal from a solution with an initial DOC of 19.2 mg L⁻¹).

Similarly Bolto *et al.* (1999) compared the removal of UV absorbing material in isolated fractions of alum with a range of cationic polyacrylamides, cationic polymethacrylates, polyDADMAC and chitosan all of which had varying MW and charge densities. The results showed that the polymers on their own were not as effective at removing the UV absorbing material from the fractions. However a combination of a lower than optimum dose of alum and polymer did produce an equal or better result when treating two of the three unfractionated water sources. A major difference between the two papers is that Kam and Gregory reported that there was very little effect on removal with varying polymer MW indicating that bridging plays little or no part in the removal process. Contrary to this Bolto *et al.* (1999) demonstrated that for all four isolated fractions an improvement in the removal of UV absorbing material was observed for polymers of higher MWs.

2.5.1.6 Coagulant aids

Whilst polymers have shown promise when used as primary coagulants they have also been shown to perform more effectively when there is particulate matter present (i.e. clays or inorganic metal salts). This has been explained as the presence of clay allows the dissolved NOM to adsorb to the particle so removing it from solution and the polymer can then coagulate the organically covered particles due to the increase of the negative surface charge (Bolto *et al.*, 2001; Kam and Gregory, 2001). The most complete study was undertaken by Bolto *et al.* (2001) who studied the effect of a number of clays including palygorskite, illite, Arumpo bentonite and Wyoming bentonite and polyDADMAC on the removal of colour and UV absorbing material from both raw and fractionated waters. The results of the addition of 20 mg L⁻¹ of illite to 4-5

mg L⁻¹ polyDADMAC on a reconstituted raw water showed an increase in the removal of colour and UV₂₅₄ from 65 to 81% and 49 to 68% respectively.

Walker and Kim (2001) reported that the use of polymers as coagulant aids along with ferric chloride greatly increased the removal of the UV absorbing fraction of the NOM, however as reported previously UV₂₅₄ removal increased with increasing cationic polymer charge density. Although the UV absorbing species removal was greatly increased due to the addition of cationic polymers the DOC in the treated water actually increased. This is explained by the polymer being used (polydiallyl dimethyl) being a source of carbon which may be of concern if the contributed carbon has a propensity to form DBPs. Bolto *et al.* (2001) also used polymers in partnership with alum to determine optimum colour and UV removals for three raw waters and also for four fractions isolated from Moorabool River. The results demonstrate that in general the use of polymers does not greatly increase the removal efficiency in terms of UV or colour at optimum alum dosages, but the addition of a polymer at lower alum doses can greatly increase the removal efficiency of both the UV and colour (Figure 2.15).

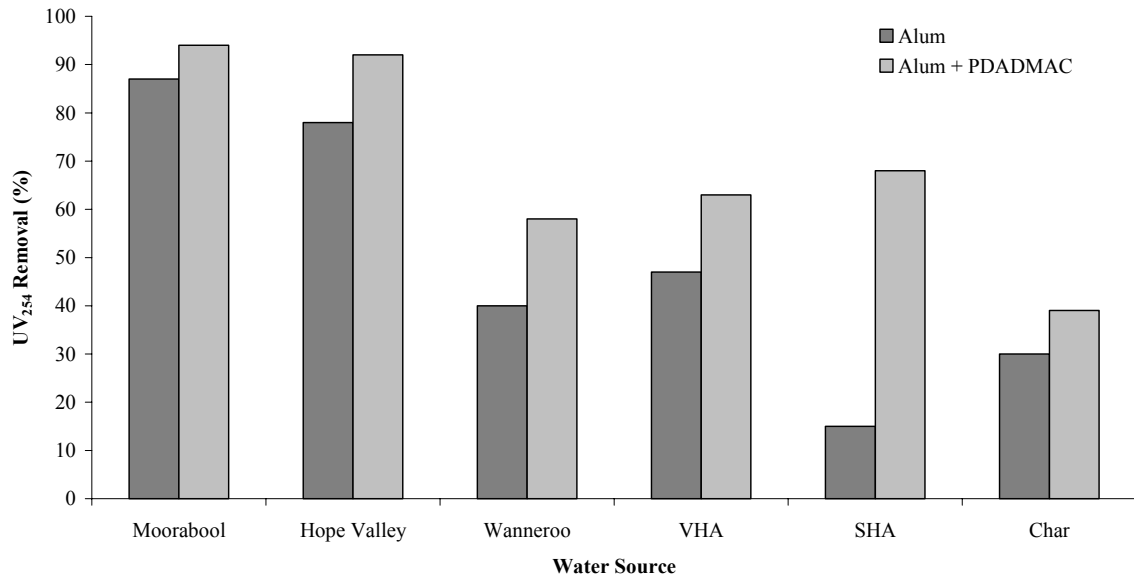


Figure 2.15 Summary of polymer effects on UV_{254} removal (Source; Bolto *et al.*, 2001)

Multivalent metal ions are known to complex with NOM and a study by Dempsey and O'Melia (1983) reported that more than 50 per cent of the negative charge associated with fulvic acid was neutralised by the addition of calcium at increasing pHs. O'Melia *et al.* (2000) put forward that this reduction in charge may reduce the coagulant demand and hence reduce sludge production. Results of their study on a range of water sources showed that the addition of calcium to “favourable” sources i.e. waters that were high in DOC, low in turbidity and did not contain hardness prior to the addition of calcium allowed for the reduction in coagulant dose for some of the waters tested.

2.5.2 Adsorption

2.5.2.1 Introduction

Adsorption of NOM onto particle surfaces is an important geochemical process in aquatic systems, where the surface characteristics of the particle can influence coagulation, flocculation and sedimentation rates (Stevenson, 1985; Malcolm, 1985;

Tipping, 1981). Due to the tightening of THM and HAA standards in the US the use of adsorption or polishing treatments such as adsorption are gaining more importance. A review of the literature shows a wide range of media has been investigated for DOC removal including:

- activated carbon;
- anion exchange resins;
- carbonaceous resins;
- metal oxides;
- preformed metal hydroxides; and
- ion exchange resins.

2.5.2.2 Activated carbon

Granular activated carbon (GAC) adsorption is considered the ‘best available technology’ for DOC removal (Karanfil *et al.*, 1999; Koechling *et al.*, 1997). Activated carbon is the most widely applied adsorption material used in drinking water treatment and is used to control pollutants such as pesticides and pharmaceuticals (Fettig, 1999). It has been reported that when initially running a GAC unit process the effluent contains virtually no humic fraction, this increases as time goes by indicating the pores are becoming saturated with NOM and by studying the DOC, UV₂₅₄ and fluorescence of the effluent, it was reported that over a typical run high removal efficiencies for bulk NOM are observed, 60–80% (Owen *et al.*, 1993).

The performance of the adsorption process is governed by a number of parameters such as carbon type, organic type and pH. Therefore any upstream processes at a water treatment works can affect the performance of GAC. For example we know that

coagulation preferentially removes hydrophobic NOM which in turn leaves a higher proportion of hydrophilic material in the feed that is less responsive to GAC (Owen *et al.*, 1993). Kilduff *et al.* (1996) observed that smaller compounds (in terms of molecular size) are adsorbed to a greater degree on an adsorbent mass basis (i.e. the greater the mass of adsorbent the greater the removal of NOM).

pH plays an important role in the adsorption on to GAC with an increase in NOM adsorption when the pH is decreased. As water pH decreases the surface charge of the carbon becomes more positive, also the degree of dissociation of the NOM functional groups decreases, the NOM molecule decreases in size by up to a factor of 2 to 3 (when pH falls from 8 to 5) and due to lower repulsive forces within the molecule the smaller pores of the activated carbon becoming more accessible to molecules (Fettig, 1999; Randtke and Jepsen, 1982). Both pH and calcium increase the amount of bridging reactions between activated carbon and the organic molecules, consequently increasing the ability of a carbon particle to react with and remove NOM (Schlautman and Morgan, 1994).

Randtke and Jepsen (1982) showed how increasing calcium concentrations lead to an increase in fulvic acid adsorption on to activated carbon from 10 to 25 mg TOC per g activated carbon. Three mechanisms were proposed:

- changes in distribution of the organics from the interaction between the calcium and organic matter;
- alteration in the packing due to the interaction between calcium and adsorbed organics; and

- neutralisation of repulsive forces between adsorbent and adsorbate due to interactions between calcium and adsorbent.

2.5.2.3 Carbonaceous resins

Carbonaceous resins have no functional groups and act similarly to GAC with surface areas of $100 \text{ m}^2 \text{ g}^{-1}$ although they have the benefit of being easily regenerated on site with steam (Fettig, 1999). They have proved to have relatively low capacities for NOM, possibly due to their hydrophobic nature, but this behaviour does lead to high performance as micro pollutant adsorbents as they are subject to less fouling by NOM than GAC (Hand *et al.*, 1994).

2.5.2.4 Metal oxides

Activated alumina and iron oxides have been tested extensively as a media for the adsorption of bulk organics (Fettig, 1999; Teermann and Jekel, 1999; Korshin *et al.*, 1997; Tipping, 1981; Schlautman and Morgan, 1994; Kung and McBride, 1989) and it is widely established that adsorption of NOM occurs by ligand exchange or surface complexation (Davis, 1980).

Gamma aluminas ($\gamma\text{-Al}_2\text{O}_3$) make up the majority of commercially available granular or powdered aluminas, with surface areas of $100\text{-}300 \text{ m}^2 \text{ g}^{-1}$ and in aqueous solution the surface is predominantly covered with hydroxyl groups which can bind the weak acid groups found in NOM (Fettig, 1999). Iron oxides tend to be in the form of fully hydrated iron oxy hydroxide granules (FeOOH) with surface areas ranging from $25\text{-}200 \text{ m}^2 \text{ g}^{-1}$ (Zhou *et al.*, 2001; Teermann and Jekel, 1999) or sand coated in iron oxide

(Korshin *et al.*, 1997). Typical physical and performance data of aluminium and ferric oxides are shown in Table 2.8.

Table 2.8 Typical data of aluminium and ferric oxide compounds

Adsorbent	Mean particle size (μm)	Surface area ($\text{m}^2 \text{g}^{-1}$)	pH	DOC (mg L^{-1})	Performance (mg g^{-1})	Reference
$\beta\text{-FeOOH}$	11	180	6	5	30	Teerman and Jekel, 1999
$\gamma\text{-Al}_2\text{O}_3$	0.03	120	6	3.3	1.82	Davis and Gloor, 1981

Davis and Gloor (1981) found the optimum capacity at pHs between 5.0-6.5 with performance falling at both lower and higher pHs. This was thought to be due to the increase in surface positive charge countered by the decrease in acid dissociation at lower pHs and *visa versa* (Kung and McBride, 1989). Schlautman and Morgan (1994) investigated the adsorption of humic and fulvic acid on colloidal size aluminium oxide particles and similarly to Davis and Gloor (1981) reported that the amount adsorbed decreases with increasing pH. They also showed how the amount of humic acid adsorbed was greater than that seen for the fulvic acid, which also showed a greater dependence on pH than the humic acid. They postulated that the greater absorbance of humic acid over fulvic acid might be due to the variation in location and distribution of the carboxyl groups (see Figures 2.4 and 2.5).

Schlautman and Morgan (1994) also observed that high MW compounds i.e. humic acid were more readily removed than fulvic acid and was related to their relative hydrophobicities. Zhou *et al.* (2001) similarly reported on the adsorption of isolated fulvic acid fractionated from a water source of high DOC content (24.2 mg L^{-1}). Adsorption isotherms of the fulvic acid onto goethite ($\alpha\text{-FeOOH}$) showed that all large

MW molecules and a portion of the smaller molecular compounds were adsorbed indicating that the larger the MW the more preferential the adsorption, probably due to the greater aromaticity of the compounds in the high MW portion and hence hydrophobicity. Likewise Meier *et al.* (1999) concluded through HPSEC and molar absorptivity data that the MW of NOM collected from two very hydrophobic water sources (37 and 41.5 mg L⁻¹ DOC) decreases in the presence of goethite indicating larger MW and aromatic compounds are preferentially adsorbed. This is not surprising given the earlier results for iron and aluminium coagulants.

Tipping (1981) reported that the adsorption of humic acid onto goethite could be more than doubled from 15% to 35% by introducing bivalent cations such as calcium to a water of 14 mg L⁻¹ DOC at pH 7 compared to water containing only monovalent ions.

Seida and Nakano (2000) investigated the removal of humics on to a variety of metal oxides and hydroxides and showed that bivalent metals exhibited high removals of humic substances with the exception of ferrous oxide, which does not hydrolyse in water (Table 2.9).

Table 2.9 Humic removals by metal hydroxides and oxides from a 100 mg L⁻¹ DOC solution (Seida and Nakano, 2000)

Compound	Weight (g)	Humic Removal (%)	pH
Mg(OH) ₂	0.15	92	10.5
Ca(OH) ₂	0.10	95	12.4
Fe(OH) ₂	0.15	47	8.3
MgO	0.15	98	10.6
CaO	0.15	97	12.4
FeO	0.15	0	8.7

Korshin *et al.* (1997) studied the adsorption of six isolated fractions on to iron oxide coated sand (IOCS). The results of the study showed that there is interaction/adsorption of all of the isolated fractions with the exception of the neutral fractions. The hydrophilic and hydrophobic acid fractions were the most readily adsorbed by the IOCS (42 and 51% respectively). It was also concluded that as the adsorption experiment continued the acidic fractions out competed the other fractions for the surface sites and possible desorption of previously sorbed fractions might occur to allow for adsorption of these acidic fractions.

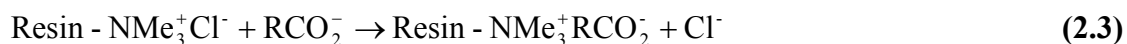
2.5.2.5 *Preformed metal hydroxides*

Although analogous to oxides, studies looking at the adsorption of NOM onto preformed metal hydroxide flocs is less well documented. Cathalifaud *et al.* (1993) presented results in an attempt to determine what reactions took place between NOM and hydroxide flocs and also to assess the influence of salts on the adsorption capacity of the hydroxide flocs. As previously shown in 2.5.1.1 the main reactions that take place are initially charge neutralisation followed by adsorption. It was also noted that similarly to Randtke and Jepsen (1982), Tipping (1981) and Seida and Nakano (2000) the addition of calcium to the system greatly increased the NOM adsorption capacity, conversely the addition of sulphate was seen to decrease the absorbance probably due to competition for the adsorption sites on the floc. Bose and Reckhow, (1998) studied the absorbance of 8 isolated fractions on to preformed aluminium hydroxide flocs and found that humic and fulvic acid had the strongest affinity for adsorption followed by weak hydrophobic and hydrophilic acid fractions and finally, the hydrophilic neutrals and bases adsorb more readily than the corresponding hydrophobic fractions. As expected results comparing SUVA with adsorption showed that the higher the SUVA

the more absorbable on to the preformed flocs. This result concurs with the findings in Figure 2.11, which proposes that fractions with high SUVA are more readily removed by coagulation in terms of DOC. Again correspondingly to previously reported data Bose and Reckhow noted that high MW fractions were preferentially adsorbed compared to lower MW fractions.

2.5.2.6 Ion exchange resins

The use of anion exchange resins for the treatment of humic rich waters is well published (Brattebø *et al.*, 1987; Ødegaard *et al.*, 1999; Symons *et al.*, 1995). They are normally very proficient at NOM removal as a large fraction of NOM can be characterised as anionic polyelectrolytes (Fettig, 1999; Ødegaard *et al.*, 1999) and this can exchange with the chloride found on a quaternary ammonium resin in the following reaction.



The efficacy of an ion exchange resin is subject to the nature of the organic matter and some general considerations have been published to address this:

- the size of the pores and their size distribution within an ion exchange resin are important when considering large MW NOM fractions; and
- the hydrophilic character of the resin is most important when addressing intermediate fractions and the exchange capacity is the major factor when low MW fractions are considered (Fu and Symons, 1990).

Published research has shown that water content is an important factor in choosing a resin for the removal of NOM, a resin of high water content has been shown to be more efficient for the removal of NOM due to the more open structure allowing better entry of the larger compounds (Gottlieb, 1995). Brattebø *et al.* (1987) reported that strong base resins were more efficient than weak base resins with reference to organic loading capacity and the resins perform more efficiently if a polar group is near the quaternary ammonium exchange sites (Bolto *et al.*, 1999). Similarly Croué *et al.* (1999b) reported that the use of strong base resins achieved considerably higher DOC removals (70-77%), especially if the stock solution was at acidic pH, compared to weak base resins (~42%) for isolated HPI-A, fractionated from the Suwannee River. They also showed that the MW of the fraction had a major effect on the removal efficiencies observed and that in general the higher the MW of a compound the lower the amount of DOC removed and hence hydrophilic neutral fractions were more readily removed than hydrophobic acid fractions.

Fu and Symons (1990) reported that removal efficiencies for ion exchange can be as high as 80% for a <1000 Dalton feed solution of 6.5 mg L⁻¹ TOC and up to 95% for a 5000-10000 Dalton solution with an initial TOC of 9 mg L⁻¹ if the resin used is suited to the nature of the water, i.e. pilot plant studies to assess the percentage of fractions in the water and hence choose a resin that is most capable of removing the NOM.

Ion exchange is not typical for full scale works although Ødegaard *et al.*, (1999) reported that, of 160 water treatment plants in Norway designed specifically for the removal of NOM, 12 use ion exchange. However the process has not proved to be

completely satisfactory and consequently very few plants remain in operation throughout the world (Drikas *et al.*, 2003).

Snoeyink (1987) concluded that due to the high selectivity exhibited by resins that although high removal efficiencies could be achieved of NOM that was well characterised, its application at a general water treatment plant was not suitable as it is not able to remove a wide variety of organic compounds.

The magnetic ion exchange (MIEX[®]) DOC process was developed by Orica Watercare, South Australian Water Corporation and the CSIRO specifically for the removal of DOC from drinking water (Figure 2.16). The resin is a strong base anion exchange resin with a macroporous structure and type 1 quaternary ammonium active sites attached to a magnetic core. The process was developed on a number of recognised premises:

- resins with quaternary ammonia functional groups are more effective (Bolto *et al.*, 2002; Singer and Bilyk, 2002);
- resins with a polyacrylic skeleton are the best for NOM removal (Symons *et al.*, 1995; Gottlieb, 1996; Singer and Bilyk, 2002);
- macroporous resins are more suited to continuous processes than gel resins (Kunin and Yarnell, 1997; Singer and Bilyk, 2002);
- resins need a high specific ion exchange capacity (Brattebo *et al.*, 1987); and
- smaller sized resin particles are more efficient (Meyers, 1995). The MIEX[®] resin beads have a mean particle size of 150 μm .

As the removal process is ion exchange only ionised organic matter can be removed. Although the ionisation of the active sites is equally efficient over the whole pH range humic substances by their nature of being weak organic acids with carboxylic functionality are only partially ionised below pH 7 and so acidic pHs are less efficient for removal.

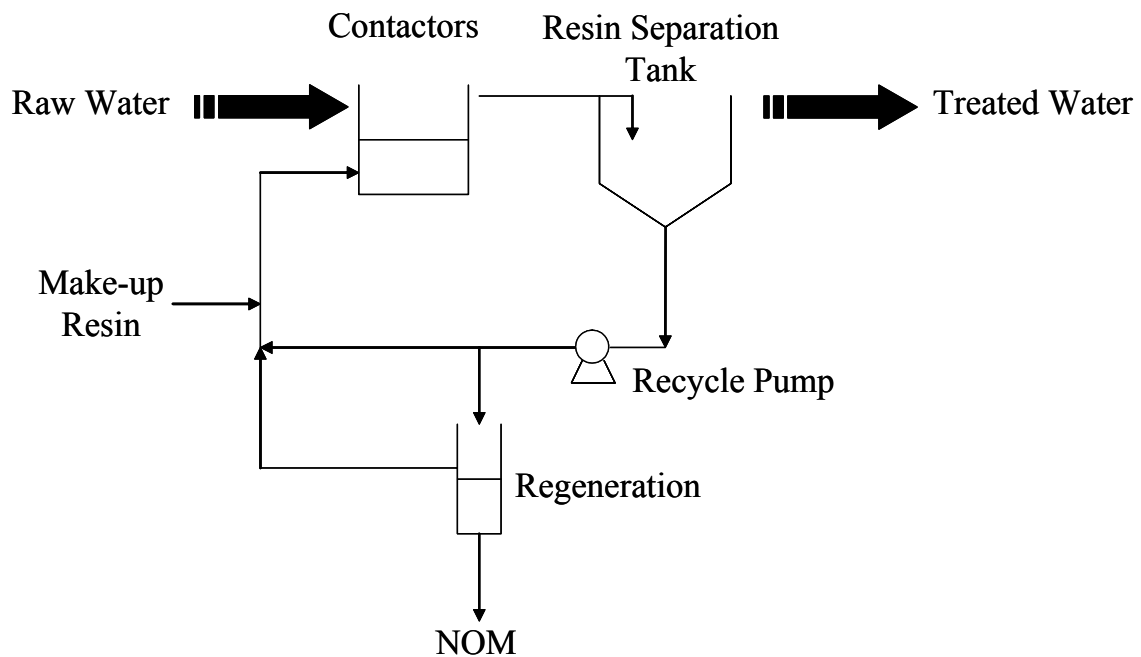


Figure 2.16 Schematic of MIEX[®] process (Orica Watercare)

The process involves adsorbing the DOC onto the MIEX[®] resin in a stirred contactor that disperses the resin beads to allow for maximum surface area. The magnetic part of the resin allows the resin to agglomerate into larger faster settling particles which allow for a recovery rate of greater than 99.9%. Any resin that is carried over is removed in downstream processes (Smith *et al.*, 2001). A further treatment stage is then required as the MIEX[®] process does not remove suspended matter, this is usually in the form of coagulation or microfiltration (Drikas *et al.*, 2003b).

Kinetic studies for the treatment of waters with MIEX[®] have shown that equilibrium is generally reached within a short contact time (10-30 minutes) (Lee *et al.*, 2003; Drikas *et al.*, 2003; Budd *et al.*, 2003). Also it has been shown that due to the large surface area relatively low doses of MIEX[®] are required to achieve maximum removals and there is more resistance to fouling on the surface (Budd *et al.*, 2003).

The bulk removal of NOM by the MIEX[®] process is relatively unpublished due to the process still being in its infancy. Published work however shows that considerable increases are generally observed in the DOC removal for a range of selected works when MIEX[®] plus coagulation is employed compared to conventional or enhanced coagulation. The removal of UV₂₅₄ is seen to be more pronounced by MIEX[®] plus coagulation for waters with a low SUVA value i.e. more hydrophilic in nature. This is due to the high SUVA waters having a high hydrophobic content which has been shown to be more readily removed by conventional coagulation. Generally the coagulant dose is greatly reduced following treatment with MIEX[®] with a reduction of up to 50% observed (Singer and Bilyk, 2002) (Table 2.10).

Table 2.10 Review of published DOC and UV₂₅₄ removal data for coagulation and MIEX[®] plus coagulated bulk waters (Drikas *et al.*, 2003; Drikas *et al.*, 2003b; Singer and Bilyk, 2002; Delphos *et al.*, 2001; Bourke *et al.*, 2001; Warton *et al.*, 2004)

	SUVA (L mg ⁻¹ m ⁻¹)	Treatment	Residual		DOC		UV ₂₅₄		Reference
			DOC (mg L ⁻¹)	DOC Removal (%)	Residual UV ₂₅₄ (m ⁻¹)	Removal (%)			
Mount Pleasant	1.32	Alum	2.6	35	2.2	49		Drikas <i>et al.</i> , 2003	
		MIEX [®] + Alum	1.5	53	1.0	77			
Hope Valley	2.4	Alum	4.2	46	7.4	46		Drikas <i>et al.</i> , 2003b	
		MIEX [®] + Alum	2.1	64	2.5	82			
Myponga	3.5	Alum	4.7	53	9.8	72		Drikas <i>et al.</i> , 2003b	
		MIEX [®] + Alum	2.4	76	3.4	90			
Mantee Co	4.5	Alum	5.3	50	10.6	78		Singer and Bilyk, 2002	
		MIEX [®] + Alum	1.4	87	2.9	94			
Tampa	4.0	Alum	9.3	65	21.9	80		Singer and Bilyk, 2002	
		MIEX [®] + Alum	2.9	86	4.1	96			
Durham	3.5	Alum	3.1	39	4.2	76		Singer and Bilyk, 2002	
		MIEX [®] + Alum	1.2	76	1.4	92			
MWD	3.0	Alum	2	29	4.8	41		Singer and Bilyk, 2002	
		MIEX [®] + Alum	1.1	71	1.6	89			
Hackensack	2.7	Alum	-	-	5.8	45		Singer and Bilyk, 2002	

					MIEX [®] + Alum	-	-	2.0	81			
					Alum	4.9	44	10	26		Singer and Bilyk, 2002	
Sioux Falls	2.7				MIEX [®] + Alum	2.4	72	3.2	76			
					Alum	2.6	7	4.1	27		Singer and Bilyk, 2002	
Austin	2.0				MIEX [®] + Alum	1.3	54	1.2	79			
					Alum	-	-	6.8	23		Singer and Bilyk, 2002	
Indianapolis	1.9				MIEX [®] + Alum	-	-	5.8	75			
					Alum	2	23	2.9	3		Singer and Bilyk, 2002	
Manchester	1.4				MIEX [®] + Alum	1.4	46	1.6	53			
					Alum	-	63	-	-		Delphos <i>et al.</i> , 2001	
Chesapeake	3.6 – 4.1				MIEX [®] + Alum	-	80	-	-			
					Fe	4.7	77	-	-		Bourke <i>et al.</i> , 2002	
Olga	~3				MIEX [®] + Fe	3.9	81	-	-			
					Alum	2.2	48	-	-		Warton <i>et al.</i> , 2004	
Wanneroo (winter)	-				MIEX [®] + Alum	1.7	60	-	-			
					Alum	2.4	65	-	-		Warton <i>et al.</i> , 2004	
Wanneroo (summer)	-				MIEX [®] + Alum	1.8	74	-	-			

Similarly the published results for the removal of isolated fractions are limited. However Lee *et al.* (2003) showed that for three isolated fractions of NOM the following removals could be achieved by the MIEX[®] process alone (Figure 2.17).

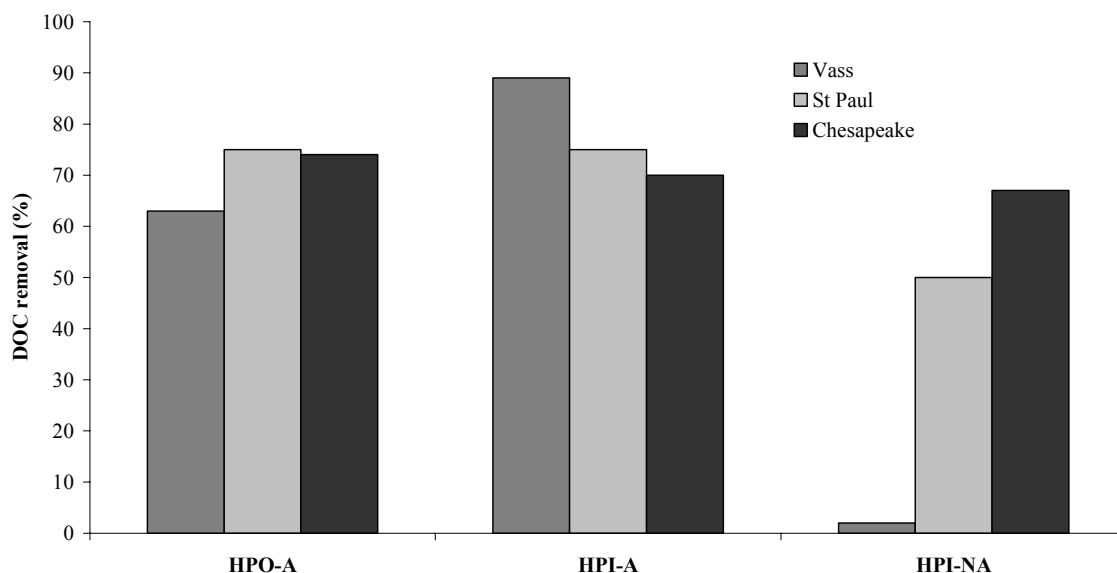


Figure 2.17 DOC removal data for the isolated fractions from 3 US water sources (Lee *et al.*, 2003)

The water sources had varying water characteristics with Chesapeake, Vass and St Paul having DOC values of 22.4, 5.1 and 8.0 mg L⁻¹ respectively. The data shows that the HPI-NA fraction is only removed to a certain level, after which no more removal is observed. This may be due to the remaining species being uncharged and consequently unsuitable to removal by the MIEX[®] process.

Furthermore it has been reported that by studying the HPSEC data for the treatment with MIEX[®] that the lower MW fractions e.g. HPI-A and HPI-NA were more readily removed than by coagulation (Lee *et al.*, 2003; Hainthaler *et al.*, 2003; Drikas *et al.*, 2003; Drikas *et al.*, 2003b)

2.5.3 Other methods

2.5.3.1 Oxidation

Oxidation is often employed as pre-treatment step in the treatment of water sources that are high in humic substances. The aim is not only to remove colour but also to react with the NOM to form products that are more susceptible to biodegradation by electrophilic addition to double bonds (Kleiser and Frimmel, 2000; Ødegaard *et al.*, 1999). The products formed after several intermediate stages are carboxylic acids, alcohols and aldehydes (Kleiser and Frimmel, 2000). Unfortunately these biodegradable products can cause a problem with regrowth of heterotrophic bacteria in distribution systems and it is therefore necessary to employ a further process to remove these products. One solution available to remedy this problem is the use of a biological step downstream of the ozonation (Ødegaard *et al.*, 1999). Combining GAC with upstream ozonation leads to significant improvements in DOC removal. Oxidation by ozone converts the NOM into smaller more biodegradable molecules which are removed in the GAC acting as biologically activated carbon (BAC) which is analogous to a biologically activated filter (BAF) (Owen *et al.*, 1993).

Hozalski *et al.* (1999) reported that the MW distribution of the NOM plays a major part in biodegradation by ozone biofiltration principally because molecules with a lower MW are more easily transported through the cell membrane, where they are consumed by metabolic enzymes (Table 2.11).

Table 2.11 Effects of SUVA and the percentage of DOC smaller than 1000 Da on NOM removal by ozone biofiltration in batch cultures

NOM Source	SUVA ($\text{m}^{-1}\cdot\text{L mg}^{-1}$)	DOC < 1000 Da (%)	DOC removal (%)
Commercial Humic Acid	9.1	10	0
Florida Ground Water	3.9	47	21
Great Dismal Swamp, VA	3.1	22	22
Soluble <i>Anabaena</i> Exudate	2.0	60	37

Source; Adapted from Hozalski *et al.*, 1999

Ozone unless applied at high doses (1.3 – 7.3 mg O₃ mg DOC⁻¹) shows no removal of DOC and from this data, it appears that there is very little benefit in ozonating water sources that have a large percentage of low MW compounds. Although those samples which contain mainly high MW (MW>1000 Daltons) taken from Great Dismal Swamp and commercial humic acid experienced a significant increase in DOC removal when ozonation was used as a pre-treatment (Goel *et al.*, 1995).

The UV absorbance is dramatically reduced and in turn so is the SUVA when ozone is used indicating that there is less aromatic content and consequently the THMFP decreases by as much as 20% for a dose of 0.5 mg ozone mg DOC⁻¹ (Table 2.12) (Kleiser and Frimmel, 2000).

Table 2.12 Changes in DOC, UV₂₅₄, SUVA and THMFP during ozonation

Absorbed Ozone (mg mg DOC ⁻¹)	DOC (mg L ⁻¹)	UV ₂₅₄ (m^{-1})	SUVA ($\text{m}^{-1}\cdot\text{L mg}^{-1}$)	Reduction in THMFP (%)
0	2.03	4.2	2.1	0
0.5	2.06	2.1	1.0	18
1	2.12	1.4	0.7	24
1.5	2.12	0.9	0.4	32

Source; Adapted from Kleiser and Frimmel, 2000

2.5.3.2 Membranes

The use of low pressure membrane processes has become of increasing interest in the treatment of water to meet stringent drinking water standards. The main interest has come in the removal of *cryptosporidium* and NOM therefore reducing DBPs (Lin *et al.*, 1999). Membrane systems have become widespread in their use across the world in a number of small scale operations (<20,000 m³ d⁻¹ - Jacangelo *et al.*, 1995). This is mainly due to their ease of operation and the decrease in the cost of employing such a process (Lin *et al.*, 1999). Recent developments in modelling ultrafiltration (UF) in particular have shown that the use of UF uses a low pressure system (40-1000 kPa), has a large pore size (0.001-0.1 µm) and a high molecular weight cut-off (MWCO) of 100,000 Da. These factors afford a higher permeate flux and hence give lower operating costs compared to reverse osmosis (RO) (Laine *et al.*, 1989).

The use of UF in the removal of NOM is dependent on the MWCO and the nature of the NOM. The use of a membrane with a MWCO of 100,000 Da appears to have very little effect on the removal of DBPs (Laine *et al.*, 1989), whereas using nanofiltration (NF) with a MWCO of 400-800 Da effectively controls DBP formation (Fu *et al.*, 1994). This can be confirmed by considering the MWs of humic material discussed in section 2.2, which states that hydrophobic material has a MW of 500 – 10,000 Daltons (Thurman, 1985).

However membrane systems are still not widely used as an alternative to other processes, possibly due to the fact that there is still limited understanding of some of the process fundamentals. There are also two problems associated with using membranes for water treatment:

1. How to enhance removal of NOM? and
2. How to control membrane fouling (Bian *et al.*, 1999)?

There are many cases showing how enhanced treatment can increase the removal of NOM i.e. UF with pre-coagulation (Bian *et al.*, 1997b, c) and microfiltration (MF) with powdered activated carbon (PAC) adsorption (Suzuki *et al.*, 1998). The membrane fouling can be attributed to any fraction of the NOM that has a size of about 0.1 μ m. NF is very effective at removing NOM, but must be used with MF and UF membranes as fouling will occur rapidly (Ødegaard and Thorsen, 1989).

The removal efficiencies that can be expected by using optimised membrane processes i.e. PAC and controlled membrane fouling is shown in a histogram (Figure 2.18). The data is taken from 18 water sources and shows the removal efficiencies obtained by using pre-treatment. Even by using pre-treatment three of the water sources failed to achieve a 50% removal of DOC, the composition of the waters in question was compared to those that achieved high removal efficiencies and it was found that the water sources that were high in colour and DOC were most easily removed whilst those with lower DOC and SUVA (3-7 mg L⁻¹ and 2-3 m⁻¹.L mg⁻¹) were harder to treat. This can be explained in that generally the lower the SUVA the smaller the molecules and hence these molecules will pass through a membrane if the pore size is not optimised for these molecules. The amount of pre-treatment, type of membrane used and nature of the water source clearly needs to be examined when considering membranes as a treatment process for the removal of DOC and THMFP (Jacangelo *et al.*, 1995).

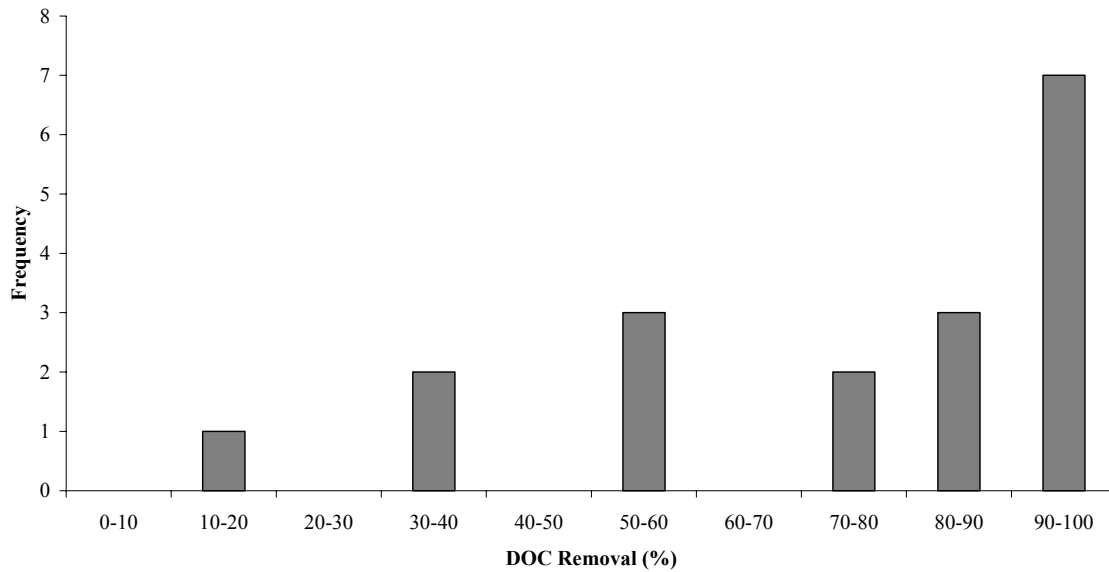


Figure 2.18 DOC removal using membranes with pre-treatment (Jacangelo *et al.*, 1995; Amy and Cho, 1999; Fu *et al.*, 1994 and Lin *et al.*, 1999)

2.6 Summary

From the published literature a summary of the findings are given:

- given the extensive literature on NOM characterisation, few researchers have linked fraction make-up to treatability;
- seasonal effects greatly alter nature of water and hence treatment options;
- bulk water analysis only suitable for a limited overview on water character;
- study of the isolated fractions allows researcher to understand which processes are suitable for individual water sources;
- HPSEC allows rapid monitoring of treatment processes on individual MW ranges of organic material;
- optimising coagulation can allow for increased removal of parts of water that lead to DBP formation;

- the use of ferric based coagulants tends to provide greater removal efficiencies compared to aluminium;
- coagulant aids can benefit the removal of the less charged material;
- adsorption can provide excellent removals of neutral and material recalcitrant to treatment by coagulation;
- ion exchange allows for high removals of humic material, but needs to be tailored for individual water sources;
- MIEX[®] is especially good for the treatment of NOM and in particular mid to low MW material found within NOM. Further trials are needed to assess its suitability to all NOM rich waters; and
- the use of membranes in the treatment of organic rich waters can afford high removal efficiencies, however pre-treatment is required and fouling can occur.

3 Objectives

The aim of the project was to investigate alternative treatment options for water containing elevated levels of NOM.

This was achieved by carrying out the following objectives:

- evaluating suitable treatment options for the removal of NOM by an extensive literature review and proposing short to medium term solutions;
- fractionating the raw and filtered water from Albert WTW to assess the most reactive fractions in terms of THM formation on the addition of chlorine in order that they may be targeted for removal;
- optimising the proposed processes for the removal of the four isolated fractions and in particular the most reactive;
- assessing the robustness of the process options on water with varying water chemistry due to seasonal changes; and
- evaluation of the proposed optimised process options on the raw water and monitoring their efficacy based on DOC, UV₂₅₄, THM and MW range removal.

4 Materials and Methods

4.1 Summary of treatment works

This section briefly describes Albert WTW from which the samples were taken for fractionation, testing and analysis. The raw water was collected from the inlet to the works and the filtered water immediately following the first rapid gravity filter.

4.1.1 Albert WTW (Yorkshire Water)

Albert WTW is a three stage plant ($33000 \text{ m}^3 \text{ d}^{-1} - 55000 \text{ m}^3 \text{ d}^{-1}$) on the western side of Halifax utilising clarification, primary filtration and manganese removal. Clarification is via 6 dissolved air flotation units (DAFs); primary filtration is via 6 rapid gravity filters and manganese removal is through 8 pressure filters. A basic process schematic is shown in Figure 4.1.

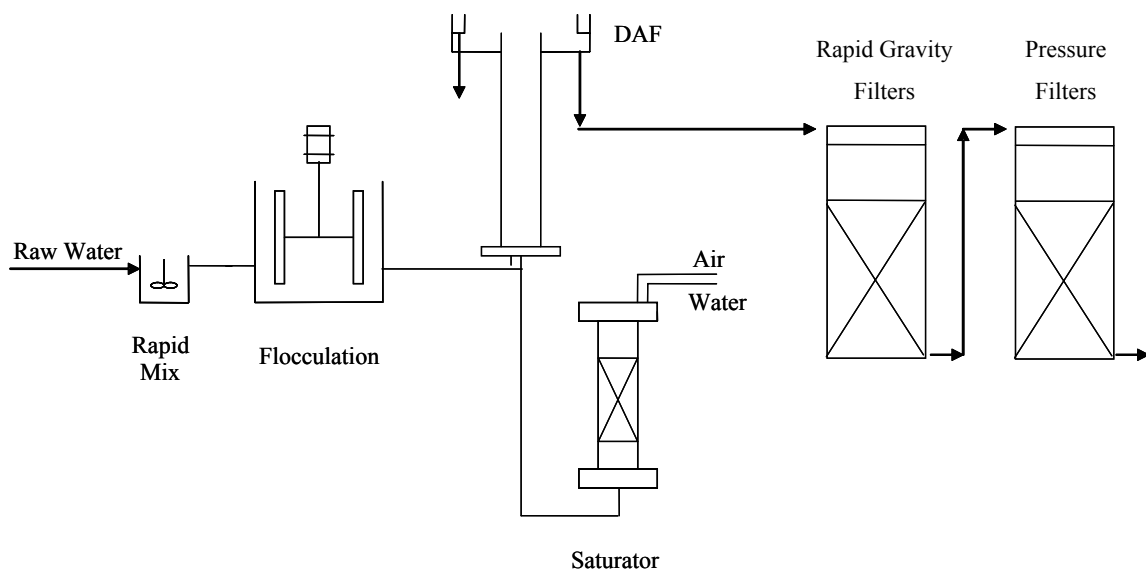


Figure 4.1 Process schematic of Albert WTW (Yorkshire Water)

4.2 Fractionation

Bulk waters were fractionated by XAD resin adsorption techniques into their HPO-A and HPI-A fractions using a method adapted from Malcolm and McCarthy (1992). A schematic of the procedure is shown in Figure 4.2. The resins used were Amberlite XAD-7HP and Amberlite XAD-4 (Rohm and Haas, PA, USA). Amberlite XAD-7HP is an acrylic ester polymer and XAD-4 is a styrene divinylbenzene polymer. Bio-Rad AG-MP-50 resin (BioRad Laboratories Ltd., Herts, UK), a non-macroporous cation exchange resin, was used to hydrogen saturate the fractions produced.

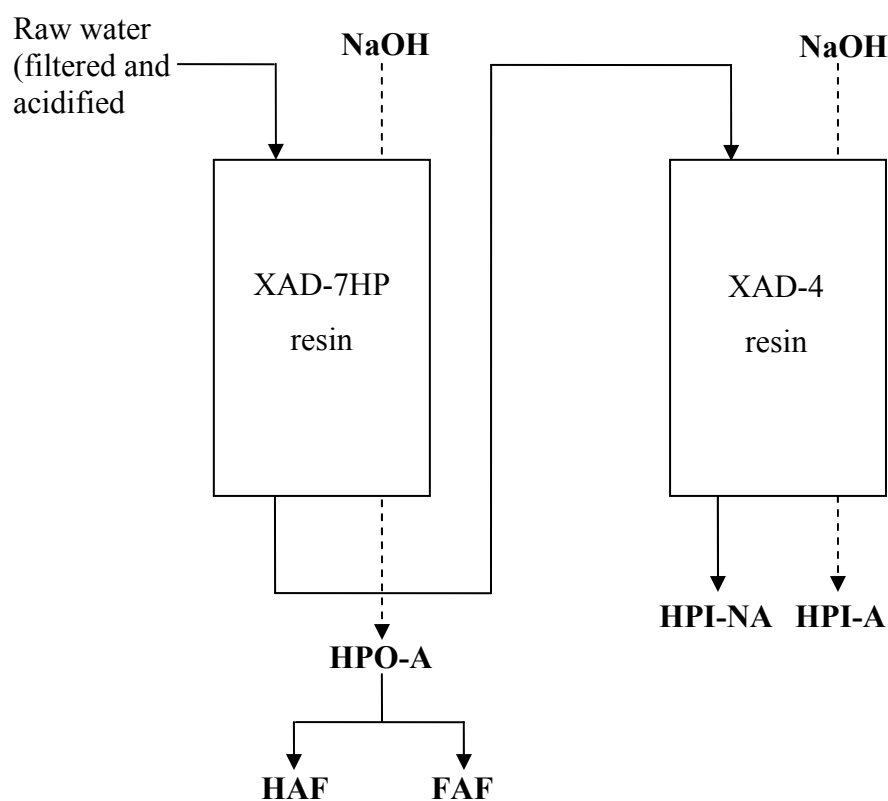


Figure 4.2 Schematic of resin fractionation process

4.2.1 Resin preparation

4.2.1.1 Amberlite XAD-7HP resin

Amberlite XAD-7HP resin (1.5 L) was slurried with sodium hydroxide (NaOH, 0.1 M, 1.5 – 2 L) and the fines decanted off, this was then repeated. The resin was stored in methanol (1.5 – 2 L) for 24 hours. The resin was sequentially soxhlet extracted for 24 hours each with methanol, diethyl ether, acetonitrile and methanol again (~ 1.75 L). The resin was packed into a glass column and rinsed with reverse osmosis (RO) water until the column effluent TOC was $< 2 \text{ mg L}^{-1}$.

The column was rinsed with 2.5 bed volumes (BV) NaOH (0.1 M) followed by 2.5 BV hydrochloric acid (HCl, 0.1 M) to remove impurities.

4.2.1.2 Amberlite XAD-4 resin

As Amberlite XAD-7HP resin preparation.

4.2.1.3 Bio-Rad AG-MP-50 resin

The resin was soxhlet extracted for 24 hours with Methanol. The resin was then slurried with RO water and packed into the column to be used. ammonium hydroxide (NH_4OH , 3 M) was pumped through the column until breakthrough of ammonia was observed. The resin was hydrogen saturated by pumping four bed volumes of HCl (2 M) through

the column. The resin was rinsed with RO water until the specific conductance of the column effluent was the same as the influent water. The resin was stored in methanol.

Each column was wrapped in aluminium foil to prevent algal growth.

4.2.2 Fractionation methodology

Raw inlet water (75 L) and treated water collected after primary filtration (300 L) from Albert reservoir was passed through a Whatman 1 μm pre-filter capsule and a Whatman 0.45 μm filter capsule and acidified to pH 2 using HCl. All of the acidified filtered water was put through the XAD-7HP/XAD-4 column pair (resin volume was 1200 mL in each column). The effluent from both columns contained the HPI-NA. The XAD-7HP column was back eluted with NaOH (0.1 M, 1800 mL). The eluate was acidified to pH 2 and passed through a 60 mL XAD-7HP column. This was the HPO-A. The XAD-4 column was back eluted with NaOH (0.1 M, 1800 mL). The eluate was acidified to pH 2 and passed through a 60 mL XAD-4 column. This was the HPI-A fraction.

The pH of the HPO-A was adjusted to 1 by adding concentrated HCl, and left to settle for 24 hours and centrifuged. The supernatant (FAF) was decanted. The residual (HAF) was dissolved in the minimum required volume of NaOH (0.1 M, ~50 mL). The HAF was hydrogen saturated by passing it through a 5 mL column of Bio-Rad AG-MP-50 resin and rinsed with RO water (5 mL). The FAF was concentrated on a 20 mL column of XAD-7HP and rinsed with RO water (20 mL) and desorbed with NaOH (0.1 M, 50 mL). The eluate was passed through a 5 mL column of Bio-Rad AG-MP-50 resin and rinsed with RO water (5 mL). The HPI-A was pumped through a 20 mL

column of XAD-4 resin and rinsed with RO water (20 mL) and desorbed with NaOH (0.1 M, 50 mL). The eluate was pumped through a 5 mL column of Bio-Rad AG-MP-50 resin and rinsed with RO water (5 mL).

The fractions produced consisted of HAF, FAF, HPI-A and HPI-NA. The recovery of the DOC was quantified by measuring the influent DOC of the water and the DOC and volume of the fractions produced. The unextracted material was assumed to be made up of the hydrophobic neutral fraction (HPO-N) as well as unrecovered material and was not quantified.

4.3 Bench scale testing

4.3.1 Coagulation

4.3.1.1 Sample preparation

Bench scale testing on solutions of water containing both the raw and treated fractions from the water collected in November 2000 were prepared to simulate the bulk water in terms of FAF, HAF, HPI-A and HPI-NA concentration. This was achieved by dosing a predetermined amount of the raw or filtered fraction into DI water (13 L) whilst stirring with a magnetic stirrer. This was equivalent to the amount of fraction present in the raw water. The pH of the stock solutions was then measured and the pH adjusted to approximately 6 (natural pH of Albert raw water) with NaOH (0.1 M) and hydrochloric acid (HCl, 0.1 M). To the stock solutions sodium hydrogen carbonate (NaHCO_3 , 20 mg L^{-1}) was added to achieve approximately 10 mg L^{-1} of alkalinity as calcium carbonate (CaCO_3), which again was approximately the amount found in the natural water sources, and the pH measured again.

4.3.1.2 *Method*

The coagulation and flocculation experiments were carried out using a Phipps & Bird PB-900 (Cambridge, UK) six-paddle jar tester. Six aliquots of the solution (1 L) previously prepared solution were taken. Whilst stirring at 200 rpm for one minute, ferric sulphate (Ferrisol XL, EA West) coagulant was dosed to five of the jars leaving the first one as a blank and the required amount of alkali to adjust the pH to 6 added; once again the pH of the aliquots was recorded. The jars were then stirred for 15 minutes at 30 rpm before settling for an additional 15 minutes before sampling. Samples of each of the jars were taken by filtering through glass fibre filter paper to remove any solids and each sample was analysed for DOC, UV_{254} and SUVA.

4.3.2 *Staged coagulation*

Staged coagulation was carried out by dosing the coagulant and pH adjusting at the start of the rapid mix stage as described previously. The second coagulant dose was added towards the end of the rapid mix stage and pH adjusted accordingly.

4.3.3 *Photometric dispersion analyser (PDA)*

A solution of DI water was prepared containing $NaHCO_3$ (20 mg L^{-1}), humic acid (Aldrich chemicals) (5 mg L^{-1}) and kaolin (2.5 mg L^{-1}). The coagulation studies were carried out using a Phipps & Bird PB-900 six paddle jar tester. A sample and return tube from the PDA (Rank Brothers, Cambridge, UK) were placed in jar containing 1 L of the previously prepared solution making sure the sample tube was placed in the same position for all experiments. The PDA logging software (PicoLog, Pico Technology Ltd) and jar tester were started simultaneously and stirred at 30 rpm for 2 minutes whilst the pH was adjusted to the desired level. The jar was then rapid mixed at 200 rpm for

10 seconds whilst adding ferric sulphate (10 mg L^{-1} as Fe) coagulant. The jar was then stirred for 15 minutes at 30 rpm to allow flocculation to occur. At this point the speed of the impeller was increased to varying values to apply a varying amount of shear for differing times, before finally re-flocculating at 30 rpm for a further ten minutes.

4.3.4 *MIEX*[®]

4.3.4.1 *Methodology*

MIEX[®] resin (Orica Advanced Water Technologies Pty. Ltd. Australia) was prepared by measuring equal doses of ‘used’ resin to water in measuring cylinders and allowed to settle for approximately two hours (the use of used resin i.e. loaded and regenerated ensured that representative results were collected). Any necessary adjustments were made using a plastic pipette before an additional settling period of approximately one hour. Samples of water to be tested (1 L) were prepared and placed on the jar tester. The jar tester was set to 150 rpm and allowed to stabilise. The resin was shaken in the measuring cylinder and added to the water sample with any residual resin being rinsed into the jar with DI water. At the end of the allotted experimental time the treated water was immediately filtered using glass fibre filter papers. If sampling was required during the process, five minute staggering of the resin additions was needed to allow for filtering.

4.3.4.2 *Resin regeneration*

A solution of sodium chloride (NaCl, 250 mL, 20%w) was prepared. An aliquot (150 mL) was removed and adjusted to pH 10 with NaOH (1 M) and diluted to 200 mL with tap water. The used resin (<50 mL) was collected and the supernatant decanted. The resin was then mixed with the previously prepared caustic NaCl solution for 1 hour and

allowed to settle. The supernatant liquid was then removed and the resin mixed in water (1 L) and allowed to settle again before removing the supernatant liquid. The regenerated resin was then re-suspended in a solution of NaCl (100 mL, 20%) and stored in a dark place for future use.

4.3.5 MIEX[®] + coagulation

MIEX[®] resin (200 mL) was prepared as in section 4.3.4 and added to the water to be treated (10 L) giving a MIEX[®] concentration of 20 mL L⁻¹. This was stirred at ~150 rpm for 5 minutes before the resin was removed via decantation and filtering. The resultant water was then subjected to the bench scale jar testing using a range of coagulant doses as described previously in section 4.3.1.

4.4 Adsorption

4.4.1 Adsorbent preparation

Activated alumina and ferric hydroxide adsorbents were prepared by taking approximately 50 g of the adsorbent and washing with NaOH solution (0.01 M) and agitating on an orbital shaker for 30 minutes, this was then washed with HCl (0.01 M) and agitated on an orbital shaker for a further 30 minutes before thoroughly rinsing with DI water and leaving for 3 days. The adsorbent was then filtered and dried for 24 hours at 105 °C.

4.4.2 Isotherm methodology

To obtain adsorption isotherms a set volume (100 mL) of water with known concentration of organic material was added to a conical flask (250 mL) containing a predetermined mass of adsorbent. Five masses of adsorbent (0.1, 0.5, 1.0, 2.5 and 5.0 g) were used to obtain the data for the isotherm and a blank containing just water was also prepared. The flasks were then pH adjusted to the desired level and gently shaken at room temperature in an orbital shaker for 24 hours. The DOC of the resultant water was then measured and the removal compared to the blank. To obtain the adsorption isotherms for the different adsorbents the results are expressed as the amount of solute adsorbed per gram of adsorbent against the amount of DOC remaining in solution relative to the blank and plotted as logarithms on opposing axes.

4.5 Analytical techniques

4.5.1 Dissolved organic carbon

Dissolved organic carbon (DOC) was measured using a Shimadzu TOC-5000A analyser (Shimadzu, Milton Keynes, UK). DOC was calculated by measuring the total carbon (TC) and the inorganic carbon (IC) and subtracting the IC from the TC. The TC standard was made by dissolving potassium hydrogen phthalate (2.125 g) in RO water (1 L). The IC standard was made by dissolving sodium hydrogen carbonate (1.750 g) in RO water (500 mL) and adding this to a solution of sodium carbonate (2.205 g) dissolved in RO water (500 mL). The standards produced had a concentration of 1000 mg L⁻¹ and working standards were diluted accordingly with RO water

4.5.2 *Ultraviolet absorbance*

UV absorbance at 254 nm was measured using a Jenway 6505 UV/Vis spectrophotometer (Patterson Scientific Ltd., Luton, UK).

4.5.3 *Specific ultraviolet absorbance*

Specific UV absorbance (SUVA) ($\text{m}^{-1}\cdot\text{L mg}^{-1}$) was calculated as a ratio of the UV absorbance at 254 nm (m^{-1}) with DOC (mg L^{-1}).

4.5.4 *Trihalomethane formation potential*

Trihalomethane formation potential (THMFP) was measured using an adaptation of procedure 5710 in ‘Standard Methods for the Treatment and Examination of Water and Wastewater’ (American Public Health Association, 1992) and is described as follows.

4.5.4.1 *Reagents*

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

$$\text{Hypochlorite Concentration, mgCl}_2 \text{ mL}^{-1} = \frac{M \times 35.45 \times \text{titrant (mL)}}{\text{Hypochlorite Added (mL)}} \quad (4.1)$$

where M is the molarity of the titrant (sodium thiosulphate).

The titration should require at least 10 mL titrant. If this is not the case, then 0.8 mL of the hypochlorite stock solution should be used. The hypochlorite concentration should be measured each time a dosing solution is made. The hypochlorite should be discarded if the chlorine concentration falls below 20 mg Cl₂ mL⁻¹.

Chlorine dosing solution (1000 mg Cl₂ L⁻¹) – The volume of hypochlorite solution required was calculated as follows:

$$\text{Hypochlorite Required (mL)} = \frac{\left(\frac{1250}{\text{Hypochlorite Conc}^n \text{ (mg Cl}_2 \text{ mL}^{-1}\text{)}} \right)}{5} \quad (4.2)$$

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., Cambridge, UK). This solution was discarded after 1 week.

Phosphate buffer – Potassium dihydrogen phosphate (KH₂PO₄, 68.1 g) and NaOH, (11.7 g) were dissolved in RO water (1 L). The buffer was refrigerated and discarded after 1 week.

Sodium sulphite solution – Sodium sulphite (10 g) was dissolved in RO water (100 mL). It was used for dechlorination. Approximately 0.1 mL destroyed 5 mg residual chlorine. This solution was discarded after 2 weeks.

Reverse osmosis water – This water was processed in the laboratory by a reverse osmosis membrane filtration unit (USF Elga, High Wycombe, UK).

DHBA solution – Anhydrous 3,5-dihydroxybenzoic acid, (DHBA, 0.078 g) was dissolved in RO water (2 L). This solution needed to be made fresh before each use.

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

Sodium hydroxide (1 M and 0.1 M).

4.5.4.2 Method

Sample chlorination – The appropriate volume of chlorine dosing solution was calculated using the formula: 5 mg Cl₂ L⁻¹ per mg DOC L⁻¹ (10 mg Cl₂ L⁻¹ was used for later samples to ensure free chlorine remained).

This volume was put in a 250 ml bottle with phosphate buffer (5 ml) and filled completely with sample. This bottle was stored in an incubator at 25 °C ± 2 °C for seven days.

Reagent blank – Chlorine dosing solution (1 mL) was placed in a 50 mL volumetric and made up to the mark with phosphate buffer with RO water. A 22 mL PTFE-lined screw cap vial was completely filled with the mixture and stored with the sample at $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for seven days.

Quality control samples – Chlorine dosing solution (1 mL) was diluted to 1 L in a volumetric flask with RO water. Phosphate buffer (5 mL) was added to each of two 250 mL bottles. DHBA solution (1 mL) was added to one of these bottles 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 $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ for seven days.

Sample analysis – After seven days storage, sodium sulphite solution (0.088 mL) was pipeted into 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 concentrated hydrochloric acid (5 drops). 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).

THMFP can be reported as a single value:

$$\text{THMFP, } \mu\text{g L}^{-1} = A + B + C + D \quad (4.3)$$

$$\text{THMFP, } \mu\text{g L}^{-1} \text{ as CHCl}_3 = A + 0.728B + 0.574C + 0.472D \quad (4.4)$$

where $A = \mu\text{g CHCl}_3 \text{ L}^{-1}$

$$B = \mu\text{g CHBrCl}_2 \text{ L}^{-1}$$

$$C = \mu\text{g CHBr}_2\text{Cl} \text{ L}^{-1}$$

$$D = \mu\text{g CHBr}_3 \text{ L}^{-1}$$

Blank analysis – after seven days storage, Sodium sulphite reducing solution (1 mL) was added to a 250 mL bottle and 5 mL of the reagent mixture added 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 $<5 \mu\text{g CHCl}_3 \text{ L}^{-1}$

Quality control sample analysis – after holding in the dark for seven days, sodium sulphite reducing solution (1 mL) 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 $119 \mu\text{g L}^{-1}$ THM as CHCl_3 . If the THM concentration of the true blank exceeds $20 \mu\text{g L}^{-1}$, purer reagent water is required.

4.5.5 High performance size exclusion chromatography (HPSEC)

4.5.5.1 Apparatus

HPSEC was performed using a high performance liquid chromatography (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

column was a TSK – gel G3000SW 7.5 mm (ID) × 30 cm and the guard column was TSK gel 7.5 cm (Tosoh Biosep GmbH, Stuttgart, Germany). For each sample a chromatogram of UV₂₅₄ (absorbance units) against time (minutes) was produced.

4.5.5.2 HPSEC calibration

The HPSEC calibration shown here was developed at Cranfield University and is as follows (Goslan, 2003). A sample of raw water taken in April 2002 from Albert Reservoir was used for the calibration.

Ultrafiltrations were performed under nitrogen pressure (30 – 60 psi) in a stirred cell reactor (model 8200, Millipore, Massachusetts, USA). Membranes with MWCO values of 0.5, 1, 3, 5, 10 and 30 kDa were used (YM1 - YM30, Millipore, Massachusetts, USA, YC05, Australia). The YM membranes were made of regenerated cellulose and the YC membrane, cellulose acetate. The YM membranes were flushed with NaOH (0.1M), NaCl (0.5M) and deionised water to remove the wetting agents before use. The YC05 membrane was flushed with NaCl (1.0M) and deionised water. 110 mL samples of the raw water were filtered through each membrane at room temperature and five 20 mL samples of permeate collected (approximately 90% of the original sample). Each sample was analysed for DOC and UV absorbance at 254 nm as well as HPSEC analysis.

4.5.5.2.1 Molecular size distribution

It can be seen that the permeate concentrations of each sample increased in proportion to the volume of sample filtered (Figure 4.3). By using the data in Figure 4.3 and Equation 4.5 (Logan and Jiang 1990), the permeation coefficients were calculated (Table 4.1).

$$\ln C_p = \ln(pC_{r0}) + (p-1) \ln F \quad (4.5)$$

where C_p is the concentration of the permeate, p is the permeate coefficient, C_{r0} is the initial concentration of the sample (where $p > C_p/C_{r0}$) and F is the fraction of the original sample filtered. By plotting $\ln C_p$ against $\ln F$, $\ln pC_{r0}$ is the y intercept and $(p - 1)$ is the gradient (Figure 4.4).

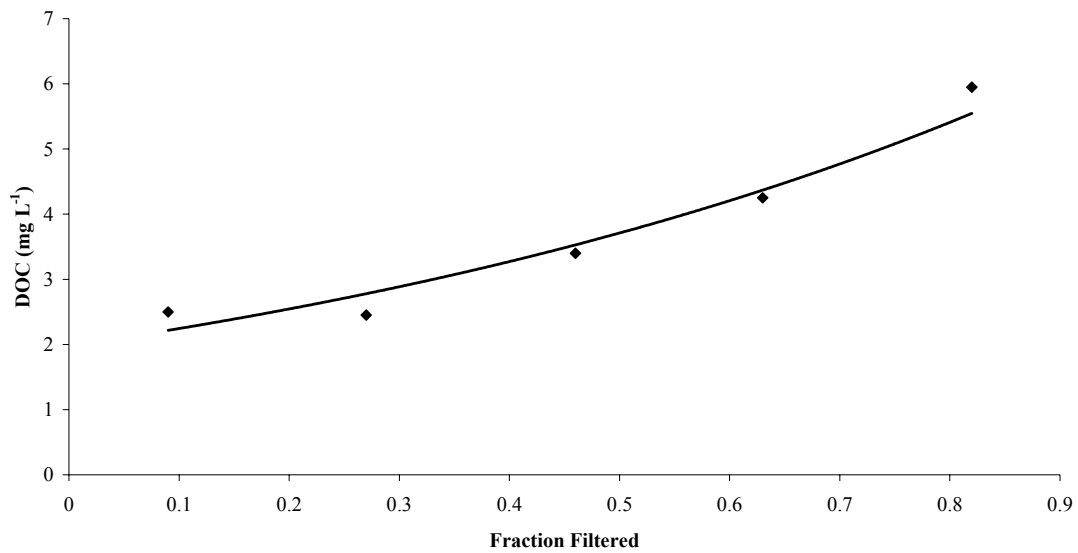


Figure 4.3 Permeate concentration as a function of fraction filtered

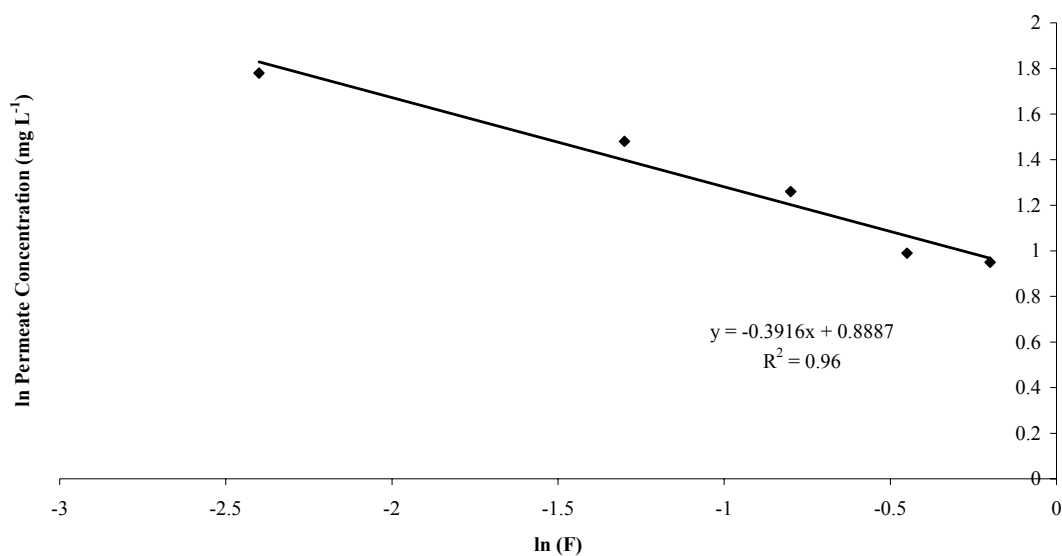


Figure 4.4 ln transformed data used to determine permeate coefficient

An average permeation coefficient, p , of 0.50 was calculated for all the membranes. This is similar to the expected value of $p = 0.60$ calculated from the manufacturer's rejection coefficient of 0.4.

Table 4.1 Permeate coefficients for each membrane for different natural water samples (adapted from Logan and Jiang, 1990)

Membrane cut-off (kDa)	p reported (1)	p reported (2)	p calculated (3)
30	0.97	0.99	0.60
10	0.73	0.36	0.58
5	0.56	0.28	0.66
3	nr	nr	0.71
1	0.54	0.22	0.27
0.5	0.80	0.20	0.18

nr – not reported

(1)– Orange County Water District (California groundwater)

(2)– Biscayne Aquifer (Florida groundwater)

(3)– Albert Raw Water April 2002

It is demonstrated that the average concentration of material measured after a batch filtration is a function of the volume collected as well as the permeation coefficient (Equation 4.6). This is illustrated in Figure 4.3.

$$C_f = C_{r0} \frac{(1 - F^p)}{(1 - F)} \quad (4.6)$$

where C_f is the final concentration of the sample.

The extent that membrane rejection contributes to underestimation of material less than the membrane cut-off can be estimated using Equation 4.5. For example, when 90% of the sample has passed through the membrane and $p = 0.60$ (for the 30 kDa membrane), the collected filtrate concentration will be 61% of the true concentration of the material having a smaller size than the membrane cut-off.

In general errors in C_{r0} are reduced when $p > 0.3$. A low p indicates that much of the material is about the same size as the membrane cut-off or that the material is strongly rejected by the membrane due to charge repulsion or some other effect. If $p < 0.2$ or > 0.9 , the size distribution should not be adjusted (Logan and Jiang 1990). The unadjusted (grey bars) and adjusted (black bars) molecular size distribution is shown in Figure 4.5. This adjustment is based on the UV absorbance of each sample, not the DOC concentration.

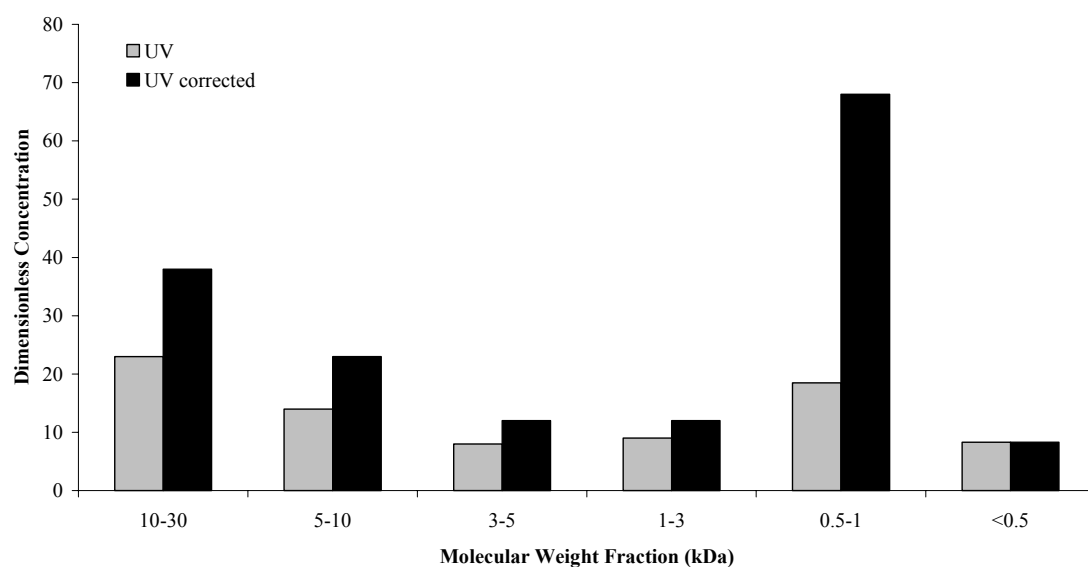


Figure 4.5 Molecular size distribution of Albert raw water (April 2002)

The UV absorbance measured is observed to fall as the MW falls. This has been reported in the literature (Collins *et al.*, 1986). The exception to the trend is molecules with the size fraction 0.5 – 1.0 kDa which had a low p value compared with the higher MWCO membranes that were made of the same material. As stated above, a low p value indicates that the material is about the same size as the membrane cut-off or that the material is strongly rejected by the membrane. It seems unlikely that the material is strongly rejected by the membrane given that the membranes were all made from the same material with the exception of the 0.5 kDa MWCO membrane. It is assumed here that adjustment is not required for the 1 kDa MWCO membrane.

4.5.5.2.2 Column calibration

Each sample collected after 90% of the sample had been ultrafiltered was run on the HPSEC. Each chromatogram exhibited five distinct peaks. The retention times for these are shown in Table 4.2 alongside the assigned molecular weight range. These

peaks corresponded to peaks observed in the raw water sample (Figure 4.6). 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 manufacturers (Figure 4.7).

Table 4.2 Assigned molecular weight range for each peak

Peak	Retention Time (minutes)	AMW (kDa)
1	8.3 – 8.6	> 5
2	8.7 – 9.0	3.5 – 5
3	9.1 – 9.7	2 – 3.5
4	9.7 – 10.4	1 – 2
5	10.5 – 10.8	0.5 – 1

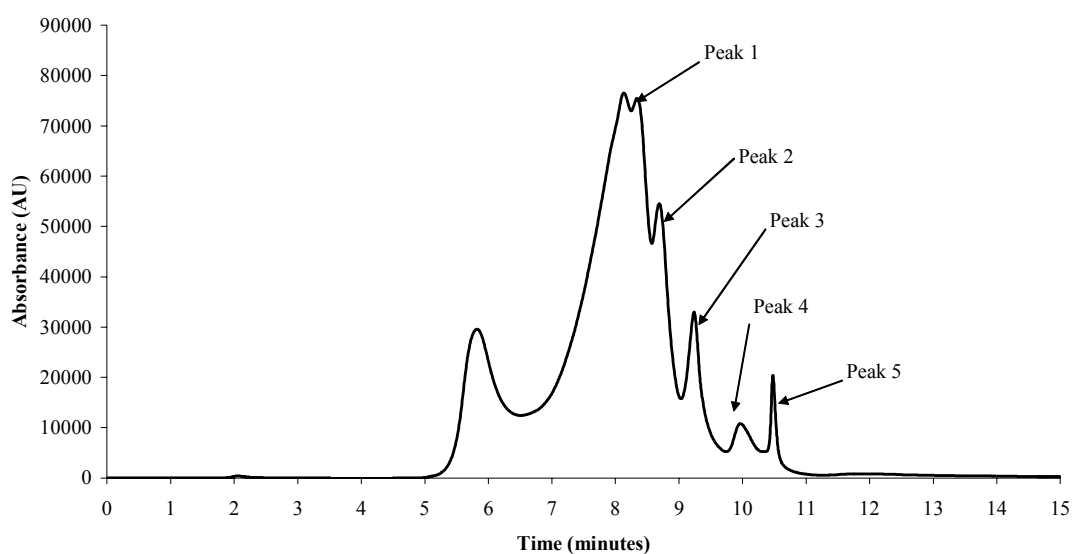


Figure 4.6 HPSEC chromatogram of Albert raw water with peaks assigned

The retention of the molecules depends on the pore size distribution of the membranes as well as the characteristics of the molecules, particularly the molecular volumes. Therefore, the retention of the molecules is not sharp. The 30 kDa membrane retains

molecules from all size ranges as can be seen in Figure 4.7. The membrane cut-off values are usually defined as the mass of a molecule whose retention is 90% on that membrane. When this retention value of 90% is applied to the peaks in an HPSEC chromatogram, the following apparent molecular weight (AMW) ranges can be assigned to each peak (Table 4.2, Figure 4.6). A range for each peak is given as each peak does not represent one specific MW.

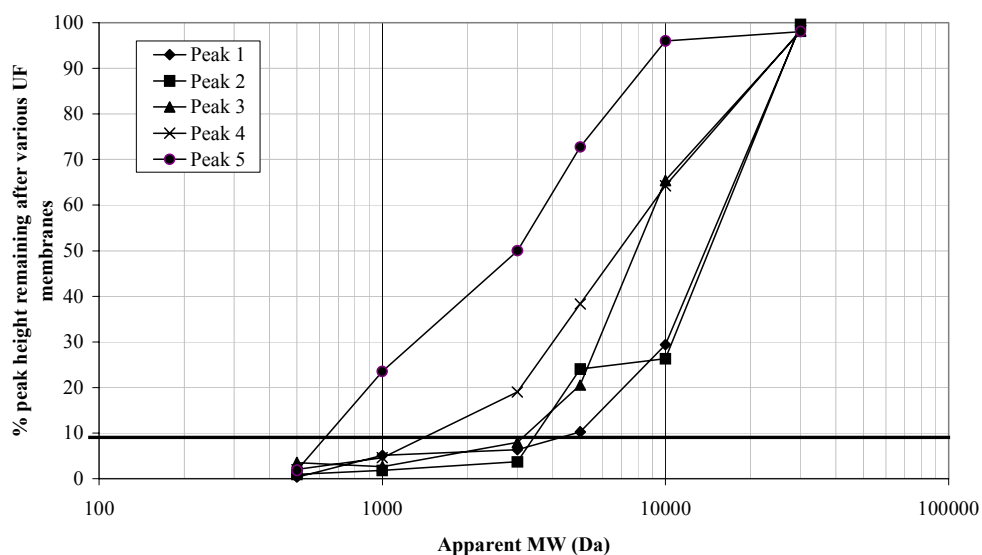


Figure 4.7 Remainder of NOM after various UF membranes measured as the reduction of peak heights in HPSEC traces

The shape of the raw water chromatogram is repeatable but the retention times for each peak can vary depending on the lengths of tubing used between the injector, the guard column and the column.

A sensitivity analysis was carried out with TOC $\pm 10\%$. No impact was observed on the AMW range.

5 Results and Discussion

5.1 Introduction

Many researchers have investigated the effectiveness of water treatment processes at removing organics by looking at bulk water quality parameters (Croué *et al.*, 1993; Dennett *et al.*, 1995; Chow *et al.*, 1999; Volk *et al.*, 2000; Bell-Ajy *et al.*, 2000). These parameters are described in detail in Section 2.4 and include measuring changes in DOC, UV₂₅₄, colour and THMFP. However when problems are encountered at a WTW in terms of meeting compliance, a more detailed idea of the composition of the NOM may be required. Bulk parameters have previously been used at Albert WTW to determine the final water quality (Banks and Wilson, 2001). For example using conventional coagulation/flocculation the colour level in final treated water can be as low as 2 Hazen units, but the THM limits can still be exceeded. It is likely that non-coloured refractory NOM is responsible for the reactivity of the treated water. In this section bulk measurements are used in conjunction with characterisation of the isolated fractions in order that problem causing organic fractions can be identified and specifically targeted. Similarly an intermediate and rapid characterisation method, HPSEC is also used to identify a particular MW range that may be recalcitrant to conventional treatment methods.

5.1.1 *Albert WTW*

The water treated at Albert WTW is typical of many upland waters found in the north of the UK having high colour and DOC levels and low alkalinity and turbidity. The character of Albert raw water is constantly changing and the water entering Albert WTW is deteriorating with respect to colour and organic content. This deterioration is

seen as a year on year increase in the organic content and colour. The latter has increased significantly over the past 10 years from an average of 40 Hazen in 1992 to 80 Hazen in 2000 (Figure 5.1).

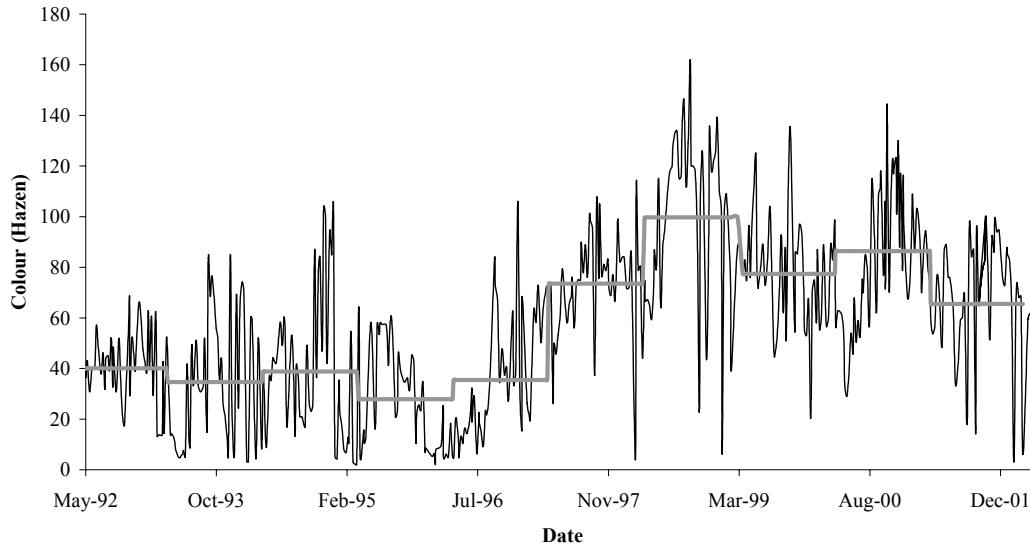


Figure 5.1 Variation in colour and average annual colour over 10 years

As well as an annual increase, seasonal changes occur generally after rainfall in the autumn. These increases have required the operators at Albert WTW to alter their coagulant dosing and control regime in order that sufficient organic material is removed to comply with current THM legislation (Figure 5.2). The target values for treated Albert water are 3.5 m^{-1} and <10 Hazen for UV_{254} and colour respectively.

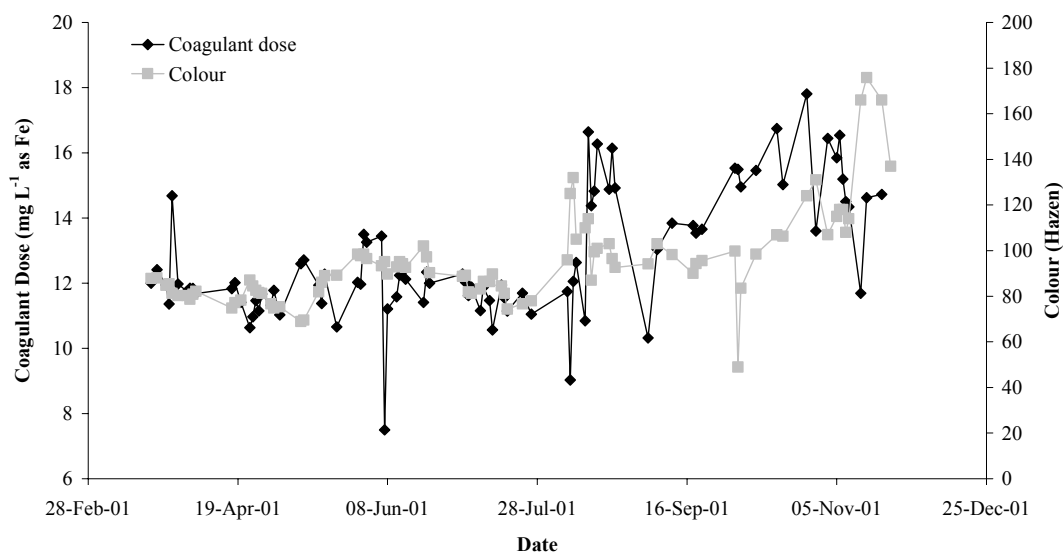


Figure 5.2 Seasonal variations in colour and coagulant dose (Albert WTW)

Alongside seasonal changes in DOC and colour the THM levels also change substantially. A summary of the THM data for 6 waters sampled during this research is shown in Table 5.1, THMs of the raw water vary from $468.3 \mu\text{g L}^{-1}$ in the summer to $907.5 \mu\text{g L}^{-1}$ in the autumn.

Table 5.1 Comparison of Albert raw water characteristics and reactivities

Sampling date	DOC (mg L^{-1})	SUVA ($\text{m}^{-1} \cdot \text{L mg}^{-1} \text{C}$)	THM ($\mu\text{g L}^{-1}$)
January 2000	7.50	4.5	632.2
June 2000	8.10	4.7	468.3
November 2000	10.24	5.9	907.5
April 2002	7.50	5.1	602.3
October 2002	10.40	5.0	511.7
January 2004	9.83	4.3	632.3

As previously described the measurement of bulk water parameters are not always sufficient to determine how a water will respond to a treatment process. Here an analysis method that determines the MW size distribution by HPSEC of the raw water for two different times is shown. It can be noted that raw water sample collected in October 2002 exhibits a high UV₂₅₄ absorbance in the area of high MW (>5000 Da) and the water collected in April 2002 is made up mostly of mid MW (1000–5000 Da) compounds (Figure 5.3).

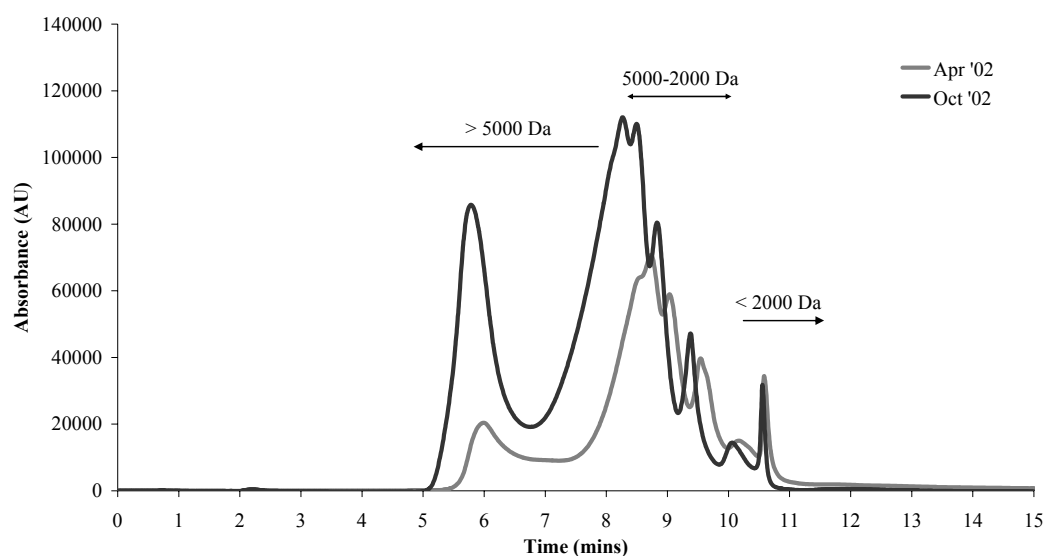


Figure 5.3 Seasonal changes in the MW profile of Albert raw water

Along with the variation in bulk water characteristics a significant variation in the fraction makeup of the raw water has been seen. During the 3 years of this study fractionations were carried out on a regular basis in order to investigate a link between fraction distribution and THMFP. As described earlier (Chapter 4) this involves splitting the bulk organic matter into hydrophobic (HAF and FAF) and hydrophilic (HPI-A and HPI-NA) material. For Albert raw water there has been a general increase in the concentration of HAF in the raw water until the autumn of 2003, during which

time a reduction in the concentration of the FAF has been seen. Although the combined distribution of the hydrophobic material has remained relatively constant ranging from approximately 60% to 75%. The distribution of the hydrophilic fractions shows no clear trends, although a decrease in the HPI-NA fraction was observed until the summer of 2003 (Figure 5.4).

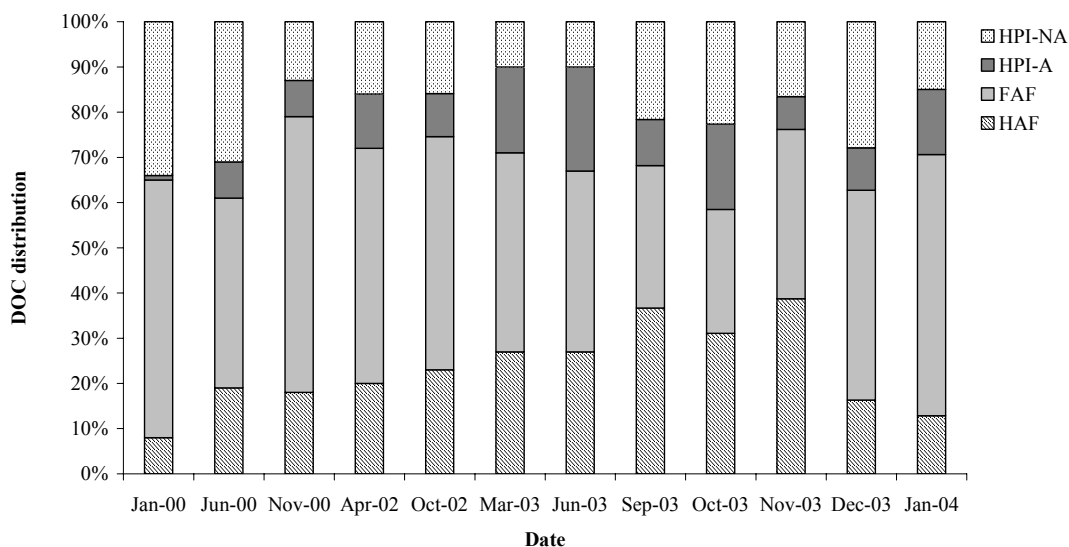


Figure 5.4 Distribution of isolated fractions by DOC during 3 year period

The MW profiles of the isolated fractions are shown in Figure 5.5. It can be seen that the HAF fraction contains compounds of all MWs. The FAF fraction contains no high MW material (5-7 minutes), the HPI-A has a similar MW range to that seen for FAF although less of the MW range 7.5 to 9.5 minutes is seen. Finally the HPI-NA fraction only contains low MW material (>9.5 minutes).

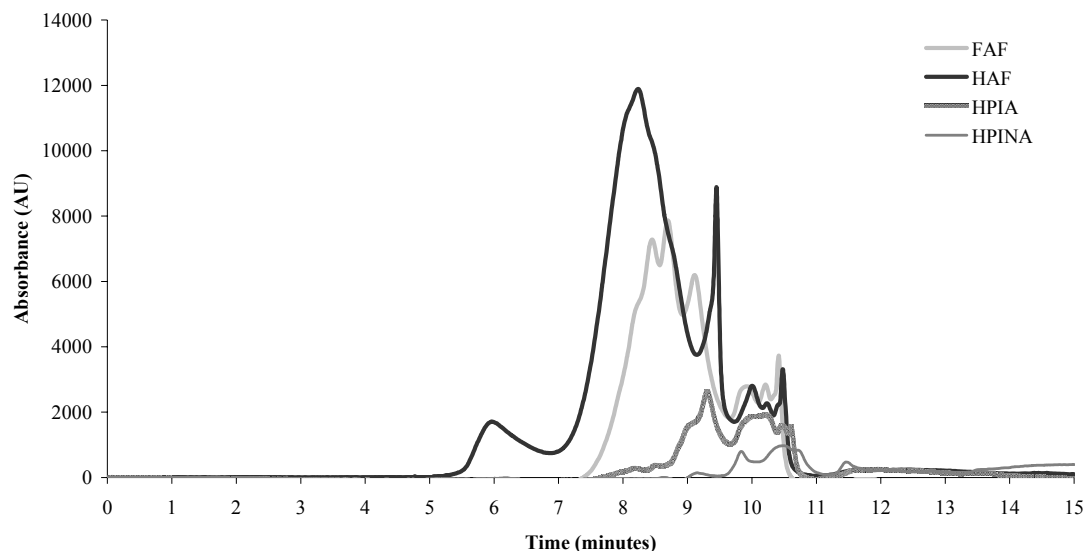


Figure 5.5 MW profiles for the 4 isolated fractions determined by HPSEC analysis (Albert, April 2002)

The water from October 2002 shows a reduction in the amount of FAF compared to the raw water sampled in November 2000 (Figure 5.4). This can be related to a reduction in the THMFP of the raw water on chlorination. Furthermore a correlation between the amount of FAF in the raw water and the raw water THMFP was found ($R^2=0.73$). This indicates that the FAF has a major effect on the reactivity of the water and consequently its removal needs to be targeted in order that THM compliance is met (Figure 5.6).

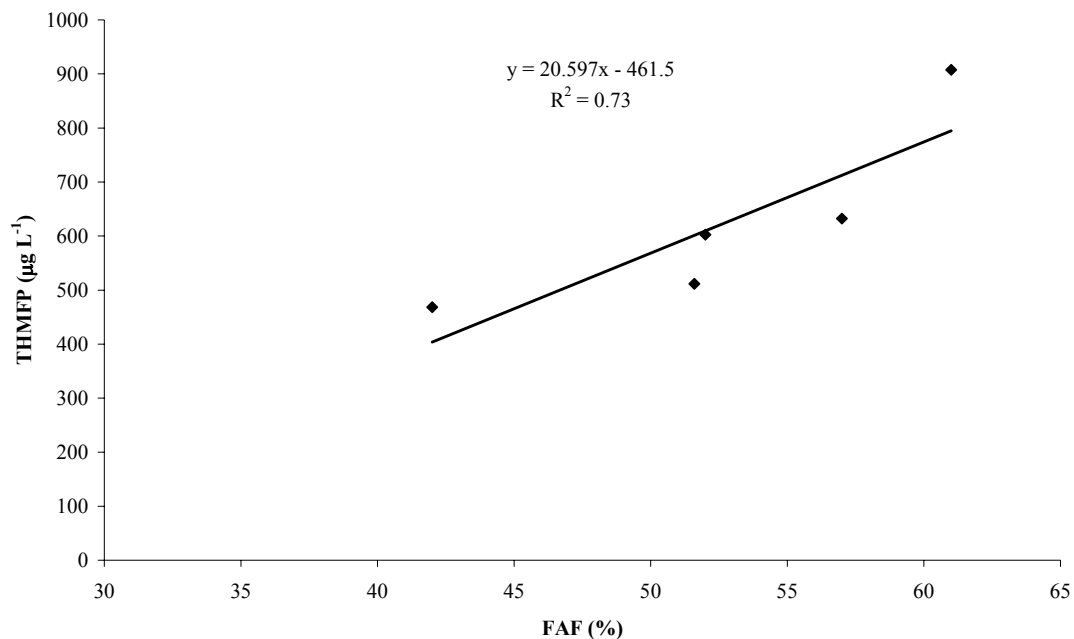


Figure 5.6 THMFP as a function of the FAF concentration in Albert raw water

All of these changes and variations have encouraged Yorkshire Water to investigate process optimisation and explore the use of novel and alternative processes. The review of the literature highlighted that by tailoring the coagulation process to target specific types of organics an increase in DOC and UV₂₅₄ removal could be achieved. Three treatment processes are presented in this section as options during these times of low water quality:

- staged coagulation;
- MIEX[®] resin as a pre coagulation treatment; and
- adsorption as a post coagulation treatment.

Here the first process option investigated was the optimisation of the coagulation process for the individual fractions and hence the use of a staged coagulation process to

target specific or difficult to treat fractions. A schematic of the proposed process is shown in Figure 5.7.

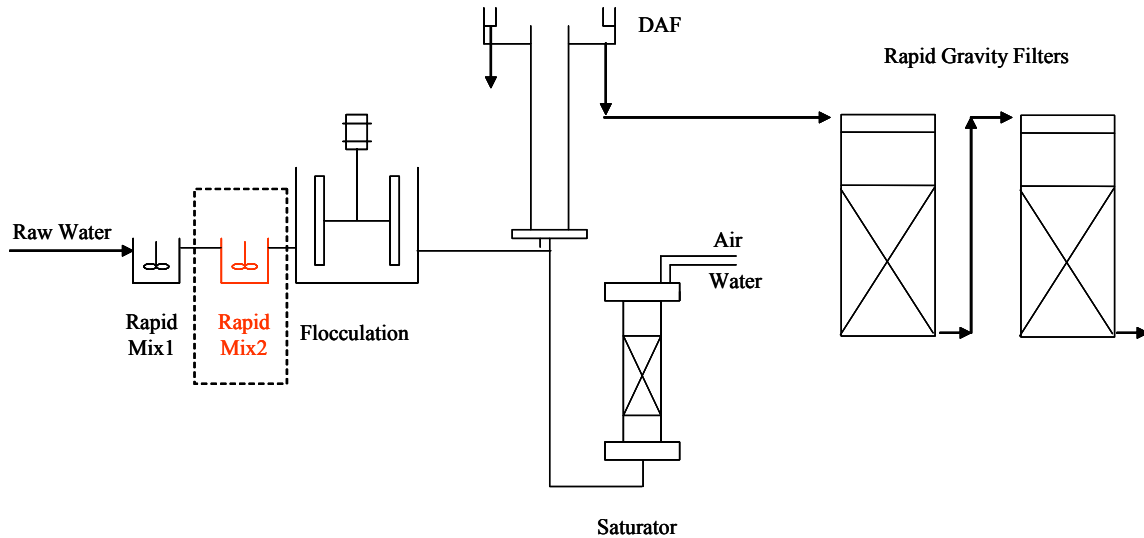


Figure 5.7 Proposed schematic for staged coagulation

The second process to be investigated is the use of MIEX[®] resin. This process was specifically designed for the removal of NOM and in particular recalcitrant NOM. A schematic for its addition to the treatment stream prior to conventional coagulation is shown in Figure 5.8.

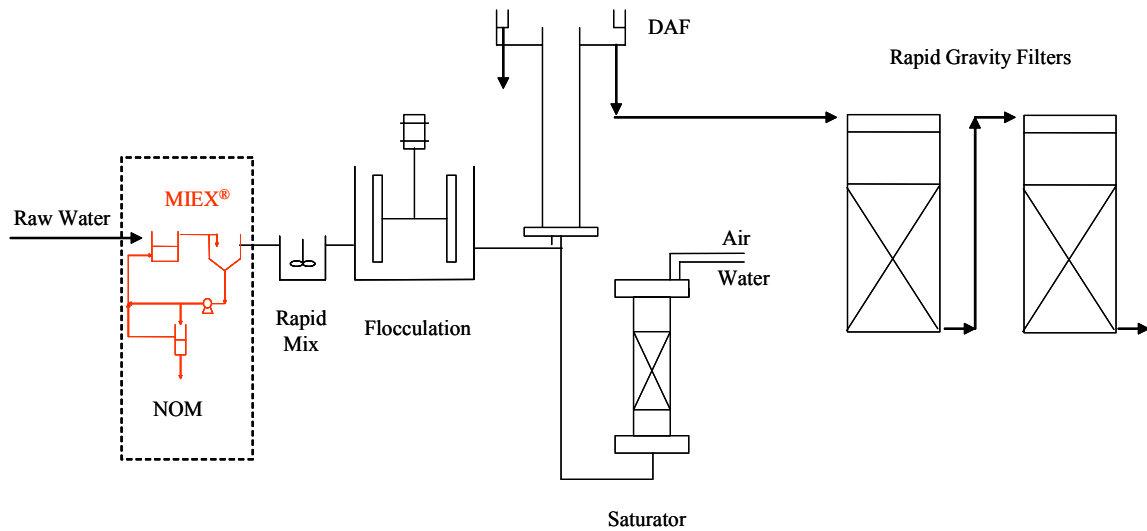


Figure 5.8 Proposed schematic for the introduction of MIEX[®] as a pre-coagulation process

Finally the addition of an adsorbent following coagulation is considered as it could allow further removal of any untreated part of the organic matter. A schematic showing its possible inclusion in to the current works is shown in Figure 5.9.

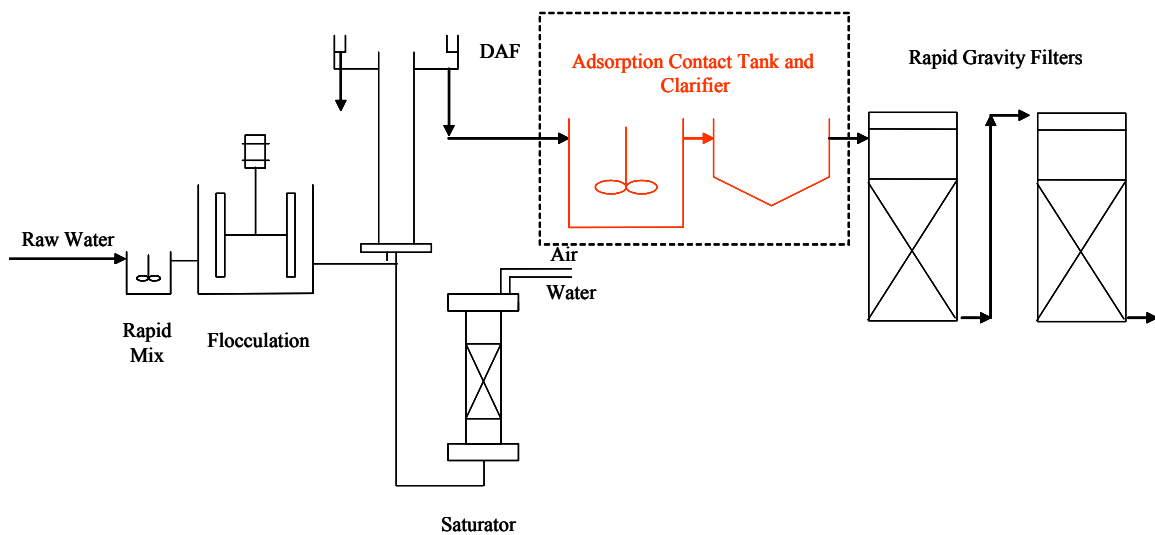


Figure 5.9 Proposed schematic for the introduction of a post coagulation adsorption process

Although there are many other options available for the removal of NOM e.g. membranes, biodegradation and coagulant aids, the options chosen for study allow the operators to choose from a short term option (adsorption) to a medium to long term option (staged coagulation) or alternatively a long term process (MIEX[®]).

5.2 Coagulation

5.2.1 Introduction

The treatment at Albert WTW currently employs ferric sulphate (Ferrisol XL, 13.5% Fe w/w, EA West) as the coagulant; the dose used is constantly reviewed so that maximum colour removal is achieved. Data supplied by Yorkshire Water shows how the coagulant dose varies throughout the year and how the average coagulant dose is increased by up to 50% during late summer and autumn (Figure 5.10).

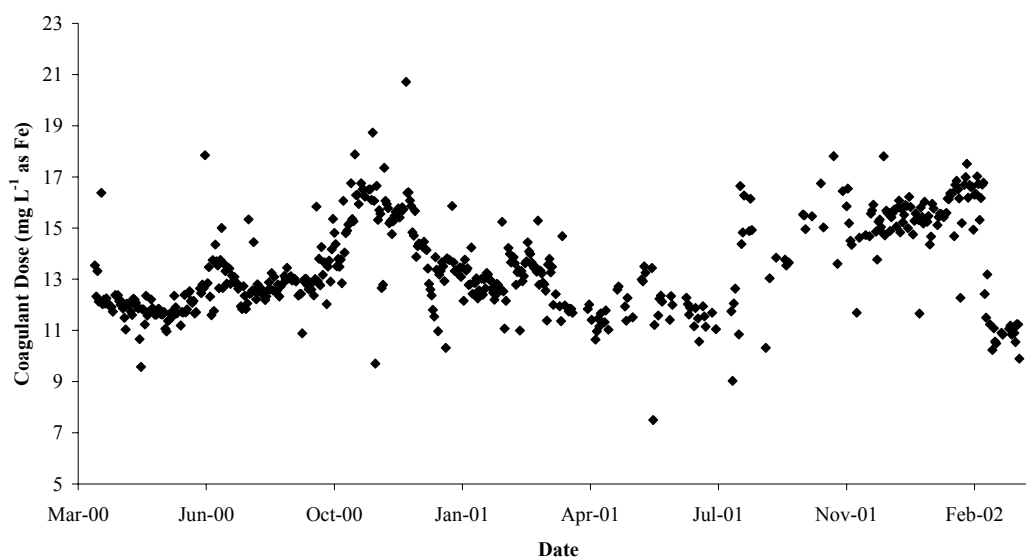


Figure 5.10 Variation in coagulant dose required for optimum colour removal (pH 4.5)

This can be linked to the increase in the FAF seen in the autumn. If we consider the sharp increase in coagulant demand seen in October-November 2000, there is a similar increase in the FAF, rising from 42% to 61% (Figure 5.6).

From this data it can be seen that the coagulant demand on the water generally ranges between 11 and 16 mg L⁻¹ with a post coagulation pH of 4.5. The following results are from water sampled during November 2000 when the coagulant demand ranged between 16 and 19 mg L⁻¹ and was particularly recalcitrant to treatment by conventional coagulation.

5.2.2 Coagulation optimisation of bulk water

5.2.2.1 pH and coagulant dose

A sample of raw water was optimised in terms of pH and coagulant dose as a baseline for the resulting optimisations. It can be seen that similarly to Figure 5.11 the optimum pH was observed as approximately 5 for a coagulant dose of 10 mg L⁻¹ Fe, and maximum UV₂₅₄ and DOC removals were observed between 10 and 30 mg L⁻¹ Fe at pH 5.2 (Figure 5.11a and b).

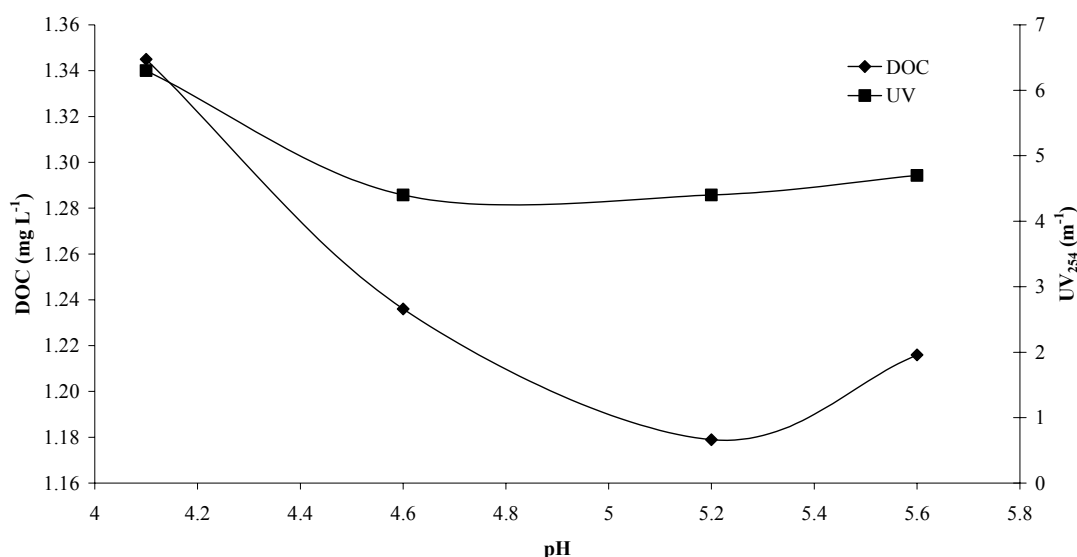


Figure 5.11a pH optimisation for Albert WTW raw water (November 2000)

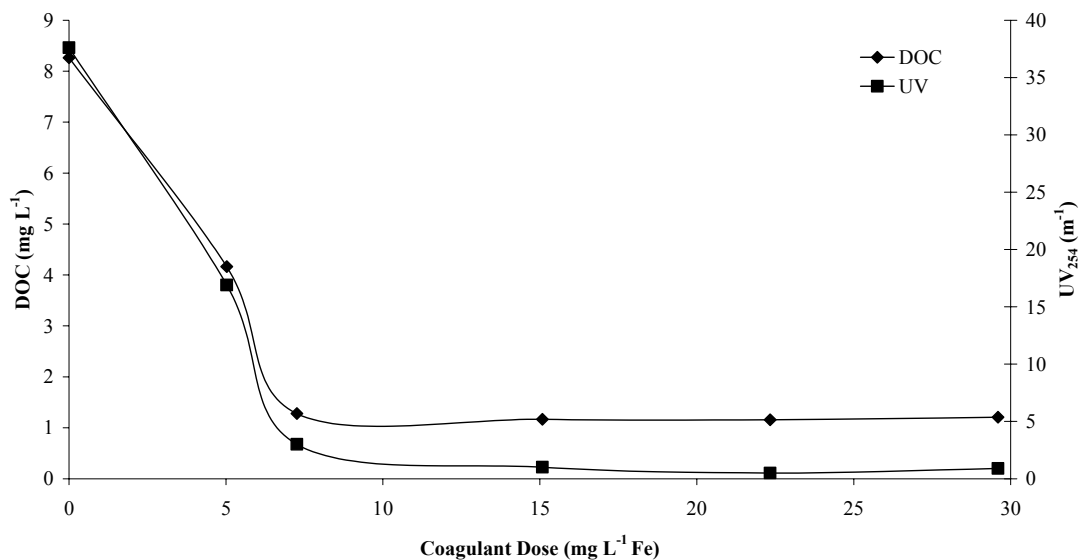


Figure 5.11b Dose optimisation for Albert WTW raw water (November 2000)

HPSEC analysis of raw Albert water and water treated with 14 mg L⁻¹ Fe at pH 4.5 shows that the high and mid MW (>2000 Da) material i.e. peaks 1-4 are completely removed. The lower MW material (peaks 5-7) is effectively removed (>50%) by conventional coagulation. However it should be remembered that the lower MW material (i.e. hydrophilics) can be responsible for the reactivity of the treated water. Also only the UV absorbing species are detected by this analysis method (Figure 5.12).

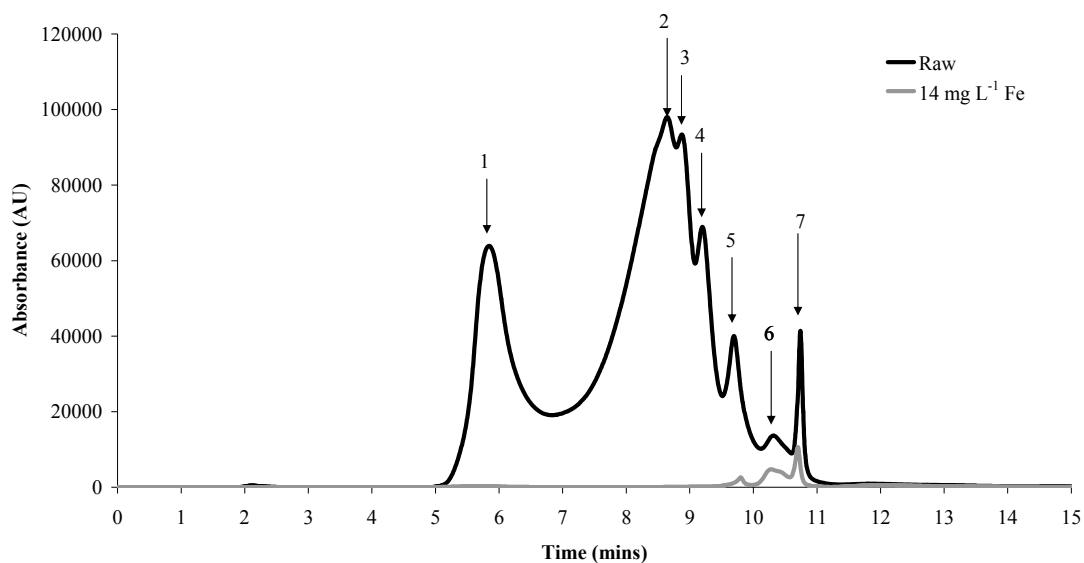


Figure 5.12 Effect of coagulation on the MW profile of raw Albert water

5.2.2.2 Properties affecting the coagulation process

Many factors are seen to affect the coagulation process i.e. coagulant choice, pH, coagulant dose and mixing time. These factors are detailed in section 2.5.1.2.

Research has shown the photometric dispersion analyser (PDA) to be a sensitive indicator of the state of aggregation of a particle suspension and an effective tool for assessing the coagulation effectiveness (Gregory and Dupont, 2001). The PDA can give dynamic, rapid measurements of microfloc size and number following rapid mixing. The PDA output flocculation index (FI) vs. time curves can be represented by a simple sigmoid curve, from which various parameters can be derived (Figure 5.13).

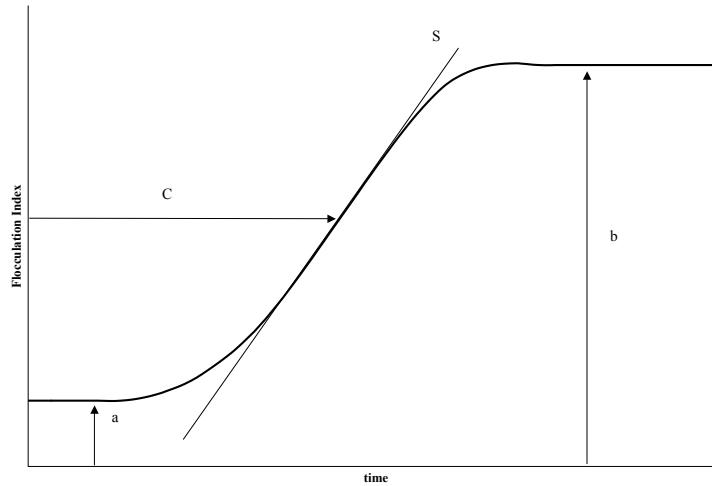


Figure 5.13 Sigmoid curve representation of PDA output (FI) vs. time

FI at time t depends on the empirical parameters a , b , c and s , as represented by the equation below (Equation 5.1).

$$FI = a + \frac{b}{1 + \exp\left(-\frac{t-c}{s}\right)} \quad (5.1)$$

The PDA facilitates dynamic investigation of coagulation parameters such as shear, temperature, water chemistry and rapid mix speeds and their effect on coagulation. Here we have used the PDA to optimise the coagulation process in terms of pH and rapid mixing time.

5.2.2.2.1 Reproducibility

The results presented are those tested on a solution of water containing 50 mg L^{-1} kaolin and 5 mg L^{-1} commercial humic acid (Aldrich). Synthetic water was used as the flocs formed from using 'real' or organic only raw water were too big for the system and the

FI was not representative of the flocs formed. The PDA method was shown to be very reproducible at constant pH (5) and the initial turbidity. Figure 5.14 shows 3 sets of data at the beginning of the coagulation process and the increase in FI value as a result of the addition the coagulant.

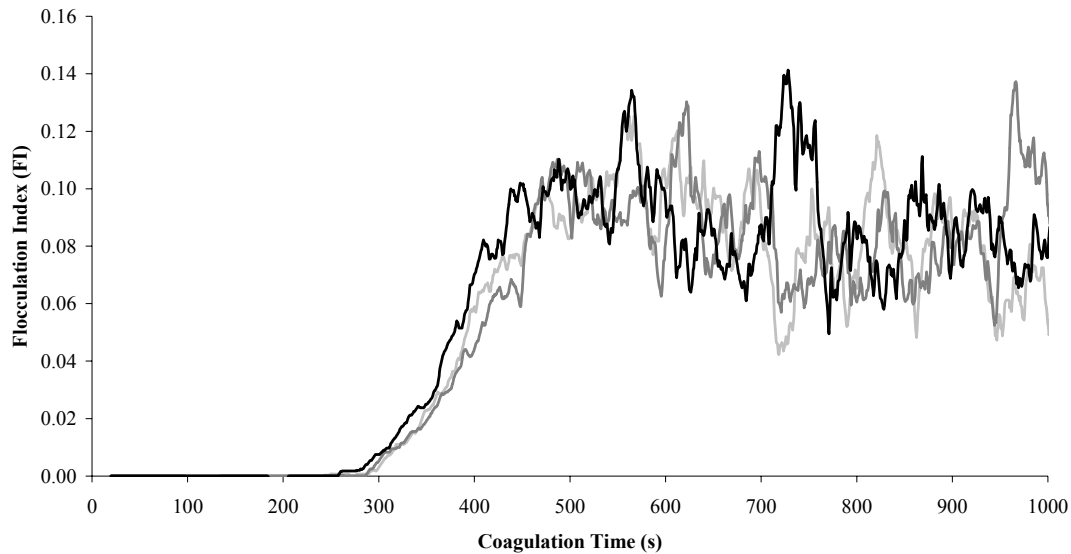


Figure 5.14 Reproducibility of results from PDA (DI water, 50 mg L⁻¹ kaolin, 5 mg L⁻¹ commercial humic acid)

5.2.2.2.2 *pH effects*

The time taken for the FI number to start to increase after the addition of the coagulant increases significantly if the pH is decreased from 6.3 to 4.3. The results of 3 experiments carried out under the same conditions except pH, show that at low pH (4.3) the time taken for there to be an increase in FI was approximately 550 s. Increasing the pH to 5.4 showed a rise in FI at approximately 250 seconds whereas the FI began to increase at about 200 seconds when the pH was increased to 6.3 (Figure 5.15).

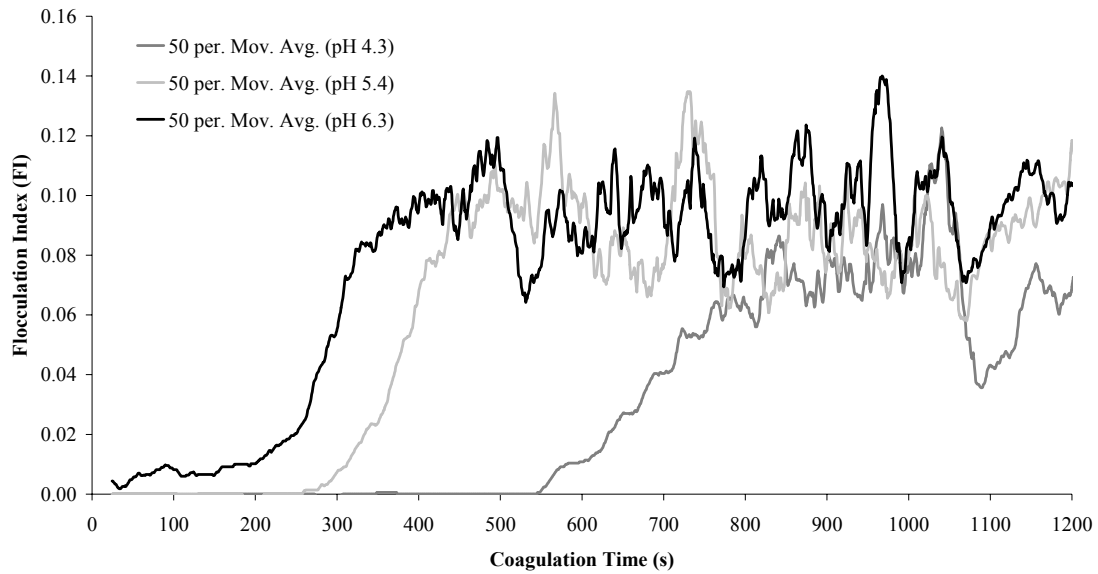


Figure 5.15 Effect of pH on the formation of flocs during coagulation/flocculation

5.2.2.2.3 Effects of shear

The flocs were subjected to rapid mix at 180 rpm for 2 and 5 minutes after 17.2 minutes to assess the relative strength of the flocs formed at pH 4 and 5. This enabled the effect of applying shear e.g. weirs and pipe bends etc. would have on the flocs following formation. In general the flocs formed at pH 5 were visually larger than those formed at pH 4 and produced a larger variation in the value of FI. In all cases following an increase in shear the variability in the FI value was reduced indicating that the flocs had been broken down to the same size and number (Figures 5.16a and b).

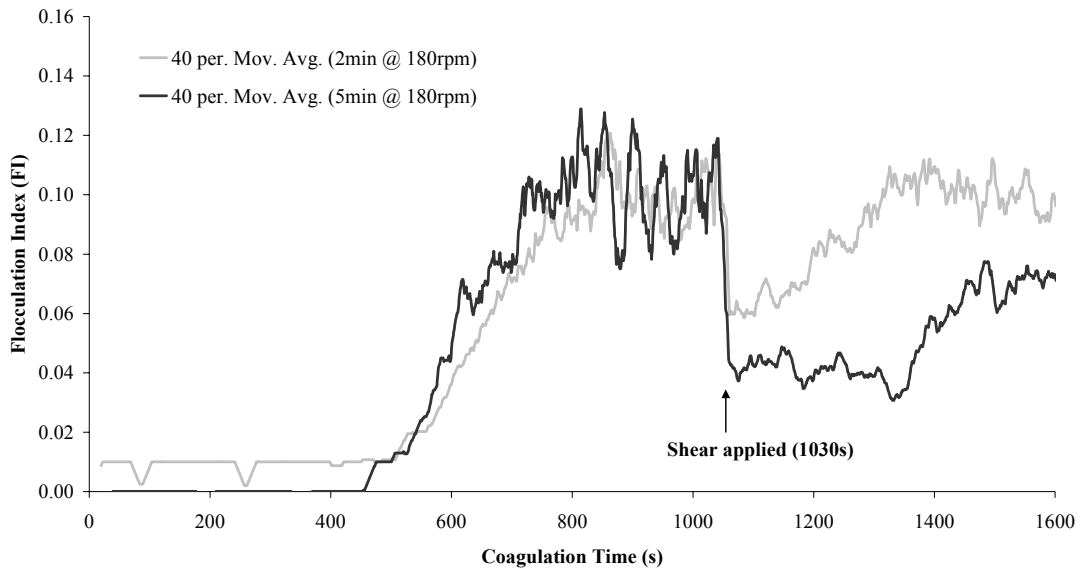


Figure 5.16a Effect of shear at pH 4.3

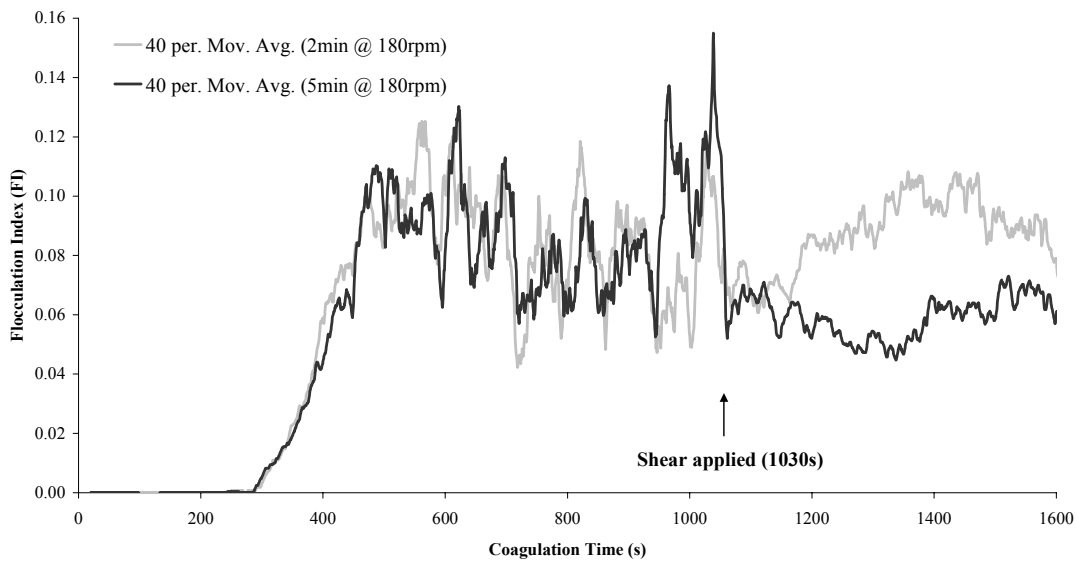


Figure 5.16b Effect of shear at pH 5.4

5.2.2.2.4 Relationships

It has been shown that there is a strong relationship between pH and coagulation time and change in FI. The general conclusions drawn from Figures 5.17a and 5.17b are that

the higher the pH the faster the FI starts to increase and also the faster the rate of change in the FI.

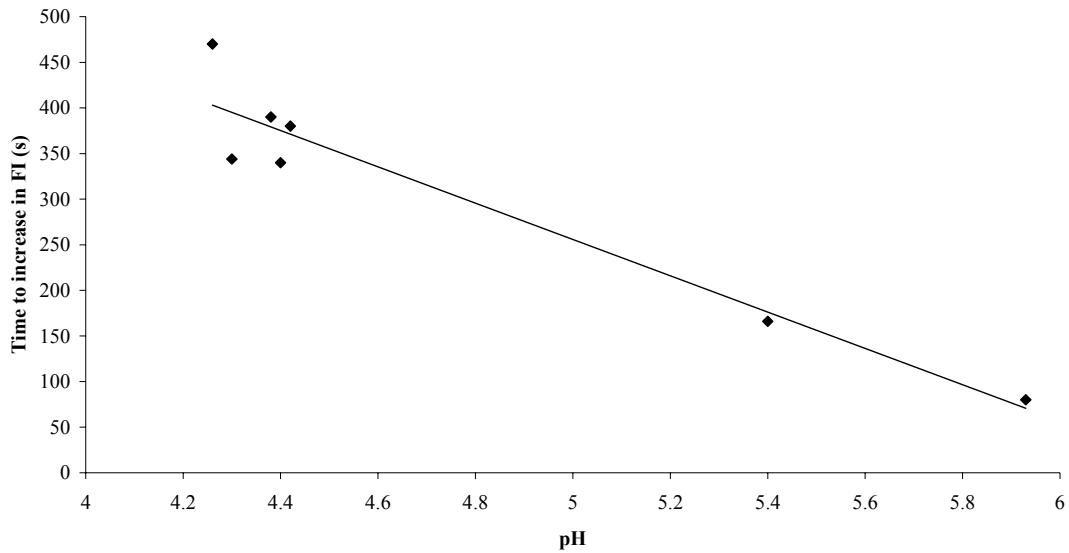


Figure 5.17a Plot of coagulation time vs. pH

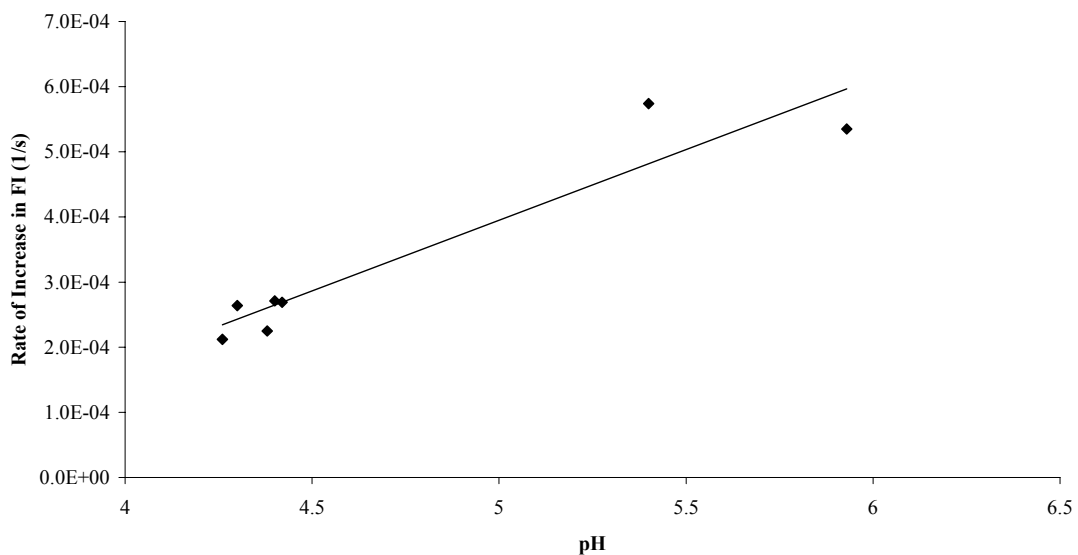


Figure 5.17b Plot of rate of floc growth vs. pH

PDA data can be used to predict the start of increase in FI and rate change of FI very easily. From these experiments it was found that the kaolin and commercial humic acid

coagulated quicker and the flocs formed faster at higher pHs. The application of shear breaks down the flocs to a greater number of similar sized flocs rather than a few large flocs, which appear to give erratic FI readings. A potential problem with the method is that large flocs are broken up in the tubing before reaching the PDA, also the significance of the FI number during these experiments could not be determined.

5.2.2.2.5 Mixing speed

A series of experiments were conducted to monitor the effect of rapid mix speed and length of rapid mix time on the coagulation of commercial humic acid by the changes in PDA output (Figures 5.18a and 5.18b).

The analysis of the effect of rapid mix time at 100 rpm gave erratic PDA data probably due to lack of homogeneity in the solution following the rapid mix time and is not shown here. At 200 rpm it was seen that the inception time and rate of change in FI is greatest for the sample mixed for 90 and 120 seconds. The samples mixed for 60 seconds had a slower inception time and growth rate. Finally the samples mixed for 10 and 30 seconds had the slowest inception time and rate of growth. It was noted that for all rapid mix times the flocs reached approximately the same maximum FI value. At 300 rpm the sample mixed for 60 seconds also has a similar inception time and growth rate to those mixed at 90 and 120 seconds whilst the data for the samples mixed for 10 and 30 seconds remained the same as seen previously (Figures 5.18 a and b)

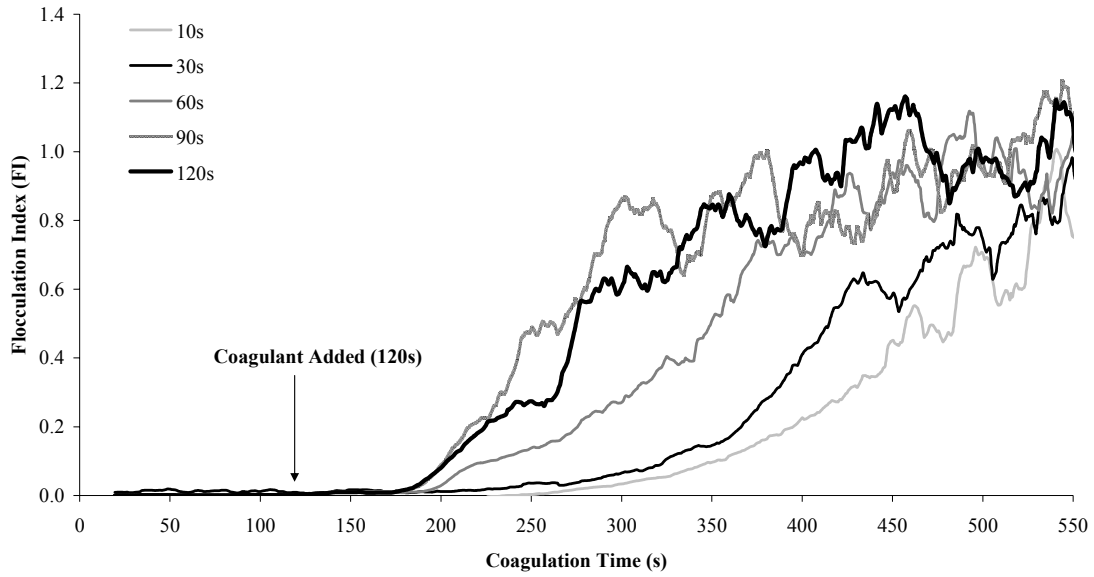


Figure 5.18a PDA output from averaged data mixed at 200 rpm for 10, 30, 60, 90 and 120 seconds

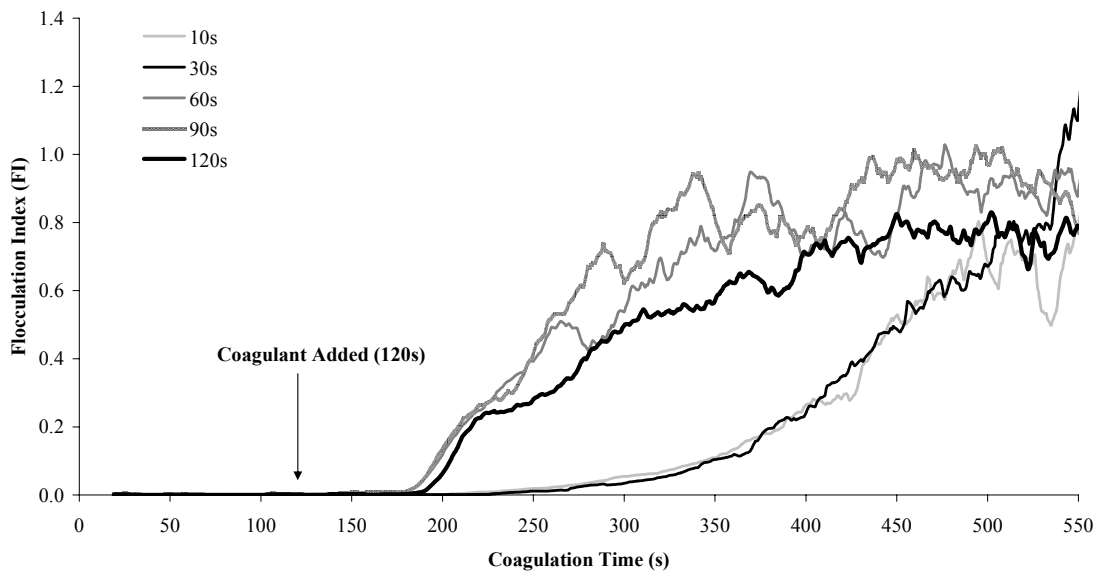


Figure 5.18b PDA output from averaged data mixed at 300 rpm for 10, 30, 60, 90 and 120 seconds

An explanation for the lower growth rate observed for both the 10 and 30 seconds mixing times is that the system is not fully mixed at low mix times. A maximum mixing is achieved when the mixing speed (G) multiplied by the mixing time (t) giving

the dimensionless number described as Camp's number reaches a certain level. The results show that at a Camp number below 30000, the time to maximum growth rate is decreasing and that after a certain amount of energy has been imparted into the system the time to reach that maximum growth rate is not increased (Figure 5.19).

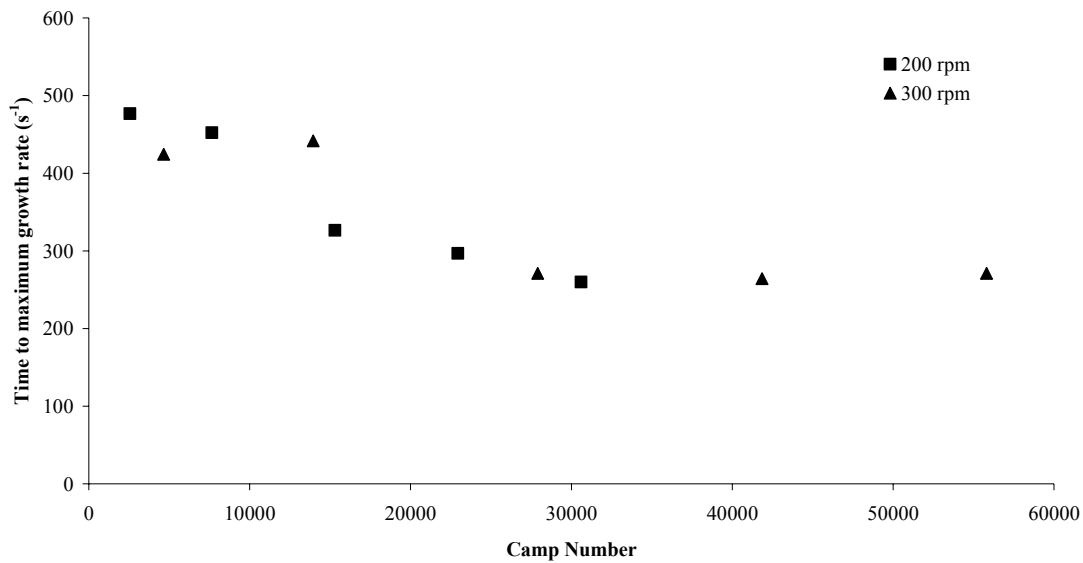


Figure 5.19 Time to maximum growth rate as a function of Camp number

From this data there was no increase in the removal of UV_{254} during the experiments (Figure 5.20). However a rapid mix speed of 200 rpm for 120 seconds was shown to be the most effective in terms of time to reach maximum growth rate. This would allow the size of rapid mix tanks to be optimised and was used in the subsequent coagulation experiments.

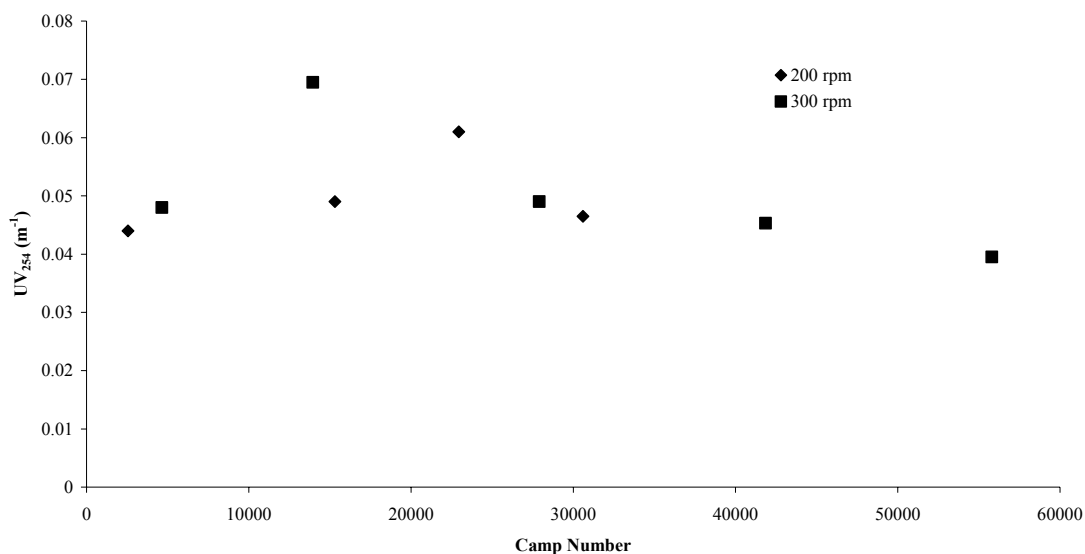


Figure 5.20 Residual UV₂₅₄ as a function of Camp number at 200 and 300 rpm

5.2.3 Coagulation optimisation of fractions

5.2.3.1 Introduction

Coagulation studies for the removal of NOM have historically been conducted using bulk water characteristics. Recently due to the need for treatment processes to improve to meet tightening legislation more studies of the major cause of THMs have been investigated. As discussed in the literature review (section 2.5.1.4) the composition of the water in terms of isolated fractions can help determine which removal methods are most effective. Here the raw and treated water from Albert WTW has been isolated in to 4 fractions by means of size and charge and hence relative hydrophobicity to determine which portion of the water has the greatest THMFP. A detailed description of the fractionation methodology is given in section 4.2.2.

The results of the organic matter fractionation for both the raw and filtered water are shown in Figures 5.21a and 5.21b. This outlines the removals achieved on site by

conventional coagulation for both the DOC and the THMFP for each of the isolated organic fractions. The principal fraction in terms of DOC and reactivity is the FAF (6.24 mg L⁻¹ and 1164.2 µg L⁻¹, respectively) followed by the HAF (1.81 mg L⁻¹ and 215.1 µg L⁻¹, respectively). It should be noted that the THMFP of the individual fractions totalled more than the bulk water (1638.1 and 907.5 µg L⁻¹, respectively). This has been observed in another study (Owen *et al.*, 1993) where fractionated substances had a combined reactivity of 100 µg THM mg⁻¹ C compared with a raw water reactivity of 38 µg THM mg⁻¹ C. The same study also looked at ultrafiltration fractions of the same water, these had a combined reactivity of 219 µg THM mg⁻¹ C. This was attributed to synergistic effects in chlorine substitution or oxidation reactions in the presence of NOM fractions compared to bulk NOM. The heterogenous nature of NOM as well as its fractions is likely to be responsible for this behaviour (Owen *et al.*, 1993) and can be explained in that the fractionation procedure has the effect of denaturing the fractions compared to when they are combined in the bulk water. Hence the relative reactivity of the isolated fractions will therefore be different compared to those in the bulk water (Peuravuori and Pihlaja, 1997).

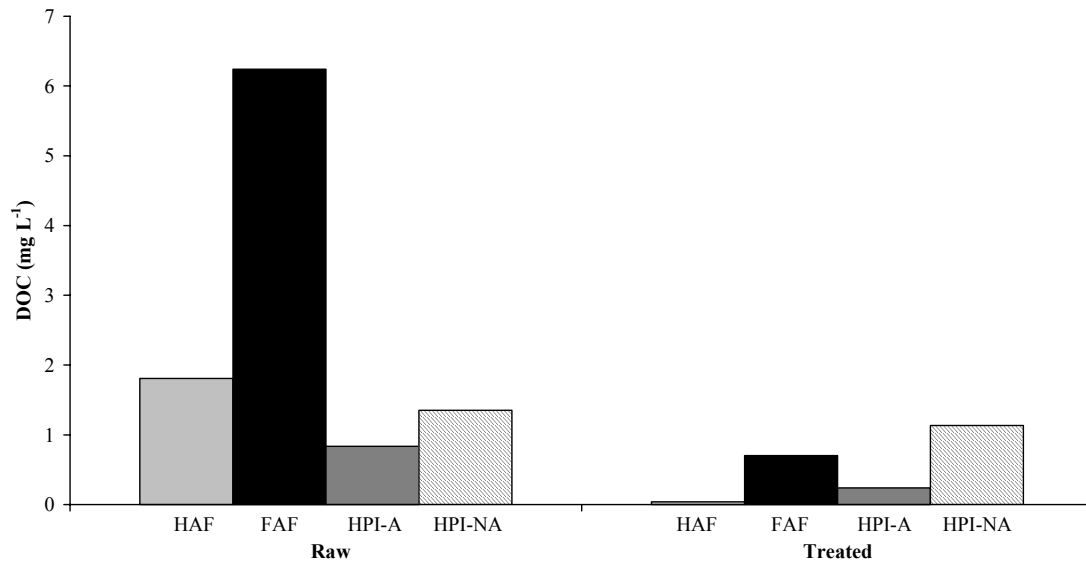


Figure 5.21a Isolated fraction DOC distribution of raw and coagulated water

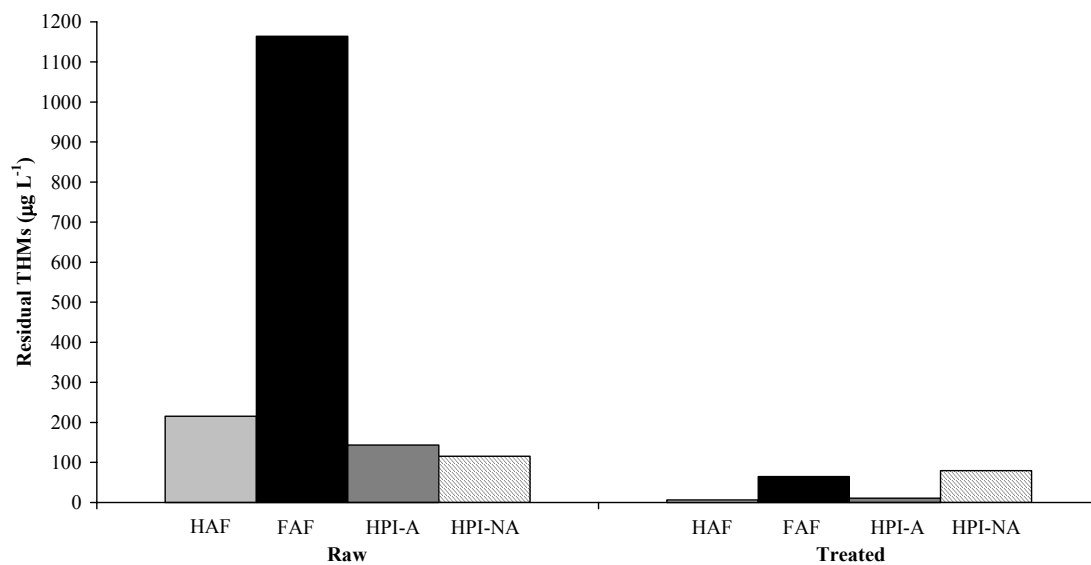


Figure 5.21b Isolated fraction THM-FP distribution of raw and coagulated water

The treatment conditions used at Albert WTW at the time of this study were able to achieve high removals of DOC for HAF, FAF and HPI-A (98%, 89% and 71% respectively), whilst the THMFP removal for those fractions is equally high (97%, 94% and 93% respectively). Removal of the HPI-NA is poor with only 16% of the DOC and 31% of the THMFP being removed by coagulation. In addition, the removal of FAF

which although as previously stated is high is still a cause for concern due to the high DOC and reactivity in terms of THMFP per mg of carbon remaining in the treated water (0.7 mg L^{-1} and $92 \text{ } \mu\text{g mg}^{-1} \text{ C}$, respectively). Table 5.2 compares the SUVA and THMFP of both raw and filtered fractions.

Table 5.2 SUVA and THMFP values of isolated fractions for raw and filtered waters

Fraction	Raw			Filtered		
	DOC (mg L^{-1})	SUVA ($\text{m}^{-1} \cdot \text{L mg}^{-1}$)	THMFP ($\mu\text{g mg}^{-1} \text{ C}$)	DOC (mg L^{-1})	SUVA ($\text{m}^{-1} \cdot \text{L mg}^{-1}$)	THMFP ($\mu\text{g mg}^{-1} \text{ C}$)
HAF	1.84	4.9	118.9	0.04	6.5	154.0
FAF	6.22	6.1	186.5	0.70	2.9	92.0
HPI-A	0.82	3.7	171.3	0.23	2.0	43.9
HPI-NA	1.32	1.6	85.4	1.13	1.3	70.2

The removal of DOC and THMFP from the raw water during autumn 2001 was 79% and 93%, respectively. This leaves a residual THMFP of approximately $70 \text{ } \mu\text{g L}^{-1}$, which means that there is very little room for error or sudden deterioration in the raw water quality. There is therefore a need to further reduce the DOC in the pre chlorinated water.

5.2.3.2 FAF optimisation

The optimisation in terms of FAF removal was seen as being key in reducing the THMFP of the treated water due to its potentially high reactivity (Table 5.2). The optimum coagulation conditions for the raw and the filtered FAF were identified from the DOC removal at a pH of 6 and was found to be approximately 12 mg L^{-1} as Fe and 8 mg L^{-1} as Fe respectively. When the pH was optimised it was found that at pH 4.7

optimum removal was achieved for the raw FAF and a slightly lower pH of 4.2 was optimum for removal of the filtered FAF (Figure 5.22).

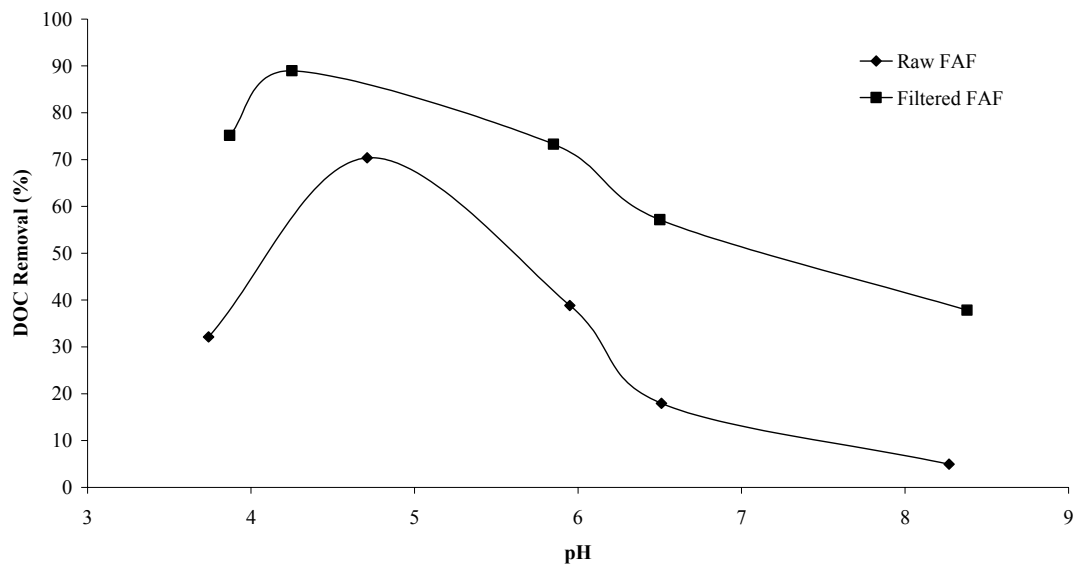


Figure 5.22 Optimised DOC removal of the raw and filtered FAF

The UV_{254} data for the raw and the filtered FAF also indicates that the optimum coagulant conditions are 12 and 8 mg L⁻¹ as Fe respectively. The majority of the UV absorbing material is removed from the raw water (92%), and a further 76% removal of the remaining 8% is observed during the optimisation of the filtered fraction. However this was achieved at a higher pH (5.85) than that considered to be optimum in terms of DOC removal (Figure 5.23).

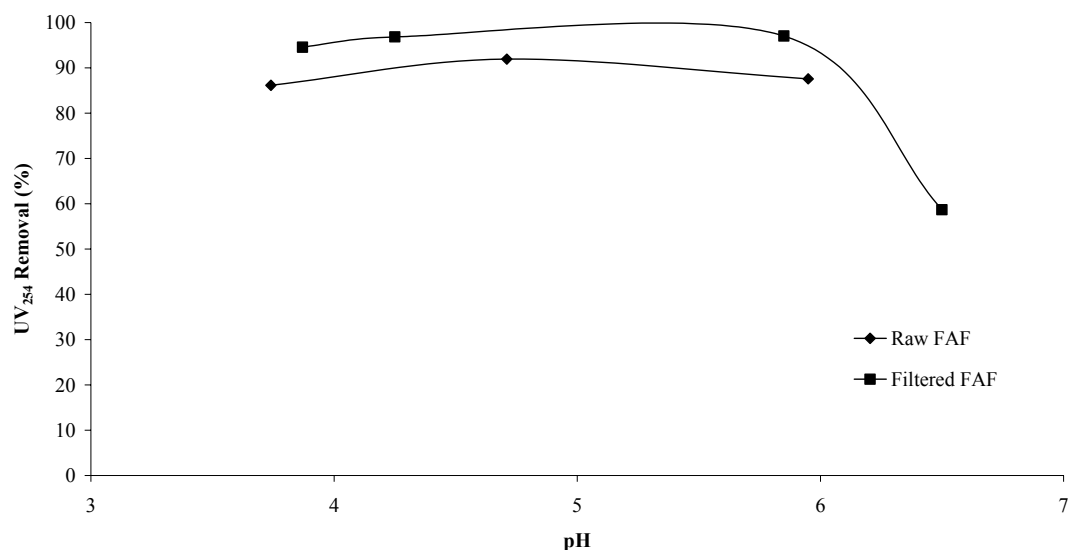


Figure 5.23 Optimised UV_{254} removal of the raw and filtered FAF

5.2.3.3 HAF optimisation

The optimum coagulation conditions for the removal raw HAF at pH 4.7 was identified as 8 mg L^{-1} as Fe, with a DOC removal efficiency of approximately 66%. The removal of the filtered HAF in terms of DOC was lower than that of the raw fraction with a maximum of 46% achieved at a dose of 8 mg L^{-1} as Fe at pH 4.25 (Figure 5.24).

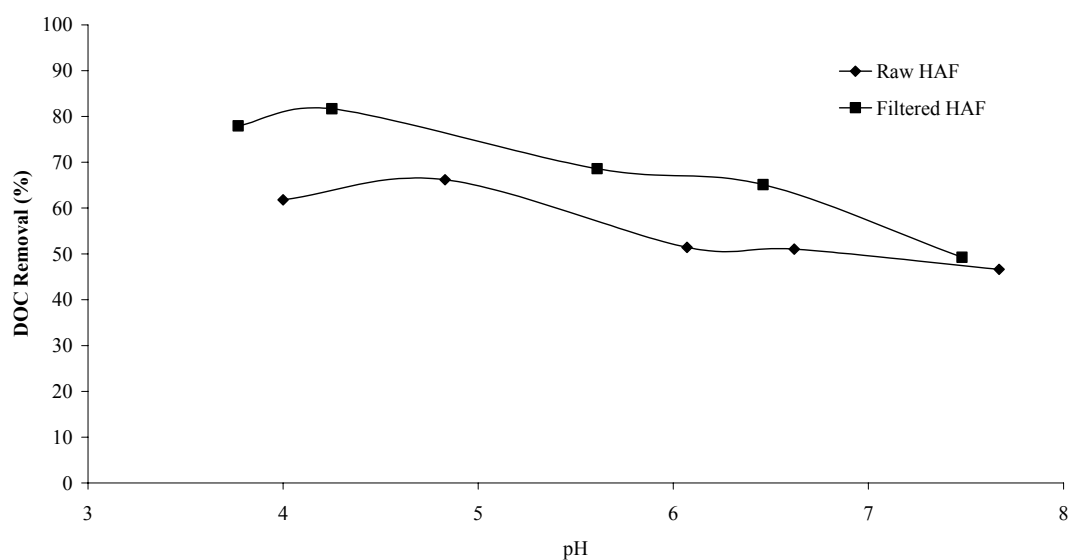


Figure 5.24 Optimised DOC removal of the raw and filtered HAF

The UV_{254} results for the coagulation also show a maximum removal for the raw HAF of 93% at pH 5. The results for the UV_{254} of the filtered HAF were so low that they were considered to be zero and are not examined here.

5.2.3.4 HPI-A optimisation

The result of the optimisation of the raw HPI-A fraction is achieved at a coagulant dose of 8 mg L^{-1} as Fe and a pH of 4. As expected for the HPI-A fraction a low DOC removal efficiency of just over 40% is observed. Surprisingly coagulation of the filtered HPI-A fraction allowed for a further 63% of the remaining DOC to be removed (Figure 5.25).

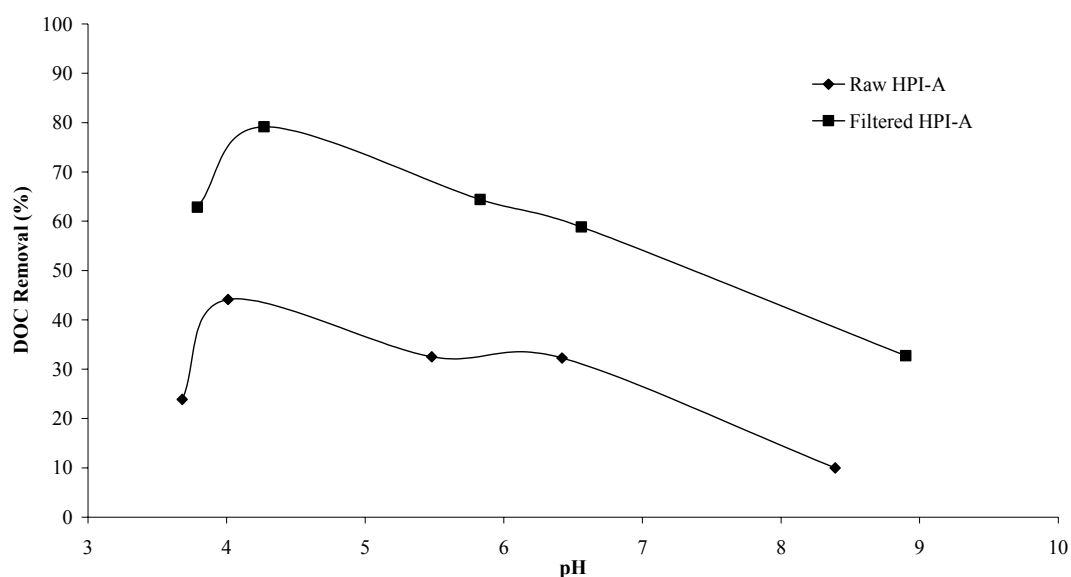


Figure 5.25 Optimised DOC removal of the raw and filtered HPI-A fractions

Similar to the filtered HAF optimisation the UV_{254} data for the hydrophilic acid fractions was inconclusive; this can be attributed to the fact that hydrophilic acid by its

very nature contains very little material that absorbs UV at 254 nm (Figure 5.5). However the data for the raw HPI-A did show a UV_{254} removal efficiency of 77% at pH 5.5 using a coagulant dose of 8 mg L^{-1} . The UV_{254} data for the filtered HPI-A was considered to be zero due to its negligible value and is not shown here.

5.2.3.5 HPI-NA optimisation

The optimum conditions for the removal of the raw HPI-NA fraction was found to be 15 mg L^{-1} at a low pH of 3.4 although the data shows that approximately 40% of the DOC is removed at a range of pHs between 3.0 and 5.5. Consequently there is no definite pH value where the DOC removal is at a maximum. The coagulant dose is considerably greater than that encountered for the previous fractions and just 43% of the raw fraction is removed during this stage. A further coagulation of the filtered fraction achieved 46% removal at a pH of 4.3 with 15 mg L^{-1} coagulant (Figure 5.26).

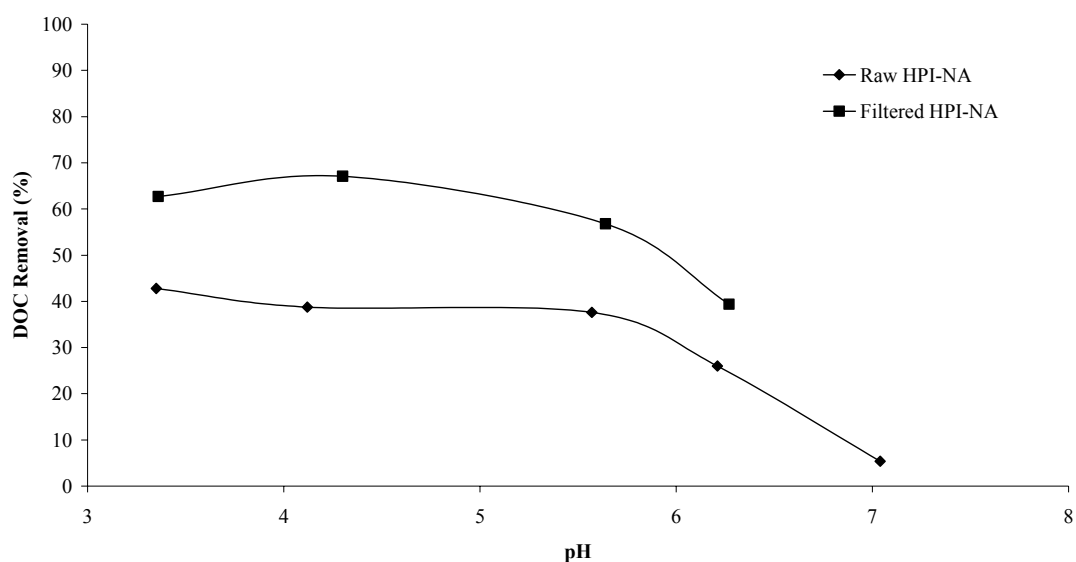


Figure 5.26 Optimised DOC removal of the raw and filtered HPI-NA fractions

The removal in terms of UV_{254} reveals that the optimum occurs at a pH of 4.1 for the raw fraction and 5.6 for the filtered fraction, using the same coagulant dose of 16 mg L^{-1} (Figure 5.27).

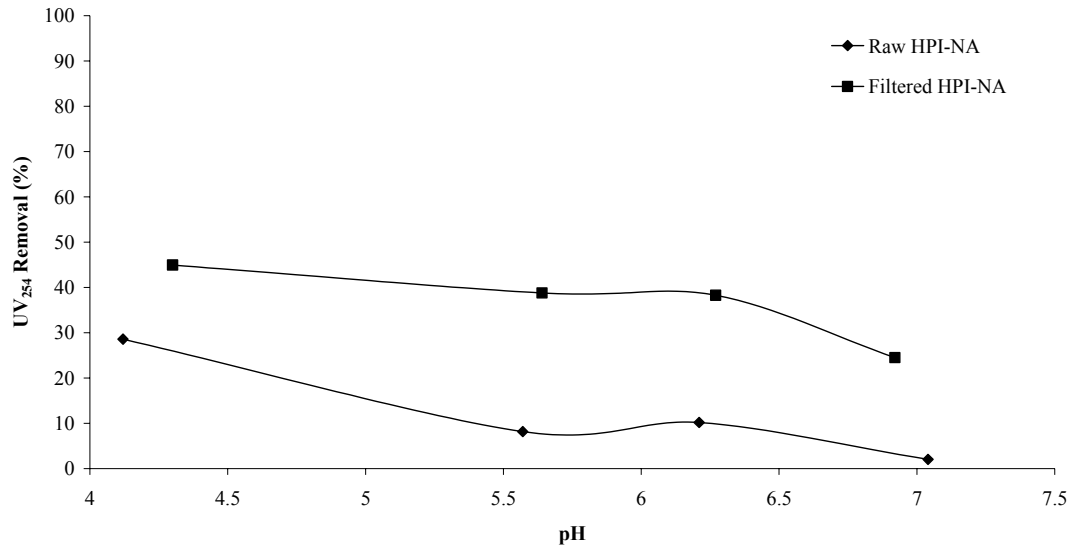


Figure 5.27 Optimised UV_{254} removal of the raw and filtered HPI-NA fractions

A summary of the optimum pH and dose condition for all the fractions and the combined removals is shown in Table 5.3.

Table 5.3 Optimum pH and coagulant doses for isolated fractions and the maximum removals observed

	Raw	FAF		HAF		HPI-A		HPI-NA	
	Water	Raw	Filt	Raw	Filt	Raw	Filt	Raw	Filt
Dose (mg L ⁻¹)	14	12	8	8	8	8	8	15	15
pH	4.5					4.0 to 5.0			
UV ₂₅₄ (% Removal)	-	92	76	93	nr	77	nr	29	23
Total UV ₂₅₄ Removal (%)	90	98		93		77		45	
DOC (% Removal)	-	70	63	66	46	44	63	43	46
Total DOC Removal (%)	80	89		82		78		69	

nr – no result

A summary of the optimised results shows an improvement in DOC removal for the isolated fractions compared to those seen under conventional un-optimised coagulation (Figures 5.28a and 28b).

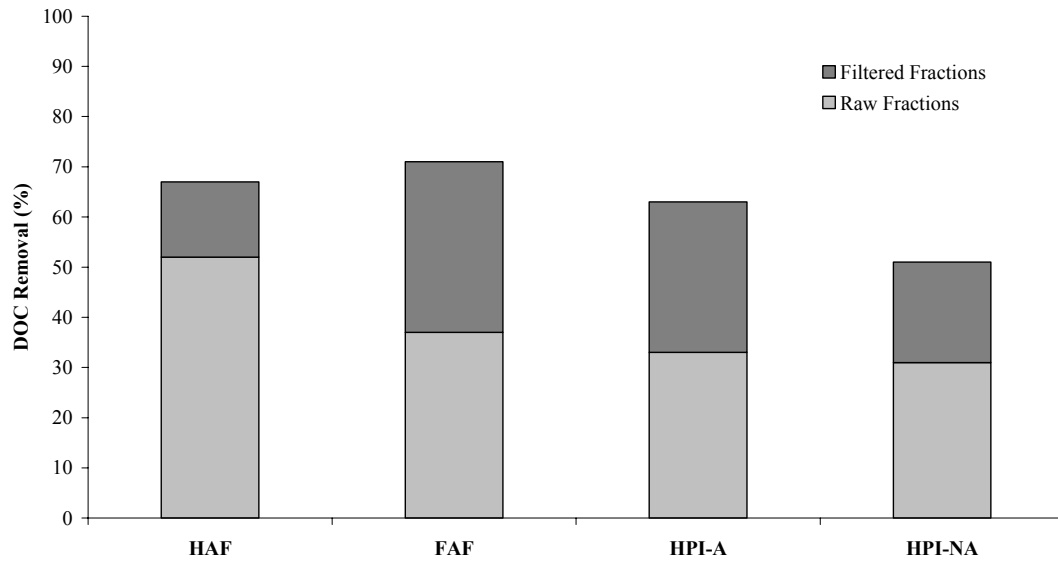


Figure 5.28a DOC removals for isolated fractions under conventional coagulation conditions

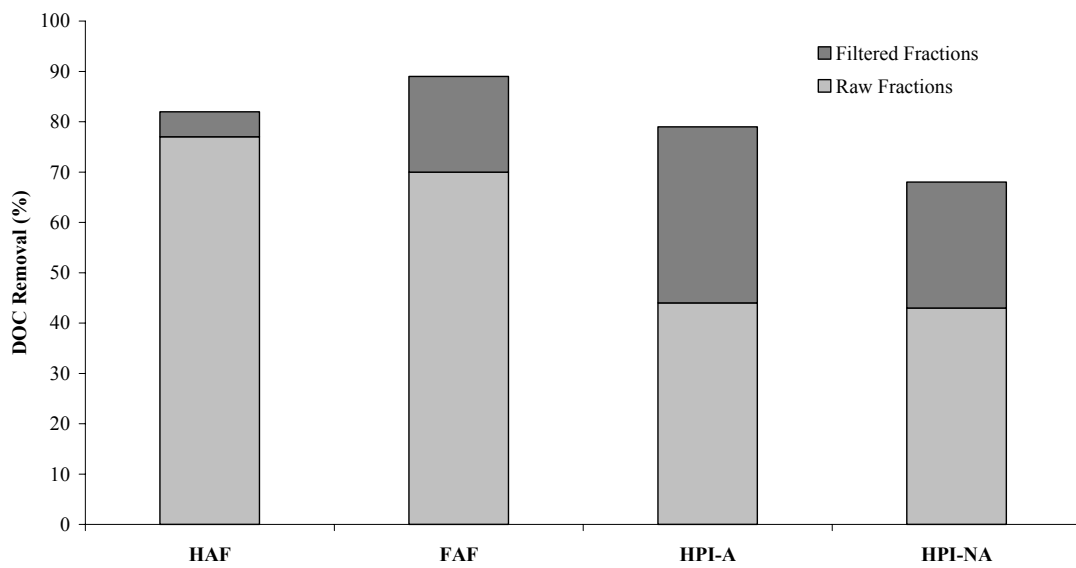


Figure 5.28b DOC removals for isolated fractions under optimised coagulation conditions

These results are comparable to those published by Croué *et al.*, 1993, where the DOC removals for HAF and HPI-A were reported as 87% and 52% respectively.

5.2.3.6 *Staged coagulation*

It was previously shown that double coagulation can improve the coagulation process in terms of DOC when organics and particles are present in the source water (Wahlroos, 1991; Carlson and Gregory, 2000) and a decrease in particle breakthrough was also observed by Billica and Gertig (2000). Here staged coagulation was employed based on the pH and dosages calculated during the optimisation of the raw and filtered fractions to determine if any increase in performance was observed. The coagulant dose and pH applied at each stage of the trial were 12 mg L⁻¹ at pH 4.7 and 8 mg L⁻¹ at pH 4.2 respectively. Model water was prepared containing the same proportion of the fractions as were isolated during the fractionation. The method employed for staged coagulation is given in section 4.3.2. Two trials were carried out method 1 was pH adjusted after both coagulant doses and in method 2 there was no pH adjustment after the second coagulant dose. The results of the two methods applied do not show any significant difference in performance and the results obtained are not as high as would be expected in terms of DOC removal. There are however high removal rates in terms of UV₂₅₄ indicating that the colour causing fractions i.e. HAF and FAF are removed leaving the non-coloured hydrophilic fractions (Table 5.4).

Table 5.4 UV₂₅₄ and DOC removal efficiencies for both staged coagulation methods

	Raw	Conventional	Method 1	Method 2
UV ₂₅₄ (m ⁻¹)	1.678	0.210	0.229	0.281
UV ₂₅₄ removal (%)	-	87.5	86.4	83.3
DOC (mg L ⁻¹)	13.06	6.423	6.478	6.593
DOC removal (%)	-	52.8	50.4	49.5

This may be explained as the removal efficiencies observed in Table 5.2 are for the individual fractions alone and when the fractions are combined in the model water there will be competition for the coagulant. It is likely that the highly charged hydrophobic material found in HAF and FAF will be more conducive to interactions with the coagulant than the less charged hydrophilic fractions (Bolto *et al.*, 1999)

Method 1 was then applied to ‘real’ raw water and compared with optimised conventional coagulation. The results showed that the staged coagulation did not appear to show any performance improvement in terms of DOC and UV₂₅₄ removal (Figure 5.29).

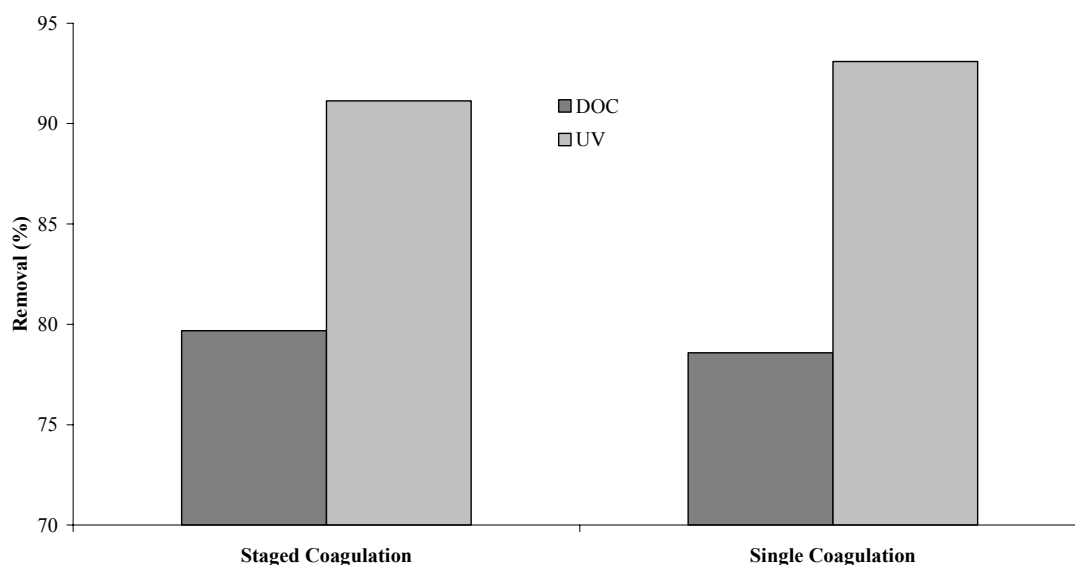


Figure 5.29 Comparison of UV₂₅₄ and DOC removals for staged and conventional coagulation

The staged coagulation method was then trialled at Albert WTW to determine if improvement in the filter performance was seen. As expected no improvement in the removal of DOC and UV₂₅₄ was seen. However a slight improvement in the reduction of THMFPS for the water treated by staged coagulation compared to conventional coagulation was observed (82% and 77% respectively) (Table 5.5).

Table 5.5 Residual UV₂₅₄, DOC and THMs for raw water, conventional and staged coagulation

	DOC (mg L ⁻¹)	UV ₂₅₄ (m ⁻¹)	THM (µg L ⁻¹)
Raw water	10.16	43.4	632.3
Conventional coagulation (12 mg L ⁻¹)	1.50	3.1	187.6
Staged coagulation (3 mg L ⁻¹ and 9mg L ⁻¹)	1.85	2.9	148.3

The THMFP values quoted are absolute values and an excess amount of free chlorine remains in the water. This explains why the treated water values are higher than those

seen previously at Albert WTW. The trial showed that a considerable improvement in the floc filterability occurs and a reduction in the size of turbidity spikes observed on site during staged coagulation (Figure 5.30). These results were similar to those published by Carlson and Gregory (2000) in which the settled turbidity of water treated by a two stage coagulation process was reduced by 25% and particle breakthrough was not observed during a typical filter run.

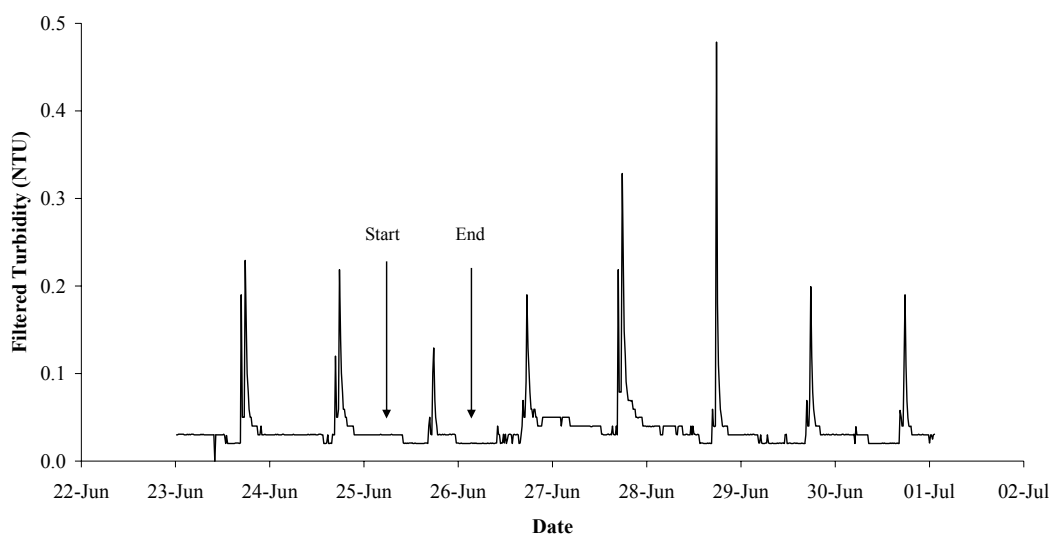


Figure 5.30 Effect of staged coagulation on the turbidity of filtered water (Albert WTW, June 2003)

A potential reason for the reduction in settled turbidity and longer filter run times is hypothesised. For a floc to be filterable the zeta potential (ZP) of the flocs formed is required to be within certain limits. Research has shown that the range of zeta potentials required to achieve maximum turbidity removal is approximately between 0 and -12 mV (Jefferson and Parsons, 2004) (Figure 5.31).

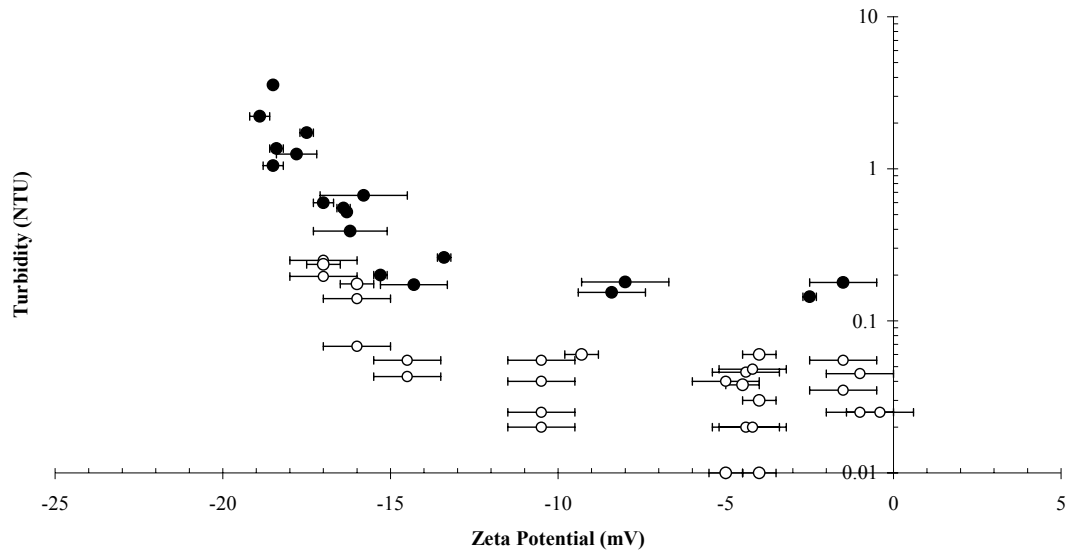


Figure 5.31 Filtrate turbidity vs. zeta potential during depth filtration (Jefferson and Parsons, 2004)

Here mechanisms for single and dual coagulation are proposed. During single stage coagulation the ferric dose is immediately followed by pH adjustment to 4.5-5. This would lead to the formation of ferric hydroxide particles and the NOM would adsorb on to the surface of the hydroxide. At pH 4.5-5 the zeta potential of the system would be 0 (similar to the 1:1 FAF to Fe line in Figure 5.32) but if the pH is then increased to approximately 6.5 prior to filtration the zeta potential of the system would become increasingly negative and in the case of FAF the zeta potential would fall outside the operational window for filterability (Figure 5.32).

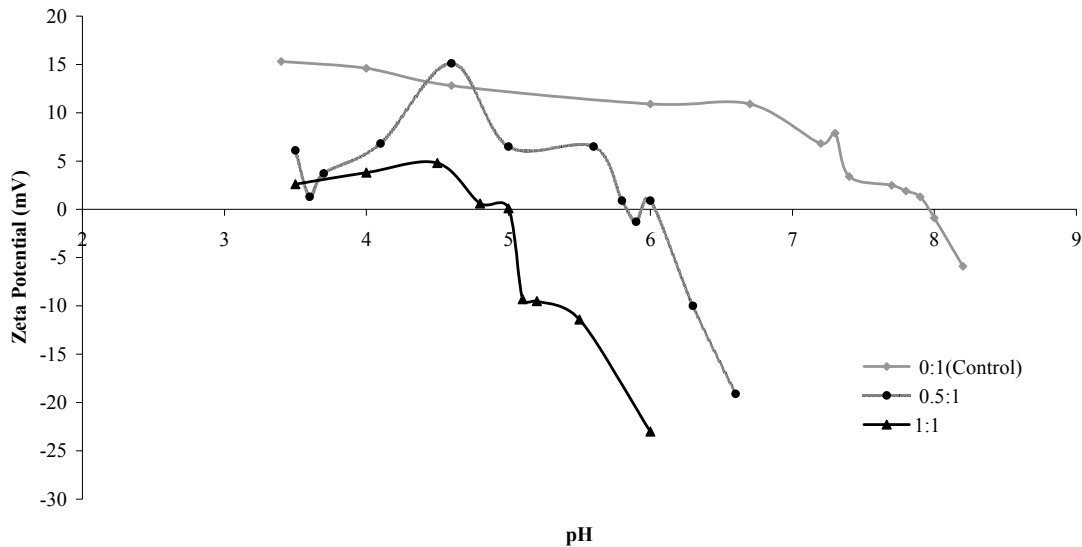


Figure 5.32 Zeta potential of ferric based coagulant with FAF at varying ratios and pH (adapted from Sharp *et al.*, 2004)

When dual coagulation is used the initial coagulant dose is not pH adjusted and therefore the likely mechanism is complexation of the ferric ions and negatively charged NOM which has an overall neutral charge associated with it. On the addition of the second coagulant dose immediately followed by pH adjustment the same adsorption mechanism as proposed for single stage coagulation would occur. However at this stage there would be significantly less NOM in the water and consequently the NOM:Fe ratio would be reduced. This in turn would lead to a more positively charged system with respect to zeta potential at pH 4.5-5 (similar to the 0.5:1 FAF to Fe ratio in Figure 5.32). Now when the pH is increased prior to filtration the zeta potential is less sensitive to pH changes and remains within the operational window for filterability.

5.2.4 Summary

As reported in the literature review (section 2.5.1.2) the optimisation of the coagulation process is vital in order that maximum efficiency is achieved in terms of NOM removal. Currently Albert WTW is optimised on the bulk water parameters. The FAF and HPI-

NA were specifically targeted during these experiments and removal efficiencies for both could be increased significantly for both (Figures 5.28a and 5.28b) when optimised individually. However tailoring the process for these fractions saw no significant improvement in the overall bulk water removal efficiencies. This may be due to competition reactions between the fractions. The process robustness was improved in terms of filter run times and a reduction in the turbidity spikes seen on the filters. This may be of considerable benefit during the months of the year when the water quality deteriorates and THM compliance and filterability problems occur. A mechanism for the improved filter performance observed during staged coagulation was proposed. Currently the staged coagulation process evaluated here is being evaluated as a full scale option at Albert WTW but results are not available for inclusion in this thesis.

5.3 Magnetic ion exchange (MIEX[®])

5.3.1 Introduction

Ion exchange is not necessarily a new process for the treatment of NOM, and due to its ability to remove anionic species such as NOM should be very effective. However very few ion exchange plants are in operation for the treatment of humic rich waters due to the costs associated with operating a pressurised bed system. It was with this in mind that the magnetic ion exchange (MIEX[®]) DOC process was recently developed by Orica Watercare, South Australian Water Corporation and the Commonwealth Scientific and Industrial Research Organisation (CSIRO) specifically for the removal of DOC from drinking water. Currently there are few published studies on the use of MIEX[®] and all the published data is based on waters in the US and Australia. Here a study on a range of waters from the UK including removal of fractions, MW ranges and process optimisation is presented

The MIEX[®] process is described in detail in section 2.5.2.6 and involves adsorbing the DOC on to the MIEX[®] resin in a stirred contactor that disperses the resin beads to ensure maximum surface area availability. The magnetic core of the resin allows the resin to agglomerate into faster settling particles which allow for a recovery rate of greater than 99.9% (Smith *et al.*, 2001). Any resin that is carried over is removed in downstream clarification processes.

The factors that may affect the performance of MIEX[®] are dose concentration, contact time, raw water quality, temperature, pH and mixing speed. Here the optimisation of dose and contact time were carried out and the performance of the resin evaluated by

trailing it on raw waters from differing geographical locations and catchments with widely variable characteristics in terms of DOC, UV₂₅₄, THMFP and MW. Also its effectiveness on the isolated NOM fractions from Albert WTW was assessed.

5.3.2 MIEX[®] optimisation

A series of experiments to determine optimum dose and contact time for the MIEX[®] on Albert raw water shows that the best DOC and UV₂₅₄ removal (90%) for both occurs at maximum dose (30 mL L⁻¹) and contact time (60 minutes). However the use of a relatively high MIEX[®] dose (20 mL L⁻¹) for a shorter contact time (30 minutes) shows that approximately 80% DOC and UV₂₅₄ removal is achievable compared to 60% and 40% DOC and UV₂₅₄ removal for a low MIEX[®] dose of 2 mL L⁻¹ for the same contact time (Figures 5.33a and 33b).

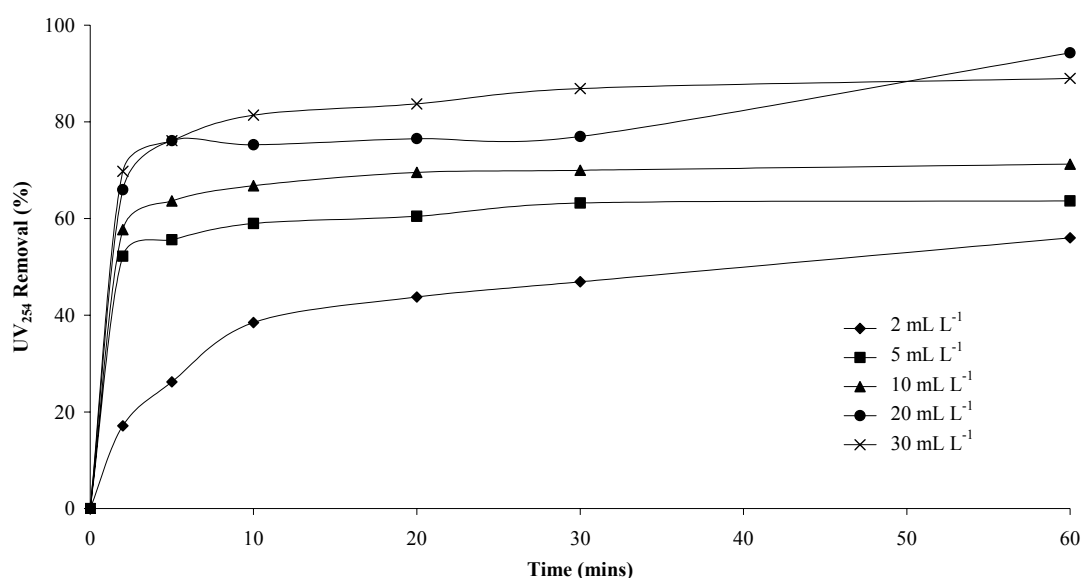


Figure 5.33a UV₂₅₄ optimisation of MIEX[®] for the treatment of Albert raw water

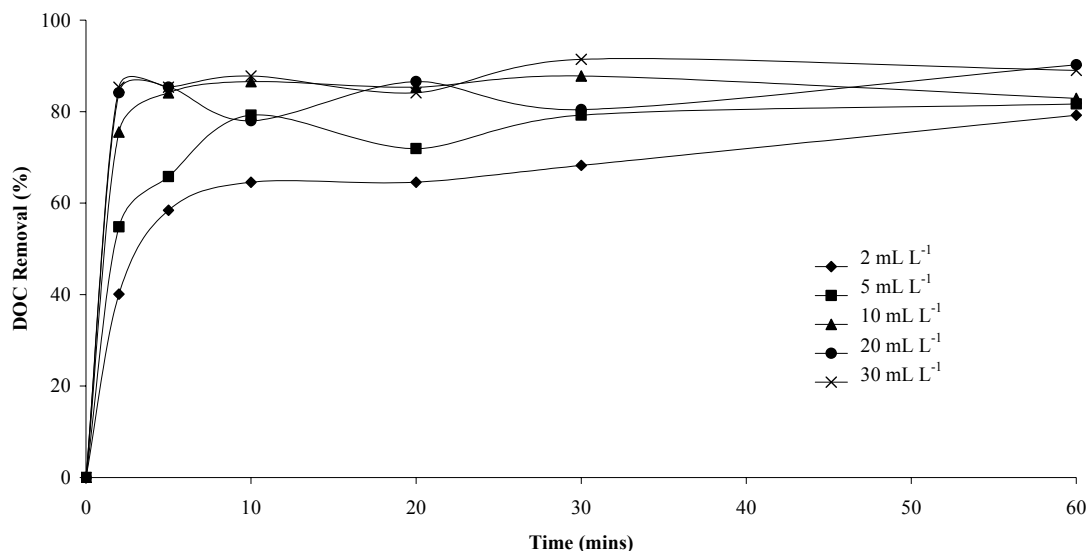


Figure 5.33b DOC optimisation of MIEX[®] for the treatment of Albert raw water

The HPSEC data for raw water treated with 20 mL L⁻¹ MIEX[®] for 30 minutes shows that peak 1 at 5.7 minutes (>5000 Da) is relatively unchanged by the addition of MIEX[®]. Peaks 2, 3, 4, 5 and 6 at 8.7, 8.9, 9.3, 9.7 and 10.3 minutes respectively (<5000 Da) are reduced significantly. However peak 7 at 10.7 minutes is less well removed (Figure 5.34).

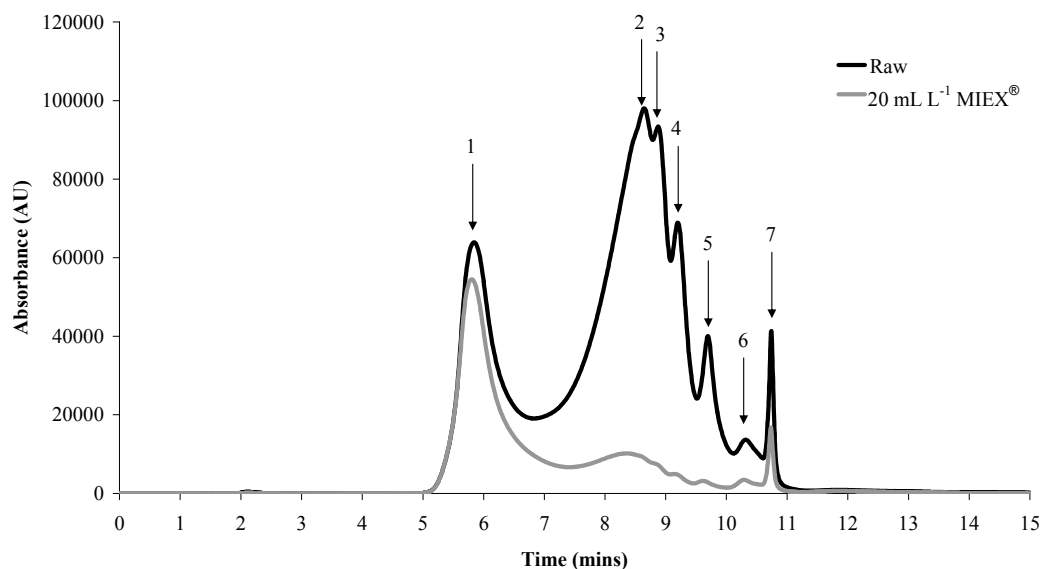


Figure 5.34 Effect of MIEX[®] treatment on the MW profile of Albert raw water

From this data an optimum MIEX[®] dose and contact time of 20 mL L⁻¹ and 30 minutes respectively was chosen for further studies. Finally another basis for using a higher MIEX[®] dose (>20 mL L⁻¹) is that at low concentrations there is high dispersion of the resin beads and less agglomeration leading to slower settling rates.

5.3.3 MIEX[®] + coagulant optimisation

The addition of a ferric based coagulant to Albert raw water showed that the maximum removal efficiencies were seen for a coagulant dose of approximately 15 mg L⁻¹ at a pH of 4.5. The removal efficiencies achieved under these conditions were 94% and 95% for DOC and UV₂₅₄ respectively. Coagulating water previously treated with the optimised dose of MIEX[®] (20 mL L⁻¹, 30 minutes) showed that for a coagulant dose of 4 mg L⁻¹ as Fe at a pH of 4.5 the maximum removal efficiencies for DOC and UV₂₅₄ were 97% and 88% respectively (Figure 5.35). These results were comparable to waters of similar SUVA value shown in Table 2.10

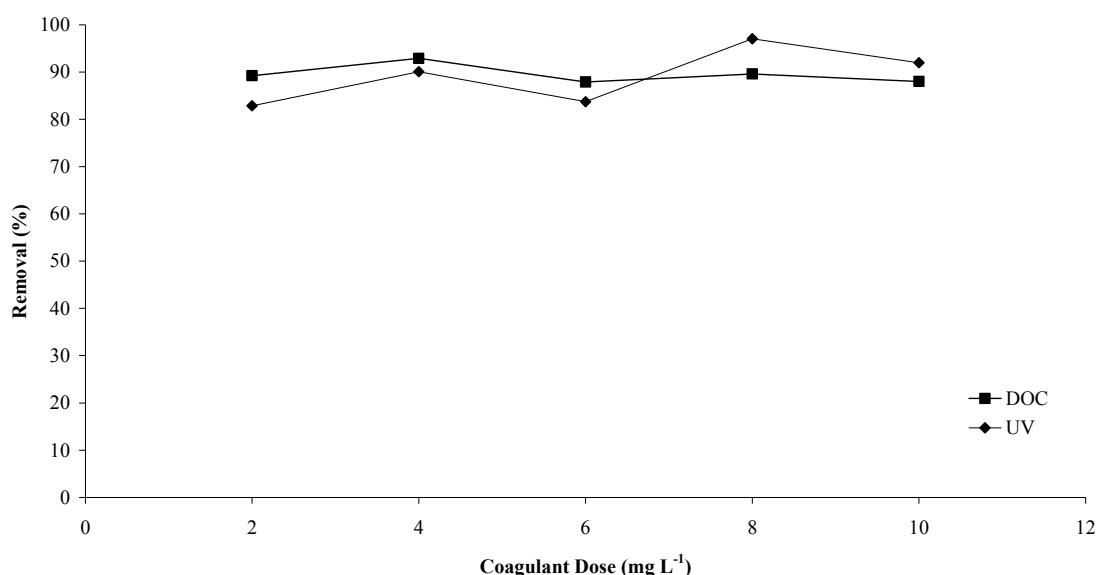


Figure 5.35 Optimisation of MIEX[®] plus coagulation treatment of Albert raw water by UV₂₅₄ and DOC removal

The HPSEC plot of MIEX[®] treated water coagulated with varying doses of coagulant show that peaks 1-4 (>2000 Da) are further removed whilst only a limited extra removal for peaks 5-7 (<2000 Da) is achieved by coagulation (Figure 5.36).

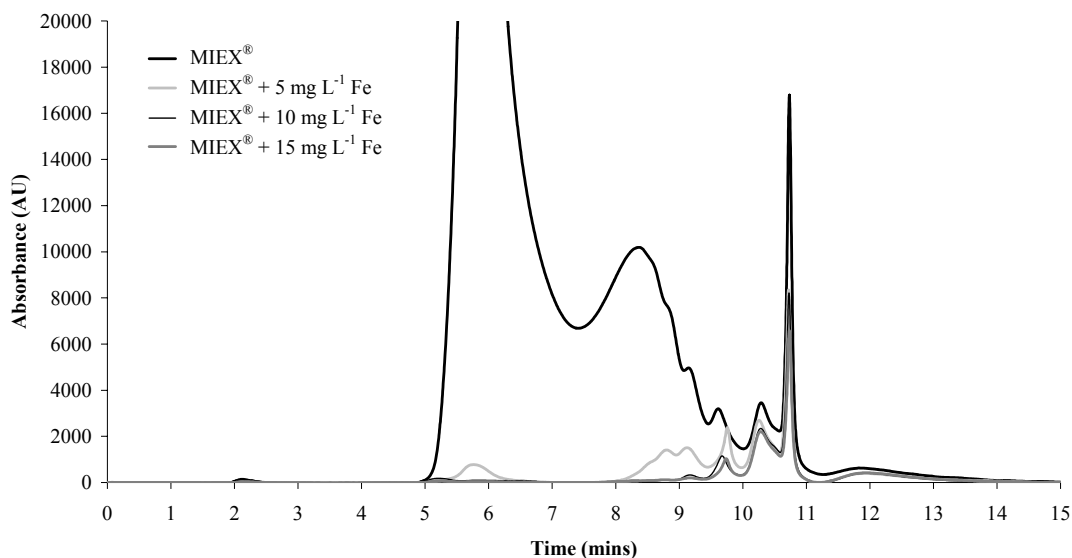


Figure 5.36 Optimisation of MIEX[®] and coagulation treatment of Albert raw water UV₂₅₄ MW profile

The results of the HPSEC show only the effect on the UV absorbing fraction of the water, and as previously stated the UV absorbing fractions (HAF and FAF) are regarded as the easiest to remove (section 2.5.1.4). Many of the recalcitrant components of the water do not adsorb UV at 254 nm or have a low MW that may be the cause of high THM levels in the treated water observed at many WTWs (Matilainen *et al.*, 2002). With this in mind it is necessary to study the removal of the DOC as well. When MIEX[®] is employed on its own approximately 60% of the DOC is removed and 70% of the UV absorbing material. When an optimum ferric dose is used the DOC and UV₂₅₄ removal is improved up to 75% and 90% respectively. A combination of MIEX[®] and a

lower dose of ferric coagulant (5 mg L^{-1}) achieved a similar DOC removal and almost complete removal of the UV_{254} (Figure 5.37).

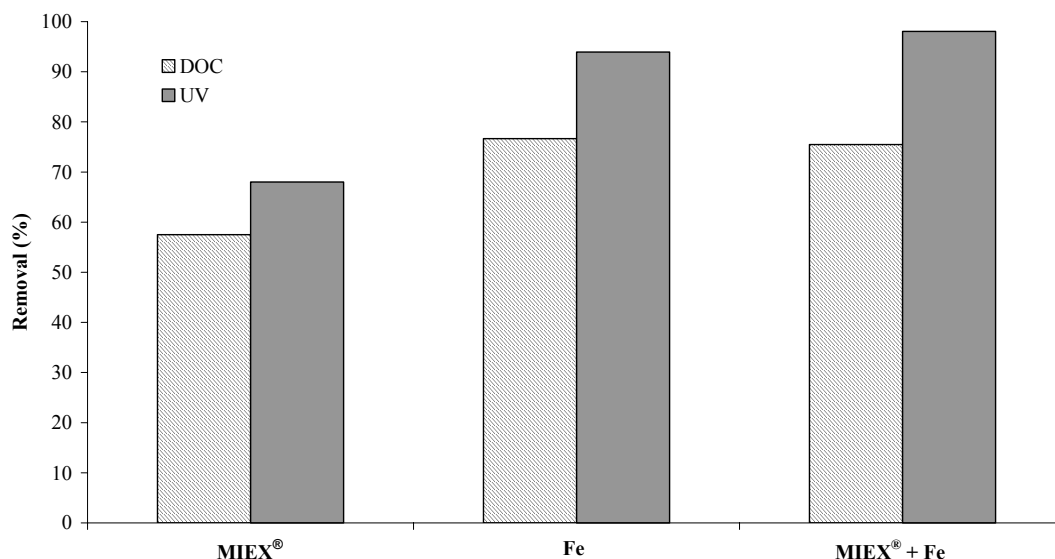


Figure 5.37 Comparison of conventional coagulation, MIEX® treatment and a combination of MIEX® and coagulation for the removal of UV_{254} and DOC

Similar results have been published where MIEX® in addition to a reduced coagulant dose of 60 mg L^{-1} ferric sulphate gave an average DOC level of 3.9 mg L^{-1} compared to an average DOC level of 5.5 mg L^{-1} when a ferric sulphate dose of 240 mg L^{-1} was used (Bourke *et al.*, 2002).

Studies were also carried out 'on site' to determine the optimum conditions for removal of THMFP precursors, it was shown that as before a lower contact time but high dose of MIEX® was equally as effective for the removal of THMs compared to low dose, long contact time (Figure 5.33b). This was combined with ferric coagulation and the amount

of coagulant required to achieve equivalent removals was considerably lower than that needed when conventional coagulation was employed (Figure 5.38).

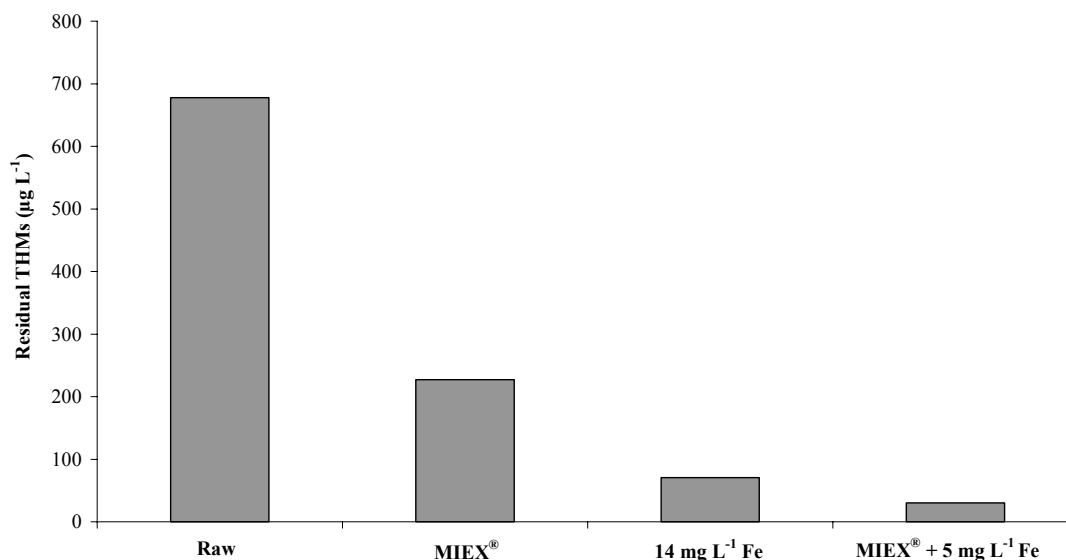


Figure 5.38 Residual THMs of raw, MIEX[®] treated, conventional coagulation and a combination of MIEX[®] and coagulation

5.3.4 *Seasonal effect on the use of MIEX[®]*

Previous research has focussed on the treatment of waters at one time during the year (Singer and Bilyk, 2002; Drikas *et al.*, 2003 and Drikas *et al.*, 2003b). Here the effect of MIEX[®] on the treatment of water was tested on Albert raw water at three different times during the year. The nature and quality of the water varies considerably throughout the year as does the fraction distribution (Table 5.6).

Table 5.6 Seasonal changes in DOC, UV₂₅₄ and fraction distribution for Albert raw water

	pH	DOC (mg L ⁻¹)	UV ₂₅₄ (m ⁻¹)	SUVA (L mg ⁻¹ m ⁻¹)	Fraction Distribution			
					FAF (%)	HAF (%)	HPI-A (%)	HPI-NA (%)
Apr 02	5.9	7.5	38.1	5.08	52	20	12	16
Oct 02	6.9	11.7	52.3	4.47	52	23	9	16
Mar 03	6.6	11.0	58.3	5.30	44	27	19	10

Consequently the maximum removals achievable using MIEX[®] (10 mL L⁻¹, 60 minute contact time) for both DOC and UV₂₅₄ also vary markedly and ranged from 66% to 82% removal for DOC and 66% to 87% for UV₂₅₄ removal (Table 5.7).

Table 5.7 Removal efficiencies for the MIEX[®] treatment of seasonally different waters

	DOC			UV ₂₅₄		
	Initial (mg L ⁻¹)	Final (mg L ⁻¹)	Removal (%)	Initial (m ⁻¹)	Final (m ⁻¹)	Removal (%)
Apr '02	7.8	1.4	82.1	32.5	4.4	86.5
Oct '02	11.2	3.8	66.1	50.7	17.5	65.5
Mar '03	11.0	3.2	70.9	51.3	11.5	77.7

These removals generally relate to the fact that the highest removal (April 2002) is seen when both the DOC and UV₂₅₄ are at their lowest and likewise when the DOC and UV₂₅₄ are at their highest (October 2002) the lowest removals are seen.

5.3.5 Fraction removal

The effect of MIEX[®] on the individual isolated fractions was examined in this study to assess the removal efficiency on each of them and relate this to the assumptions

regarding preferential removal of lower MW material. It also enabled the MIEX[®] to be directly compared to the optimum removal achievable via single optimised coagulation (Section 5.2.3). The results confirm that MIEX[®] removes a large amount of the FAF (90%) with respect to the UV₂₅₄ and achieves similar removals to ferric for both the HAF and HPI-A (90% and 75% respectively). It was also noted that MIEX[®] performs better at removing the HPI-NA fraction which has been shown in the past to be the most recalcitrant fraction when coagulation is employed (Bolto *et al.*, 2001). In terms of DOC removal the FAF and HAF fractions are readily removed by both the MIEX[®] and conventional coagulation (60%-70% respectively) which in itself is slightly unexpected as the MIEX[®] previously appeared to be less adept at removing high MW compounds that would be expected to be found in HAF. A disadvantage of MIEX[®] compared to coagulation is its reduced removal efficiency of DOC for the HPI-A fraction (Figures 5.39a and 5.39b).

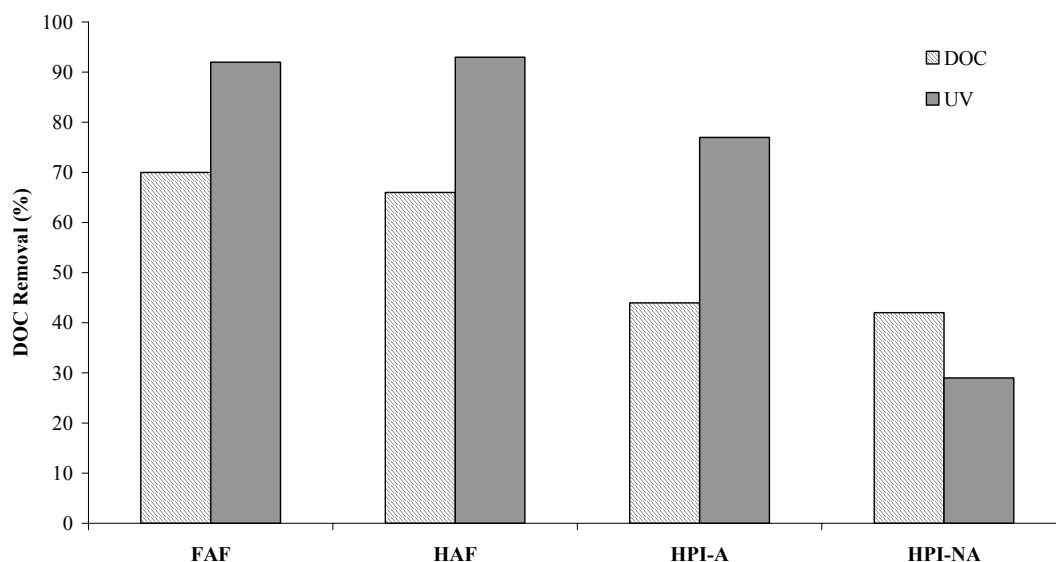


Figure 5.39a. Maximum DOC and UV₂₅₄ removal for the isolated fractions using MIEX[®] treatment only (10 mL L⁻¹, 60 minutes)

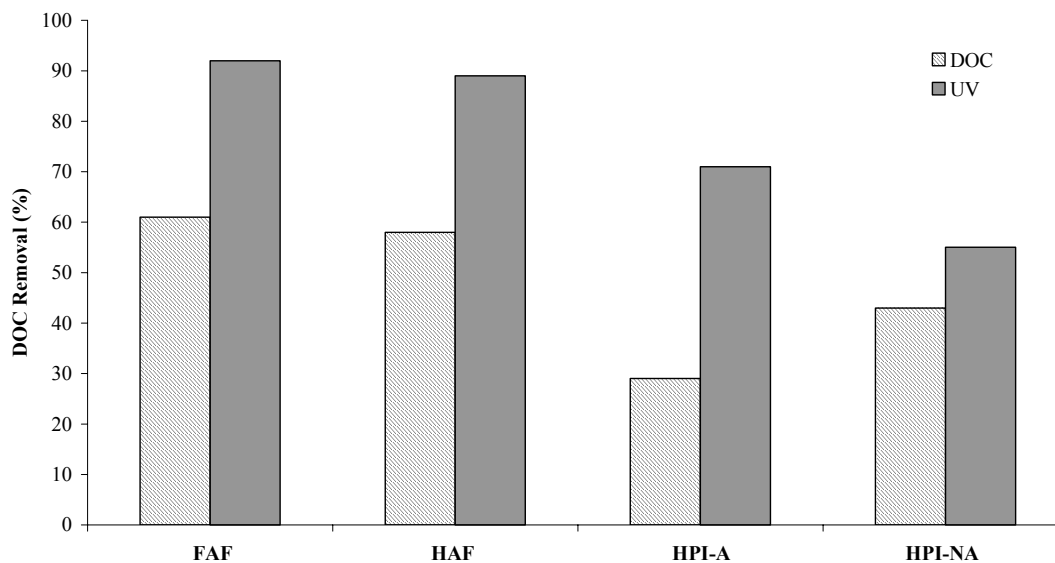


Figure 5.39b. Maximum DOC and UV₂₅₄ removal for the isolated fractions using ferric treatment only (each fraction optimised for dose and pH)

Although there are no published data on the effect of MIEX[®] on isolated NOM fractions, results published by Singer and Bilyk (2002) show that the effect of treating a high SUVA water ($4.5 \text{ m}^{-1} \cdot \text{L} \cdot \text{mg}^{-1}$) with MIEX[®] prior to conventional coagulation increases the DOC removal from 50% to 87%. It can also be seen that the effect of MIEX[®] on the treatment of low SUVA water also shows an increase in DOC removal from 23% to 46%.

5.3.6 Evaluation of other UK water sources (2003-2004 survey)

Water from five different WTWs was treated with MIEX[®] to assess the effect of differing water quality and catchments (moor land reservoir, low land river and upland impounded) have on performance.

The moor land water sources are from Albert (Yorkshire Water) and Bamford (Severn Trent), the low land river samples are from Draycote (Severn Trent) and Loftsme

Bridge (Yorkshire Water). The upland impounded water is from Amlaird (Scottish Water). A summary of the main water chemistry characteristics are shown in Table 5.8.

Table 5.8 Raw water chemistry characteristics of trialled water sources

Water Source and Sampling Date	Albert (10.06.2003)	Bamford (3.09.2003)	Draycote (10.11.2003)	Loftsome Bridge (22.2.2004)	Amlaird (17.12.2003)
pH	6.0	5.7	8.2	7.8	6.0
DOC (mg L ⁻¹)	8.18	8.06	15.63	4.30	20.85
UV ₂₅₄ (m ⁻¹)	47.3	34.7	34.0	19.5	86.3
Turbidity (NTU)	5.02	1.35	0.75	14.6	3.08
SUVA (L mg ⁻¹ m ⁻¹)	5.78	4.31	2.18	4.53	4.14

The HPSEC data for the raw waters studied are shown in Figure 5.40. The waters from Albert and Bamford show similar MW ranges although peak 1 (>5000Da) for Bamford is approximately 50% of the intensity compared to that of Albert. The water from Amlaird has significantly higher absorbance intensity than the other waters due to its high colour and UV₂₅₄ absorbance shown in Table 5.8. The water collected from Draycote is mainly composed of compounds that have a mid to low MW range and has no absorbance in the high MW region (5-7 minutes). Finally the MW profile of Loftsome Bridge raw water exhibits a very low intensity throughout the MW range and therefore HPSEC with UV₂₅₄ detection would be of little use as an indicator for removal efficiency.

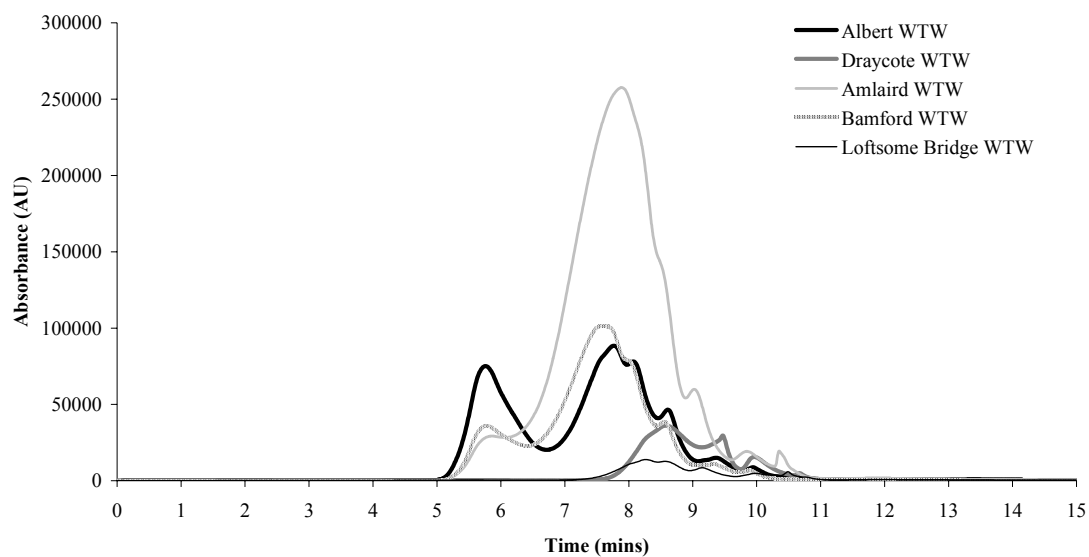


Figure 5.40 Comparison of MW profile for the trialed raw waters

Initially the MIEX[®] optimisation of the trialed waters was carried out to determine the contact time and dose required to achieve optimum removal. The optimum was not necessarily the highest removal efficiency but rather the lowest dose and contact time that achieved comparable removals (Figure 5.41). The results for Loftsosome Bridge WTW are not shown here due to the low UV_{254} absorbance.

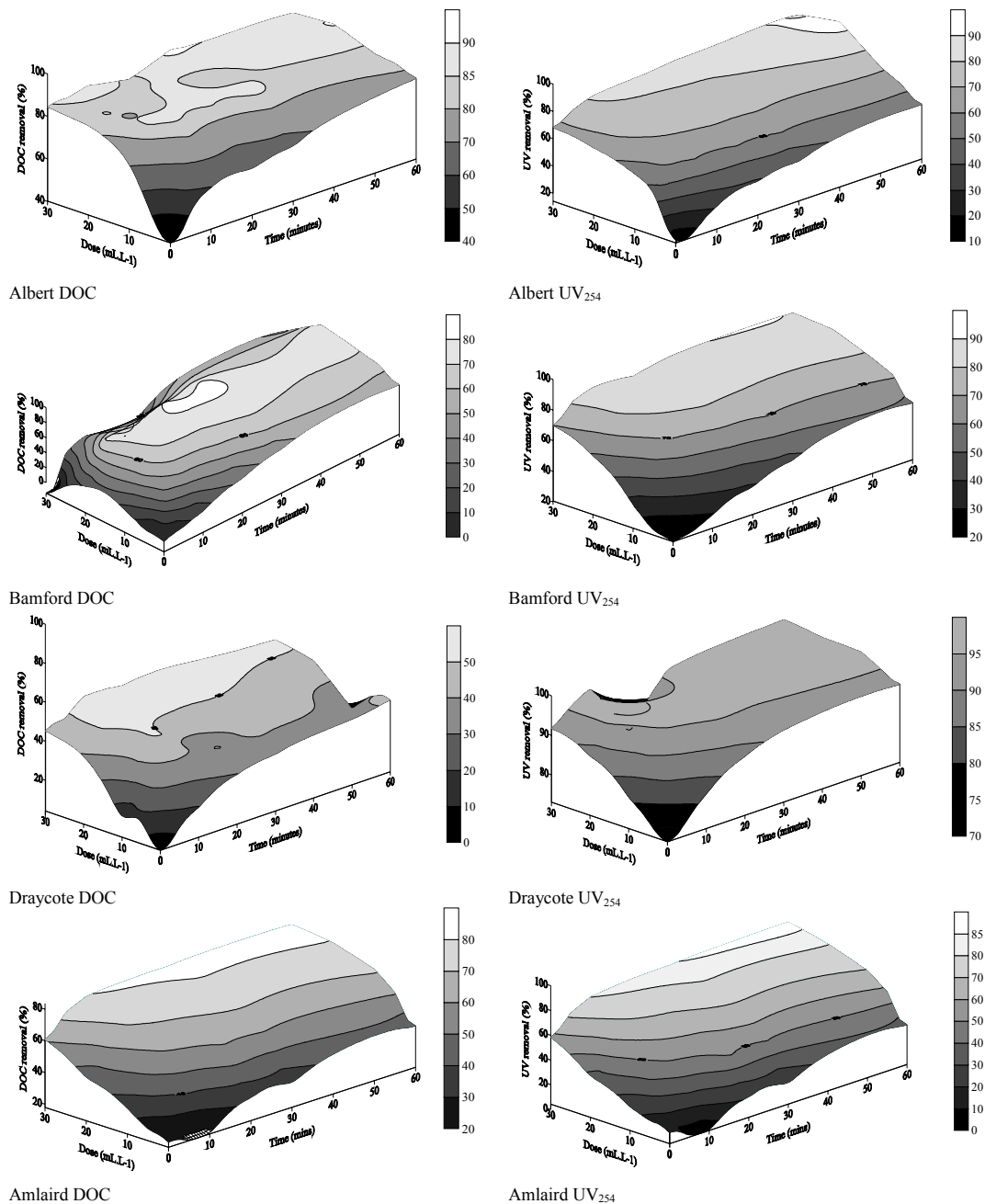


Figure 5.41 MIEX[®] optimisation of waters studied during evaluation

5.3.6.1 Albert WTW

The results achieved by coagulation and, MIEX[®] plus coagulation for the removal of DOC on water collected in June 2003 are similar with over 90% removal being achieved. Similarly the optimum UV₂₅₄ removal for coagulation and, MIEX[®] plus

coagulation is approximately 96%. These removals are higher than experienced previously with conventional coagulation during other seasonal periods (Table 5.7). This may be attributed to a higher proportion of hydrophobic material in the water during this period which as seen previously (Figure 2.12) leads to higher observed removal efficiencies.

This data along with further HPSEC data for raw water treated with MIEX[®] and ferric individually shows that MIEX[®] is better suited to removing mid and lower MW parts of the raw water and less effective for the high MW portion. Ferric coagulation at optimum dose and pH (14 mg L⁻¹ as Fe at pH 4.5) shows excellent removals of the high and mid MW material in the water. Although comparable removals of the lower MW compounds is also observed a decrease in efficiency would be seen if the dose was reduced in order that coagulant costs and sludge are to be minimised or there was an increase in DOC levels (i.e. coagulant to DOC ratio reduced). A combination of both MIEX[®] and a considerably lower dose of ferric (5 mg L⁻¹ as Fe) show an improvement in UV₂₅₄ removal in terms of HPSEC analysis (Figure 5.42).

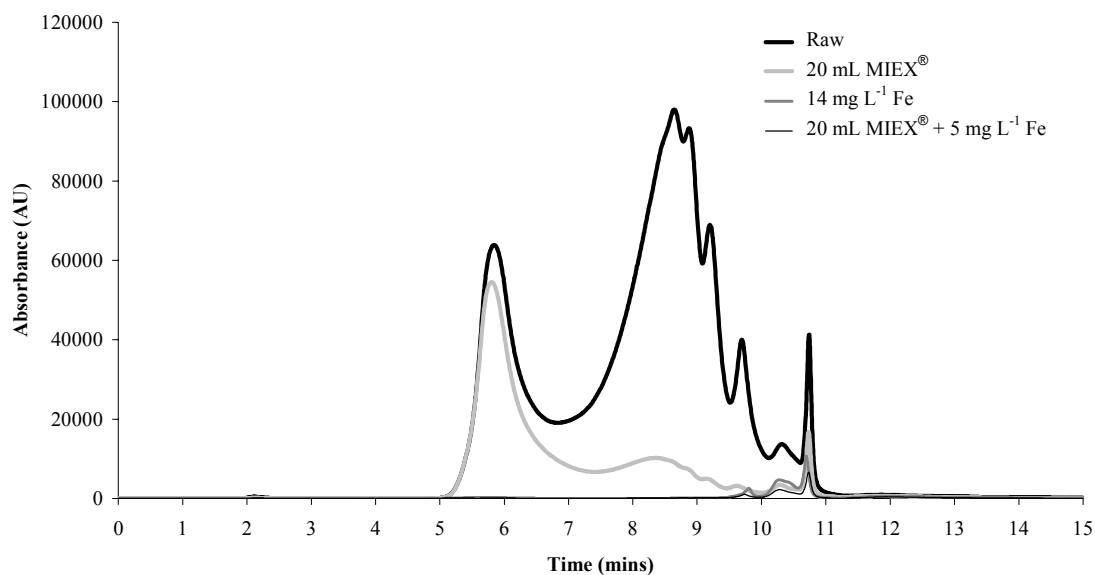


Figure 5.42 Comparison of MIEX[®], ferric and a combination of MIEX[®] plus ferric on the removal of UV₂₅₄ found within raw reservoir water (Albert)

5.3.6.2 Bamford WTW

From the raw water characteristic data shown in Table 5.8 and the HPSEC of the raw water in Figure 5.40 it can be seen that Bamford raw water is similar to that of Albert with the exception of SUVA which is lower ($4.31 \text{ L mg}^{-1} \text{ m}^{-1}$ compared to $5.78 \text{ L mg}^{-1} \text{ m}^{-1}$ for Albert). The DOC removals achieved by both coagulation and MIEX[®] plus coagulation show that a lower dose of coagulant (6 mg L^{-1}) when combined with MIEX[®] achieve similar removals ($\sim 80\%$) to that of conventional coagulation (15 mg L^{-1} as Fe at pH 4.5). Similarly the UV₂₅₄ removal shows that the use of MIEX[®] prior to coagulation does not significantly increase removals (87% and 84% for MIEX[®] treated and conventional coagulation respectively).

5.3.6.3 Draycote WTW

Draycote raw water has considerably different characteristics to the other waters reported previously in that the UV_{254} is comparatively low when compared to the DOC indicating that the water contains more low MW hydrophilic material ($SUVA = 2.18 \text{ L mg}^{-1} \text{ m}^{-1}$). This leads to coagulation not being as effective for the removal of the DOC with only approximately 46% removal efficiency observed for a coagulant dose of 10 mg L^{-1} as Fe at pH 4.5. Whereas a considerably lower coagulant dose (2 mg L^{-1}) following treatment with MIEX[®] (20 mL L^{-1} for 30 minutes) achieves a DOC removal of approximately 76%. Comparable results are observed for the UV_{254} removal where 71% and 97% removals are observed for coagulation (10 mg L^{-1}) and MIEX[®] plus coagulation (20 mL L^{-1} , 30 minutes plus 2 mg L^{-1} Fe) respectively.

The HPSEC data for coagulation, MIEX[®] treatment and combination of both confirms that coagulation alone achieves the lowest UV_{254} removal over the full MW range. This is to be expected as coagulation is usually less effective for low SUVA waters (Figure 2.12). Also the absence of the high MW material usually seen at 5.7 minutes is most effectively removed by coagulation (Figure 5.43).

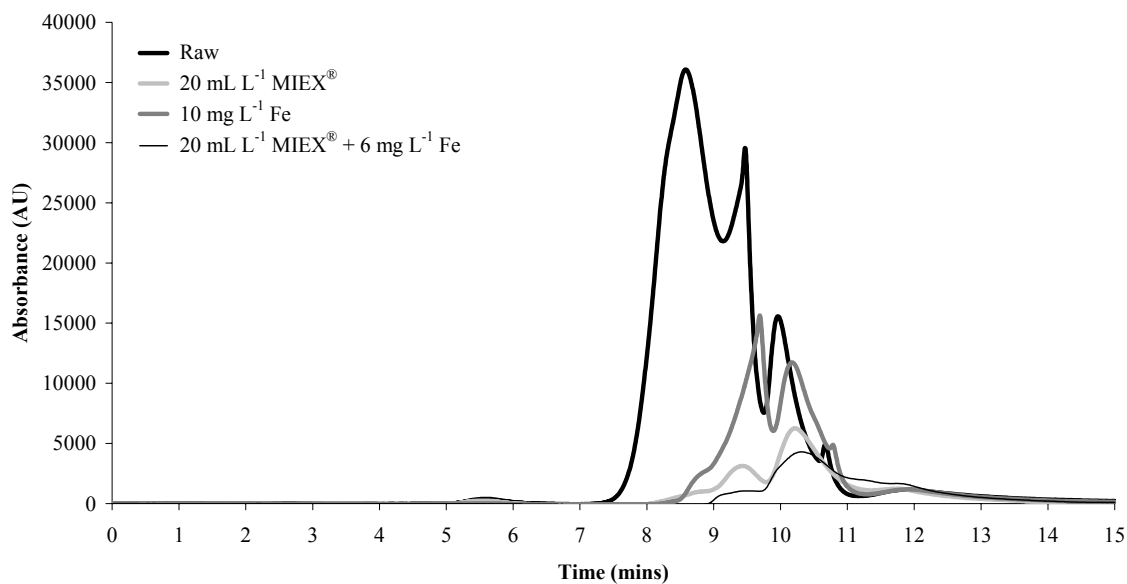


Figure 5.43 Comparison of MIEX[®] and ferric on the removal of UV₂₅₄ found within raw reservoir water (Draycote)

5.3.6.4 Loftsome Bridge WTW

Loftsome Bridge water is low in both UV₂₅₄ absorbing compounds and DOC but has a relatively high SUVA value ($4.53 \text{ L mg}^{-1} \text{ m}^{-1}$) suggesting that it should be suitable for treatment by coagulation (Figure 2.12). Surprisingly though only 30% removal of DOC is achievable by coagulating with 10 mg L^{-1} Fe at pH 4.5. Slightly higher removals are achievable by coagulation following MIEX[®] treatment (33%), with a reduced coagulant dose of 1 mg L^{-1} .

Loftsome Bridge has a high alkalinity content ($\sim 250 \text{ mg L}^{-1}$ as CaCO_3) and exhibited some peculiar results when the DOC concentrations were analysed (Table 5.9).

Table 5.9 Organic carbon analysis by standard TOC method (Loftsome Bridge)

	Fe	MIEX [®]	TC	IC	DOC	TC Rem	IC Rem	DOC Rem
	mg L ⁻¹	mL L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	%	%	%
1	0	0	34.16	29.86	4.30			
2	10	0	9.83	6.85	2.99	71.1	77.1	30.5
3	0	20	30.80	29.69	1.11	9.8	10.6	74.1
4	2	20	6.011	3.132	2.88	82.4	89.5	33.0

The DOC removals for sample 3 (MIEX[®] 20 mL L⁻¹) shows a better efficiency than sample 4 (MIEX[®] + Fe). The spurious results can be attributed to the accuracy of the TOC analysis. The manufacturer's specification states a 5% error on both the total carbon (TC) and inorganic carbon (IC). Due to the high values for both TC and IC the combination of these errors gives a range of -1.5 to 5.1 mg L⁻¹ for the MIEX[®] treated water. The use of non purgeable organic carbon (NPOC) as an indicator for the removal efficiency was assessed. With this method the inorganic carbon is purged out prior to detection by acid digestion and nitrogen stripping and should lead to a reduction in the instrument error due to only TC being measured. The results showed that a 60% reduction in the NPOC was observed for a coagulant dose of 10 mg L⁻¹ at pH 4.5. When a coagulant dose of 2 mg L⁻¹ is used following MIEX[®] treatment (20 mL L⁻¹, 30 minutes) a 65% removal efficiency is seen (Table 5.10). Also a SUVA value of 3.46 L mg⁻¹m⁻¹ is observed when NPOC is used for the organic content, indicating the water less suitable for coagulation than was previously thought.

Table 5.10 Organic carbon analysis by NPOC method (Loftsome Bridge)

Fe	MIEX [®]	NPOC	NPOC Removal
mg L ⁻¹	mL L ⁻¹	mg L ⁻¹	%
0	0	5.63	
10	0	1.91	66.1
0	20	2.62	53.5
1.5	20	2.08	63.0

The use of NPOC as a method for determining the effectiveness of a treatment process on high alkalinity waters was shown to have less error associated with its measurement in terms of organic carbon content.

Similarly high UV_{254} removals of 87% were achieved for both coagulation (10 mg L^{-1} as Fe) and MIEX[®] followed by coagulation (1.5 mg L^{-1} as Fe). The HPSEC data for Loftsme Bridge was inconclusive due to its low initial absorbance mentioned previously.

5.3.6.5 *Amlaird WTW*

Amlaird raw water had the highest DOC of any of the waters tested (20.85 mg L^{-1}) and the highest concentration of high to medium MW species (Figure 5.40). Consequently a high dose of coagulant ($>15 \text{ mg L}^{-1}$) was required to achieve a DOC removal of 85%. The effect of treating the water with MIEX[®] prior to coagulation was that for a coagulant dose of 0.5 mg L^{-1} , a DOC removal efficiency of 93% was achievable. Due to the exceptionally high UV_{254} in the raw water 99% removal was achievable by both conventional coagulation and coagulation of MIEX[®] treated water.

However when looking at the HPSEC data for the conventional and MIEX[®] coagulation it can be seen that coagulation alone does not remove all of the material eluting between 8 and 9.5 minutes ($\sim 3000 \text{ Da}$) whereas the MIEX[®] treated coagulation appears to remove all of this material leaving only a low concentration of low MW material eluting at approximately 10 minutes (2000 Da) (Figure 5.44).

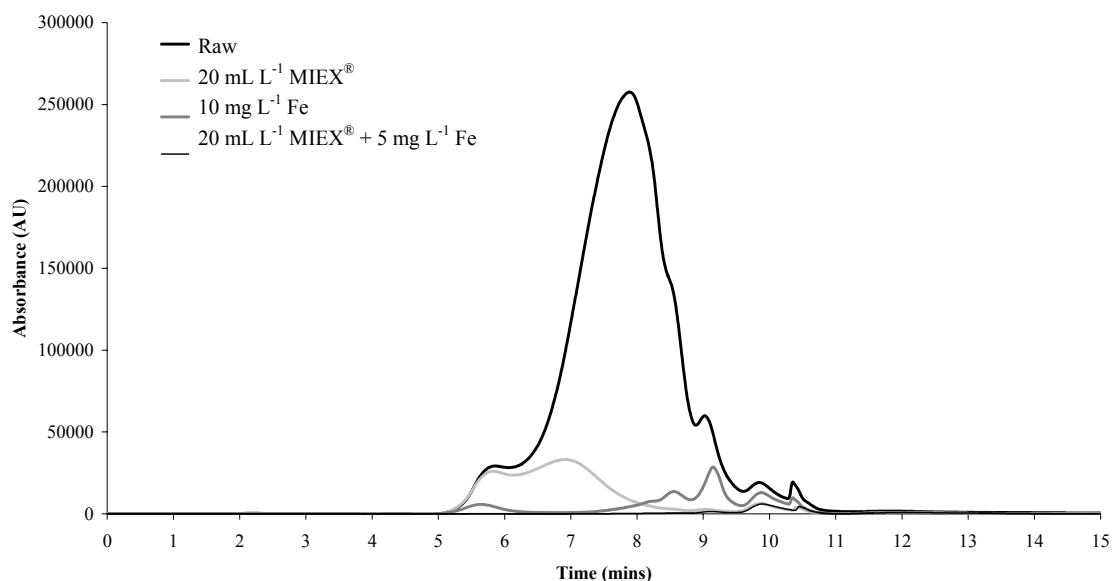


Figure 5.44 Comparison of MIEX[®] and ferric on the removal of UV₂₅₄ found within raw reservoir water (Amlaird)

5.3.7 Summary

A summary of the removal efficiencies for all of the waters studied shows that the combination of MIEX[®] and a reduced coagulant dose improves the DOC removals in all cases. The removal of the UV₂₅₄ is not so effective for MIEX[®] treated water this is because the material that absorbs UV at 254 nm is an indicator for conjugated species and not all DOC absorbs UV at 254 nm. As a result of a lower dose of coagulant being used following MIEX[®] this material is not as well removed although the differences in removal are not significant. All MIEX[®] doses and contact times used in the trials were 20 mL L⁻¹ for 30 minutes (Table 5.11).

Table 5.11 Comparison of the DOC and UV₂₅₄ removals for the studied water sources with conventional and MIEX[®] pre treated coagulation

Water Source	SUVA (L mg ⁻¹ m ⁻¹)	Treatment	Coagulant		DOC Removal (%)	Residual UV ₂₅₄ (m ⁻¹)	UV ₂₅₄ Removal (%)
			Dose (mg L ⁻¹)	Residual DOC (mg L ⁻¹)			
Albert	5.78	Fe	14	0.5	93.9	1.9	96.0
		MIEX [®] +Fe	5	0.6	92.9	1.4	97.0
Bamford	4.31	Fe	15	1.3	83.8	0.3	99.2
		MIEX [®] +Fe	6	1.1	86.9	0.6	98.7
Draycote	2.18	Fe	10	5.2	45.7	9.9	70.9
		MIEX [®] +Fe	2	2.3	75.9	1.2	96.5
Loftsome Bridge	3.46	Fe	10	1.9*	66.0	2.5	87.2
		MIEX [®] +Fe	1.5	2.1*	63.0	2.3	88.2
Amlaird	4.14	Fe	15	3.4	83.8	0.2	100.0
		MIEX [®] +Fe	0.5	1.5	92.8	1.4	98.4

*-Measured as NPOC

The data also shows that conventional coagulation as expected achieves better removals for water that have high SUVA values ($> 4 \text{ L mg}^{-1} \text{ m}^{-1}$) and that have high raw water DOC concentration ($> 8 \text{ mg L}^{-1}$). Draycote has a low SUVA ($2.18 \text{ L mg}^{-1} \text{ m}^{-1}$) and is consequently more difficult to treat with coagulation alone. This may be explained by coagulation acting as a charge neutralisation/complexation process at low pHs and hydrophilic waters are usually less charged than hydrophobic waters making this process limited (Sharp *et al.*, 2004). The pre treatment with MIEX[®] almost doubles the DOC removal efficiency.

Here an attempt to correlate optimum DOC removal achieved for the different waters against their raw water SUVA values is shown. The data shows that treating water with coagulant only is more efficient if the raw water SUVA is high. The treatment of waters with MIEX[®] followed by coagulation shows that good removals are achieved from waters with low as well as high SUVA values (Figure 5.45).

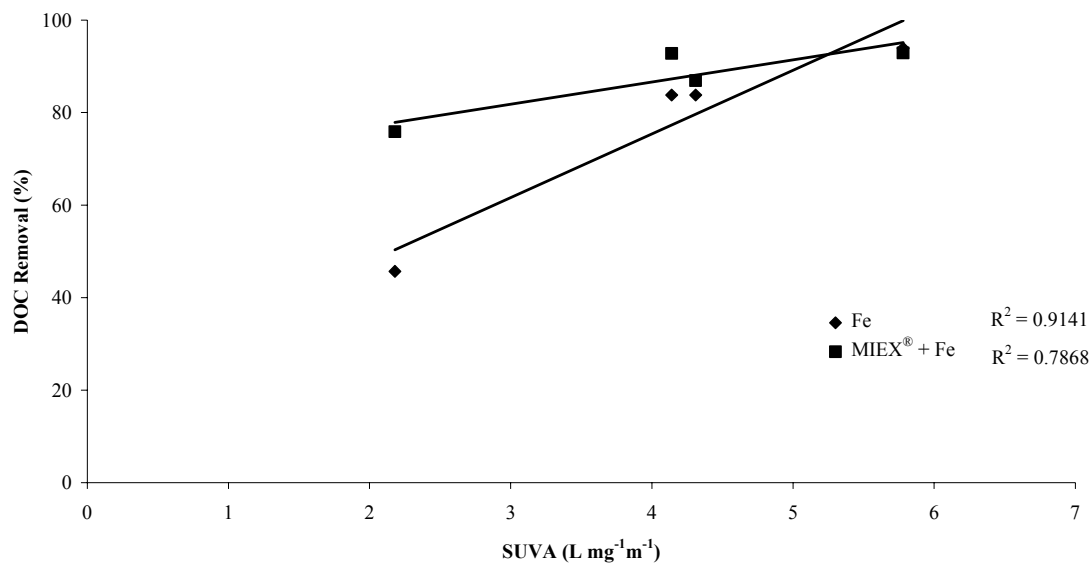


Figure 5.45 DOC vs. SUVA correlation for waters treated by conventional and MIEX[®] pre treated coagulation

From the analysis of the data it can be concluded that the MIEX[®] plus coagulant process appears to be more effective for the treatment of low SUVA raw water sources and hence indicates that a greater reduction in the more hydrophilic material is seen than when conventional coagulation is used. A similar relationship is shown for the data shown in the literature review (Table 2.10) in that the combination of MIEX[®] and coagulation achieves higher DOC removal efficiencies for low SUVA waters. However this data also shows that higher removals are seen for the waters with higher SUVA values (i.e. hydrophobic) although the removals observed are not as high for those seen with by the treatment of alum and a combination of MIEX[®] and alum (Figure 5.46).

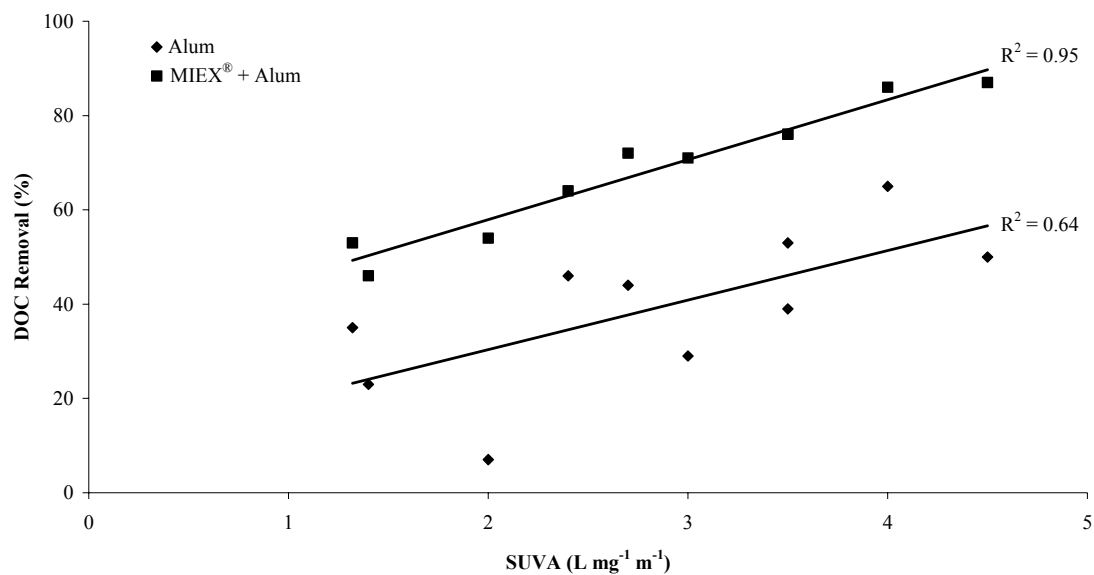


Figure 5.46 DOC vs. SUVA correlation for waters treated by conventional and MIEX[®] pre treated coagulation (Singer and Bilyk, 2002; Drikas *et al.*, 2003; Drikas *et al.*, 2003b)

The use of MIEX[®] as a pre treatment prior to coagulation can be seen as a very robust option for the treatment of humic rich waters. The advantages of its use are the reduction in costs for both coagulant purchase and sludge disposal. Also the variations in the water quality from seasonal changes and geographical location appear to have little effect in the efficacy of the process.

5.4 Adsorption

5.4.1 Introduction

Adsorption is already extensively used in the treatment of water as a tertiary or polishing process to remove trace organic pollutants such as pesticides (Nowack *et al.*, 1999). The two major adsorption mechanisms are size exclusion and electrostatic interactions, which are important in order to understand how the process can be optimised for the removal of NOM. The relationship between the size of the NOM and the pore size of the granular activated carbon (GAC) dictates that NOM compounds of similar size to the pore size are more likely to adsorb as there will be more contact points between the adsorbate and the pore. Therefore smaller low MW fractions will be preferentially removed by GAC (Newcombe *et al.*, 1997). Adsorption isotherms are generally used to model the efficiency of an adsorbent to a pollutant and therefore aid the design of the adsorbers for full scale use. The Freundlich isotherm is an empirical expression and is only valid when adsorption is purely physical. It assumes there is no change in the speciation of the NOM molecule and does not account for heterogeneity in the adsorption sites that have different energies of adsorption. An adaptation of the Freundlich isotherm was prepared in which the uptake is plotted as a function of the non adsorbed NOM per unit adsorbent mass. This model has been used by several researchers for the analysis of NOM adsorption from water and is described by Equation 5.2 (Karanfil *et al.*, 1999; Summers and Roberts, 1998; Harrington and DiGiano, 1989).

$$q_e = K_f (C_e / D_0)^n \quad (5.2)$$

q_e is the amount adsorbed (normalised to adsorbent mass), C_e is the solution concentration, D_0 is the mass of adsorbent used, K_f is the Freundlich number and

indicates the adsorbents adsorption capacity and n is related to the size of the adsorption force and the distribution of the energy sites on the adsorbent.

A linearised equation (Equation 5.3) enables the constants to be calculated from a plot of $\log C_e/D_0$ against $\log q_e$ with the y-intercept being $\log K_f$ and $1/n$ being the gradient.

$$\log q_e = \log K_f + \frac{1}{n} \log(C_e / D_0) \quad (5.3)$$

The n and K_f constants can be used to calculate the maximum amount of adsorbate that will be adsorbed per unit mass of adsorbent from a solution.

Here a range of adsorbents including metal hydroxides, carbons and clays were tested to determine their DOC and UV_{254} removal efficiencies and consequently their usefulness as a post coagulant treatment for the removal of the lower MW, recalcitrant fractions i.e. the HPI-NA fraction. The main properties of the adsorbents used are shown in Table 5.12.

Table 5.12 Adsorbent properties

Adsorbent	Particle Size (μm)	Surface Area ($\text{m}^2 \text{g}^{-1}$)	Reference
β -FeOOH	320-2000	18-292	Genz and Jekel, 2004
Activated Alumina	3-5	300	www.saiadsorbents.com
Activated Carbon	25	≤ 2500	www.cee.vt.edu
XAD-4	490-690	>750	www.rohmhaas.com
XAD-8	560-710	>380	www.rohmhaas.com
Kaolin	7	5-20	wvlc.uwaterloo.ca
Earths	~ 10	100-180	www.worldminerals.com

The surface areas of the main adsorbents, evaluated by nitrogen adsorption, ranged from 10 to $2000 \text{ m}^2 \text{ g}^{-1}$ and the particle size from 7 to $2000 \mu\text{m}$. The adsorbents with the

larger surface area to unit particle size ratio should be the most effective adsorbents, however pore size and nature of each adsorbent will dictate which is the most effective for the removal of NOM.

5.4.2 Bulk Removal

Initially the modified isotherms for the activated carbons (AC), resins and oxide adsorbents was determined and the results shown in Figure 5.47. Interpretation of the isotherms can provide some important information on the suitability of an adsorbent on a particular system. In particular:

- the fact that the carbon isotherms are not a straight line indicates that the water could contain multiple types of adsorbates which is expected in raw water;
- the downward slopes on the lines obtained for the isotherms of the resins and oxides indicate that there is material present in the system that is non-adsorbable by the particular adsorbent. The carbons do not exhibit this trend and are therefore suitable for adsorption for all components present in the raw water; and finally
- where the isotherms cross can help in the adsorbent choice and whether a batch or column system would be more suitable. For instance beyond the point on the graph indicated by ♦ the oxide has the greater capacity and below this point the carbon has the higher capacity. Consequently carbons would be preferable in column operation due to its higher capacity at influent concentration and oxides would be more suited to batch treatment.

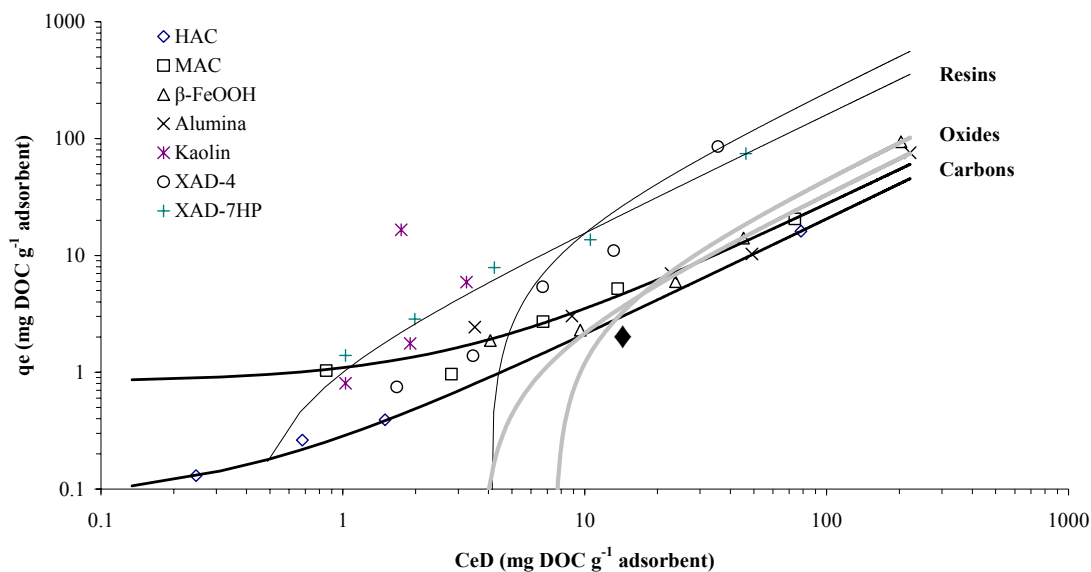


Figure 5.47 Modified Freundlich isotherms for selected adsorbents on the adsorption of Albert raw water (April 2002)

Further trials of DOC and UV_{254} removals efficiencies of all the adsorbents are compared in Figure 5.50. Here the AC proved to be the most effective giving greater than 85% DOC removal followed by the activated alumina (AA) and β -FeOOH which gave over 80% removal. The diatomaceous earths proved to be less successful for bulk organic removals with DOC removal ranging from 10-30% with the exception of Microcel T49 which achieved approximately 50% DOC removal. The XAD resins, which are specifically used for the fractionation of NOM, and kaolin achieved DOC removals between 50 and 70% (Figure 5.48).

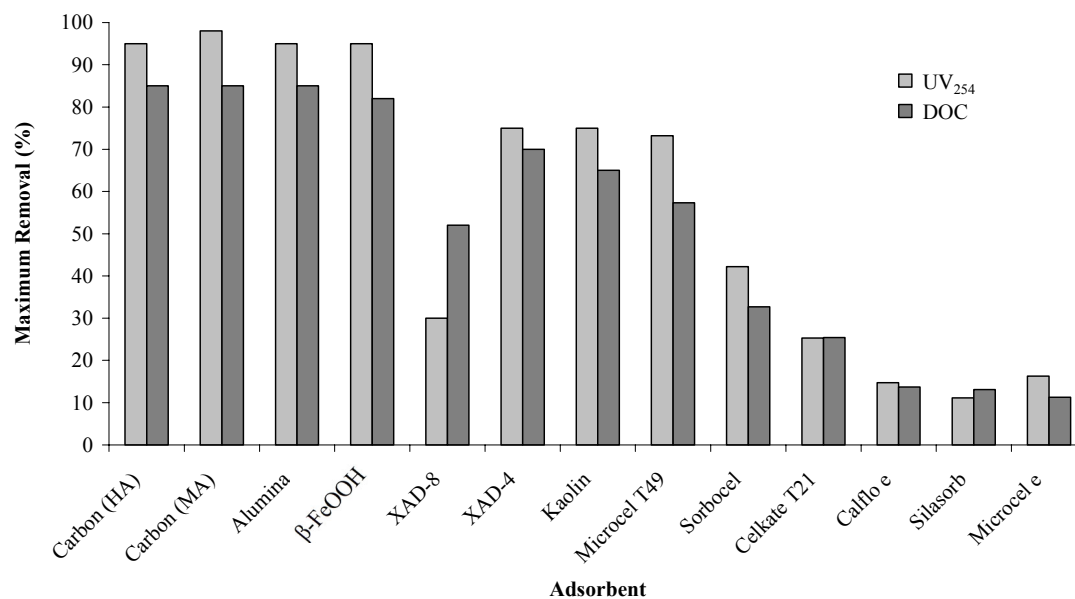


Figure 5.48 Maximum DOC and UV₂₅₄ removals of raw water using all adsorbents

Applying a Freundlich isotherm to the data allows a comparison of each adsorbent's Q_{\max} , K_f and n^{-1} values. The AC, AA and β -FeOOH all have Q_{\max} values in excess of 100 mg DOC g⁻¹; with the alumina and β -FeOOH having an adsorption capacity of 221 and 103 mg DOC g⁻¹ respectively. This would indicate their potential suitability for the treatment of NOM. The kaolin and XAD resins have Q_{\max} values between 35 and 60 mg DOC g⁻¹ but the diatomaceous earths all have Q_{\max} values less than 20 mg DOC g⁻¹, implying that their efficiency for removal of NOM is relatively low. A Freundlich isotherm plot of β -FeOOH and high activity carbon (HAC) on Albert raw water compared to published data on the adsorption of commercial humic acid, fulvic acid and a wood based carbon on a raw water source of 15 mg L⁻¹ DOC is shown (Figure 5.49). The isotherms produced here are similar although the K_f is lower here than found by Karanfil *et al.*, (1999) which is likely to be due to the type and range of organics in each water (Karanfil *et al.*, 1999).

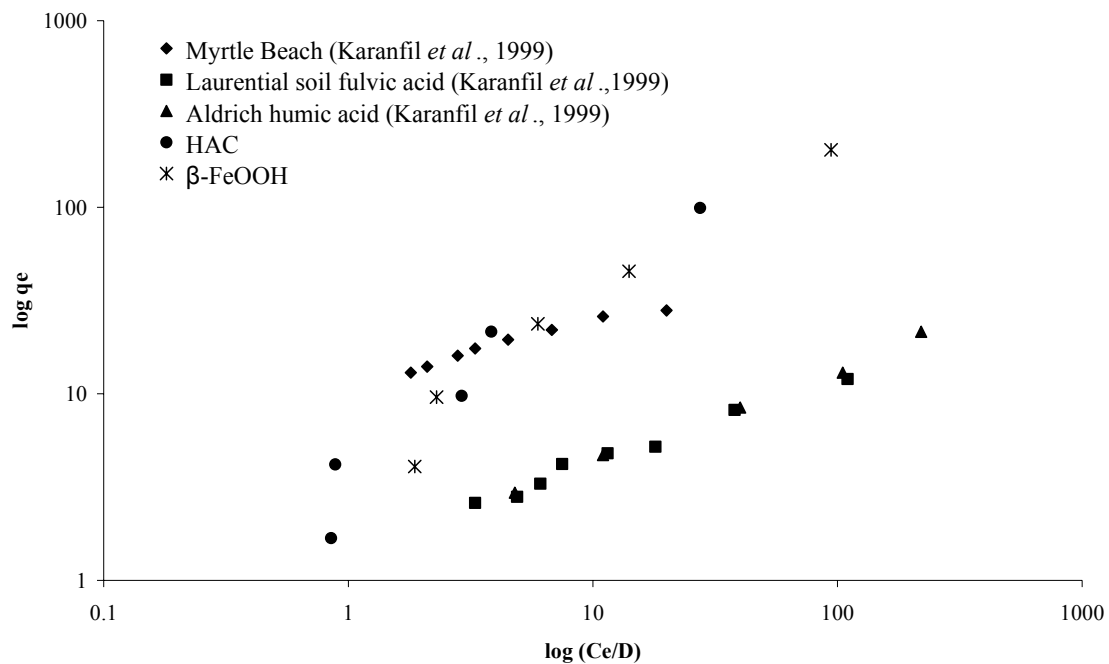


Figure 5.49 Adsorption of natural water by HAC and β -FeOOH compared to published data

Using size exclusion chromatography it is possible to fingerprint the MW profile NOM. Here we have assessed the UV_{254} removals of the 3 different MW ranges. The MW ranges are described as MW1 = >5000 Da, MW2 = 2000-5000 Da and MW3 = <2000 Da. Once again the AA, β -FeOOH and HAC achieve significant removals of all 3 MW ranges as does the XAD-8 resin. In NOM fractionation XAD-8 is used for the removal of hydrophobic material which generally has the greatest UV absorbance at 254 nm of any fraction. The remaining hydrophilic material is weakly observed by UV absorbance due to its lack of conjugated bonds which absorb at 254 nm. The kaolin performs well for the removal of the high and medium MW material (100 and 79% respectively) but is poor for the low MW material (0%). The diatomaceous earths generally provide the best UV_{254} removal of the high MW material only, with 5 of the adsorbents giving no removal for both the mid and low MW range. On the basis of bulk removals the

diatomaceous earths were excluded from any experiments on fractionated material due to their low capacity (Table 5.13).

Table 5.13 Freundlich data and HPSEC removal data

Adsorbent	pH	K_f (mg DOC g ⁻¹) ¹⁻ⁿ	n^{-1}	Q_{max} mg DOC g ⁻¹	UV ₂₅₄ Removal (%)		
					MW1	MW2	MW3
β-FeOOH	7	3.48	0.95	203.00	99.5	98.0	85.7
AA	7	1.53	1.20	221.41	98.9	96.8	37.8
HAC	7	2.73	1.14	99.25	99.4	99.7	88.7
MAC	7	1.41	1.45	105.52	99.8	99.5	89.5
XAD-8	4	7.40	0.63	46.42	56.8	84.1	32.6
XAD-4	4	3.85	0.64	35.55	55.7	47.4	0.0
Kaolin	7	2.03	0.77	58.37	99.5	78.8	0.0
Calflo e	7	8.98	1.01	14.00	78.6	0.0	0.0
Silasorb	7	12.59	0.68	2.84	74.9	0.0	0.0
Celkate T21	7	5.23	1.00	4.32	70.3	0.0	0.2
Microcel e	7	15.60	1.25	3.02	55.4	43.3	0.0
Sorbocel	7	5.55	1.00	17.50	99.8	57.0	13.0
Microcel T49	7	2.50	0.45	12.50	69.3	3.4	19.3

MW1->5000Da : MW2-2000-5000Da : MW3-<2000Da

5.4.3 Fraction Removal

Here the Freundlich isotherms for the adsorption of HPI-A, HPI-NA and Albert raw water on to AC is compared. It has been previously shown that Albert raw water is predominantly made up of hydrophobic material and the raw water is therefore analogous to the hydrophobic compounds. The isotherm for the adsorption of raw water on to AC again shows that there is more than one component present. Isotherm data for the HPI-A and HPI-NA fractions exhibit relatively straight lines indicating a one component system, this however is unlikely and the components of each fraction may exhibit similar adsorptive characteristics. From these two isotherms the relative efficiency (RE) of carbon on the two systems can be calculated. At C_0 (10 mg g⁻¹) the loading (q_e) at influent concentration of the HPI-A fraction is 6.2 mg DOC g⁻¹ carbon

and the loading of the HPI-NA fraction is $10.1 \text{ mg DOC g}^{-1}$. This gives an RE of HPI-A with respect to HPI-NA of 61%. As seen previously HPI-NA has the lowest MW profile of the isolated fractions (Figure 5.5) and will therefore be more amenable to adsorption into the active pores (Figure 5.50).

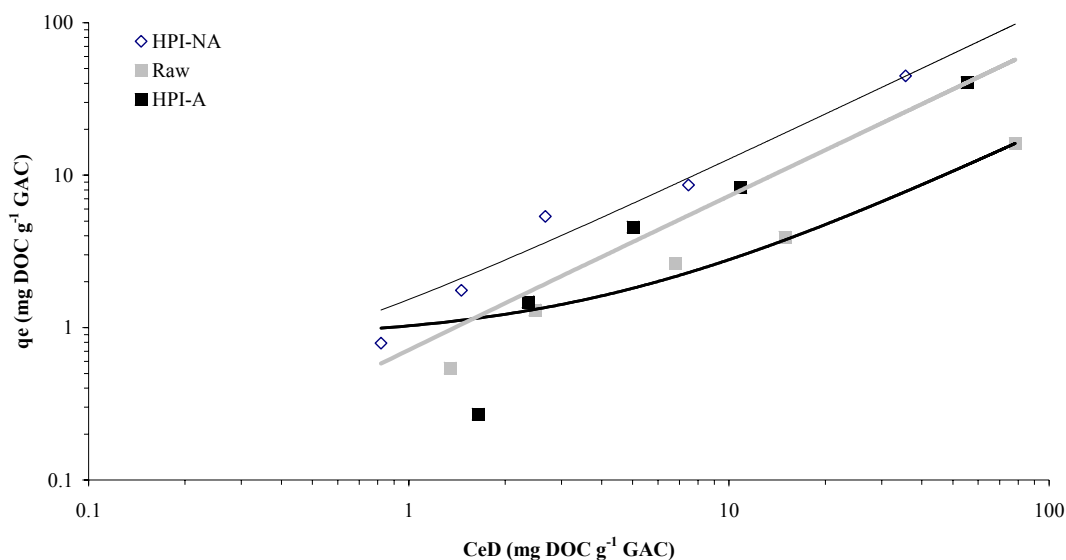


Figure 5.50 Comparison of the adsorptive abilities of carbon on different fractions

It has been previously shown that conventional treatment of NOM typically coagulation with metal salts is effective for the removal of UV_{254} for high and mid MW ranges, however the lower MW range material is left largely untouched (Figure 5.10). The HPSEC chromatograms for 4 of the adsorbents shows that the XAD-4 resin is only really effective for the mid MW range compounds and the AA is not so effective for the small MW range material (Figure 5.51). The β -FeOOH achieves good removals over the whole range of NOM and high activity carbon provides significant removal efficiencies over the whole MW profile.

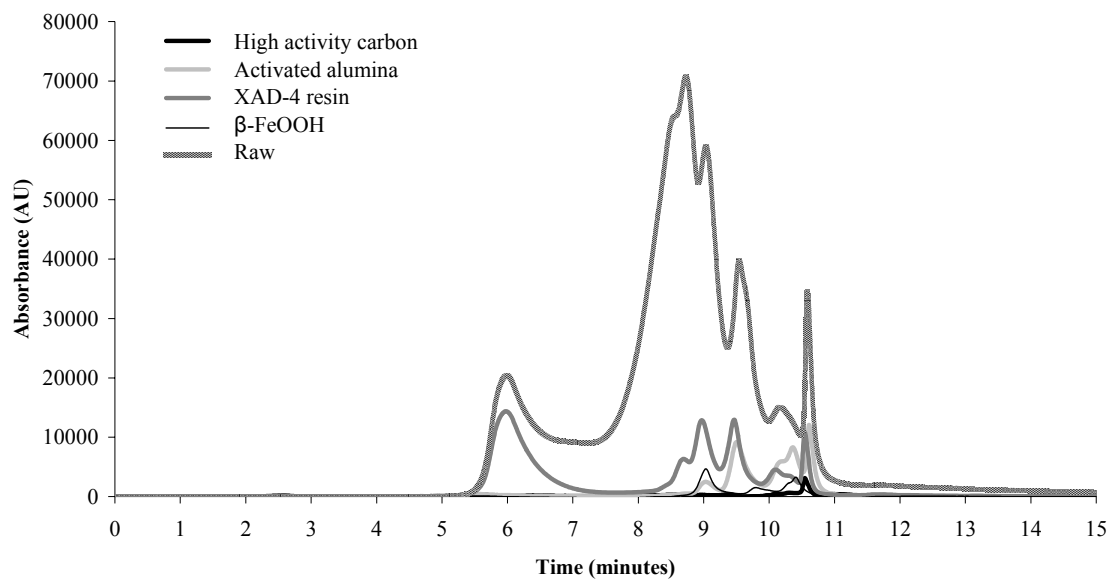


Figure 5.51 HPSEC chromatograms of maximum removals from a range of adsorbents on Albert raw water (April 2002)

Other researchers have shown the hydrophilic non charged fractions to be the most recalcitrant when treating NOM rich waters (Bolto *et al.*, 1999; Croué *et al.*, 1993; Marhaba and Pipada, 2000). HPI-NA is typical of the NOM found in coagulated waters and with this in mind the remaining adsorbents were evaluated on the filtered HPI-NA fraction isolated from Albert. The initial removal efficiencies show that once again AC is the most effective adsorbent, however all the other adsorbents with the exception of kaolin provide a 50% reduction in the DOC concentration (Figure 5.52).

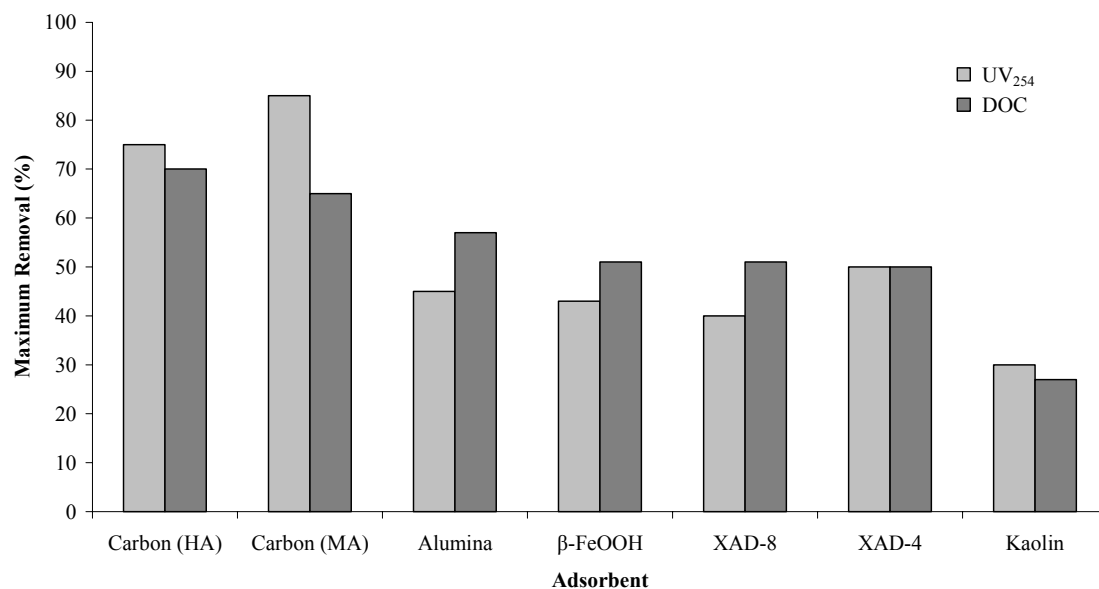


Figure 5.52 Maximum DOC and UV₂₅₄ removals for HPI-NA fraction

As the HPI-NA fraction has no or very little charge associated with it the mechanism for removal is likely to be size exclusion rather than electrostatic interaction which is probably due to the smaller MW range of the HPI-NA (Edzwald, 1993; Sharp *et al.*, 2004).

5.4.4 Summary

The bulk removal of NOM by the adsorbents evaluated showed that the AC, β-FeOOH and AA provided the best results and had the highest adsorption capacities. The remaining adsorbents provided reasonable removals for selected MW ranges but were not as effective over the whole range of MWs. The results for the NOM fraction removal shows that adsorption of the more recalcitrant fractions i.e. HPI-NA is achievable by dosing a range of different adsorbents. AC has proved to be the most efficient with up to 70% of the DOC being removed. However it can be expensive especially if the active sites become rapidly saturated leading to shortened lifetimes

between regenerations. β -FeOOH and AA achieve approximately 50% DOC removals and could be considered as a post coagulation treatment to be used during times when the water is more difficult to treat. These are lower cost adsorbents and suitable as a filter process or as a disposable adsorbent similar to the process used for addition of PAC. The theoretical adsorbent usage required to treat the HPI-A and HPI-NA fraction can be calculated from the influent concentration divided by the loading per unit weight of adsorbent at influent concentration. In the case of HPI-A this would be 0.62 g L^{-1} and 1.01 g L^{-1} for HPI-NA.

5.5 Comparison of process options

5.5.1 Introduction

The findings of the research presented previously (staged coagulation, MIEX[®] and adsorption) resulted in three processes being examined in detail. In this section the performance of the treatment processes are compared against each other in order that a more robust treatment process could be proposed for high organic waters.

5.5.2 Bulk Removal

In terms of DOC removal, there is very little difference in the removal efficiencies for each process, with only slight increases observed for the combination of MIEX[®] and coagulation, β -FeOOH and AC (Figure 5.53a).

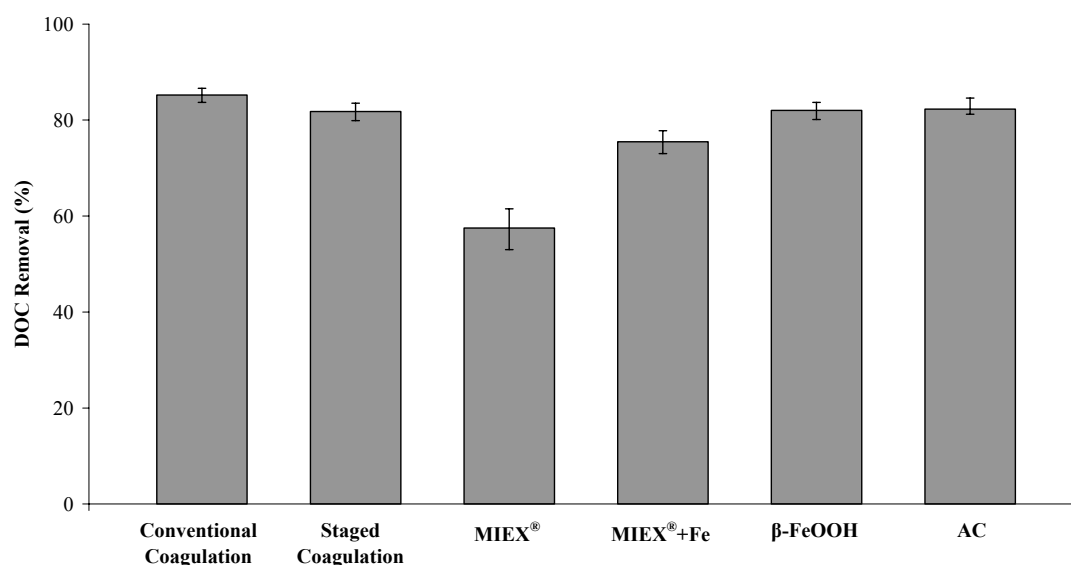


Figure 5.53a Comparison of the evaluated processes for the removal of DOC

Similarly in terms of UV_{254} removal, no process performs significantly better than another. This is as expected as the removal of UV_{254} absorbing material such as HAF and FAF is amenable to conventional processes such as coagulation probably due to its

higher charge density and is hence not considered to be as refractory compared to organics that do not absorb UV_{254} such as HPI-A and HPI-NA (Figure 5.53b).

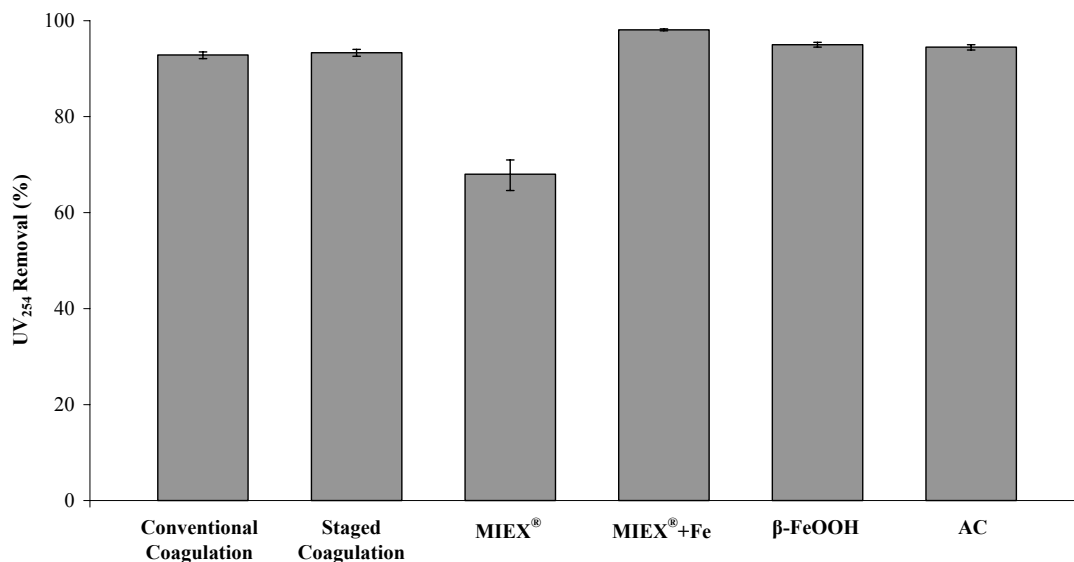


Figure 5.53b Comparison of the evaluated processes for the removal of UV_{254}

The effect of the treatment processes on the removal THMs and residual THMs is more significant. For all the processes in excess of 60% is achieved for each process, with the combination of MIEX[®] and coagulation and the adsorption onto β -FeOOH and AC achieving greater than 80% THM removal (Figure 5.53c).

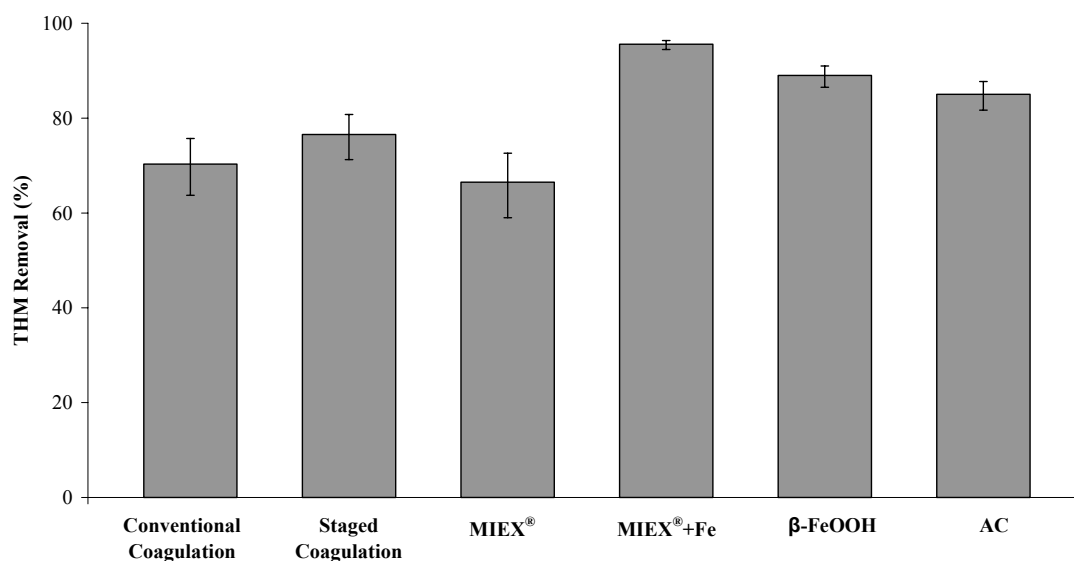


Figure 5.53c Comparison of the evaluated processes for the removal of THMs

Whilst the THM measurements have not been undertaken on a single water sample, we have taken the removal efficiencies from Figure 5.53c and applied them to the raw water of January 2004 (Figure 5.53d), which had a raw THM value of $632.3 \mu\text{g L}^{-1}$. It can be seen that the conventional, staged and MIEX[®] alone failed to meet the current UK THM regulations of $100 \mu\text{g L}^{-1}$. (These values are absolute values calculated on ensuring free chlorine remains in the water following the 7 day chlorination). The combination of MIEX[®] and coagulation and adsorption with $\beta\text{-FeOOH}$ and AC all easily meet the current regulations and will be more likely to comply with future UK regulations (Figure 5.53d).

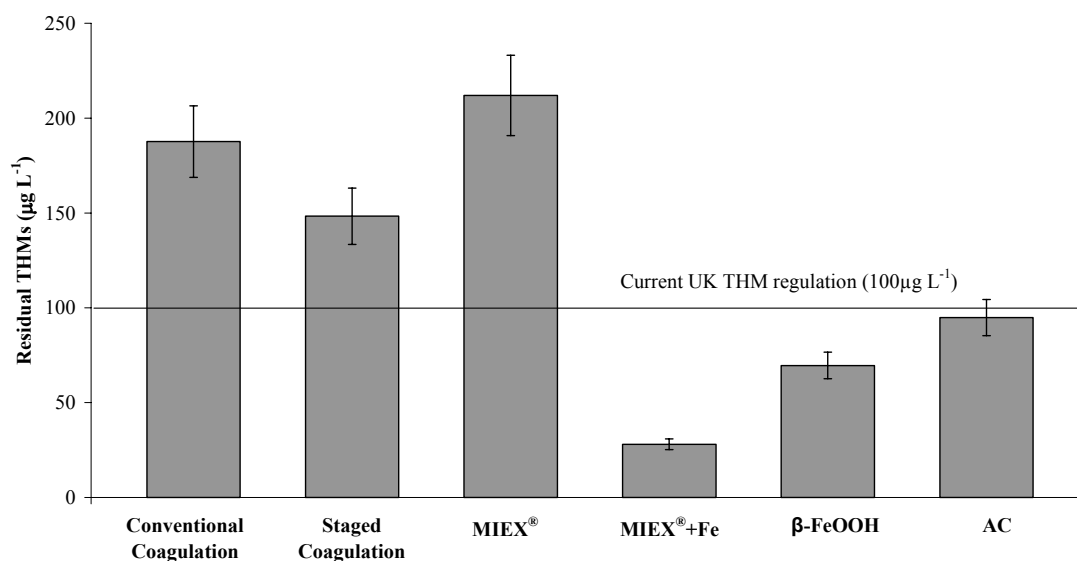


Figure 5.53d Predicted residual THMs of the treated water assuming a raw water THM of $632.3 \mu\text{g L}^{-1}$ (THM of raw Albert water in January 2004)

5.5.3 Seasonal effects

Albert raw water is susceptible to seasonal changes in character and load which leads to difficulties in treating the water and meeting THM regulations. Here the predicted residual THMs following treatment by each of the proposed processes were calculated again assuming the THM removals shown in Figure 5.53c. Conventional coagulation, staged coagulation and MIEX[®] treatment lead to high residual THMs for all the waters treated and appear to be especially susceptible to the times when the organic levels was particularly high (January and November 2000 and April 2002). The adsorbents are an effective treatment process for all months predicted with the exception of January and November 2000 when the residual THMs are on the limit of the $100 \mu\text{g L}^{-1}$ standard. Of the options the MIEX[®] plus coagulation option is the most robust process and copes with periods of high THMFP in the raw water and the residual THMs seen range from $20 \mu\text{g L}^{-1}$ in June 2000 to a maximum of $40 \mu\text{g L}^{-1}$ in November 2000.

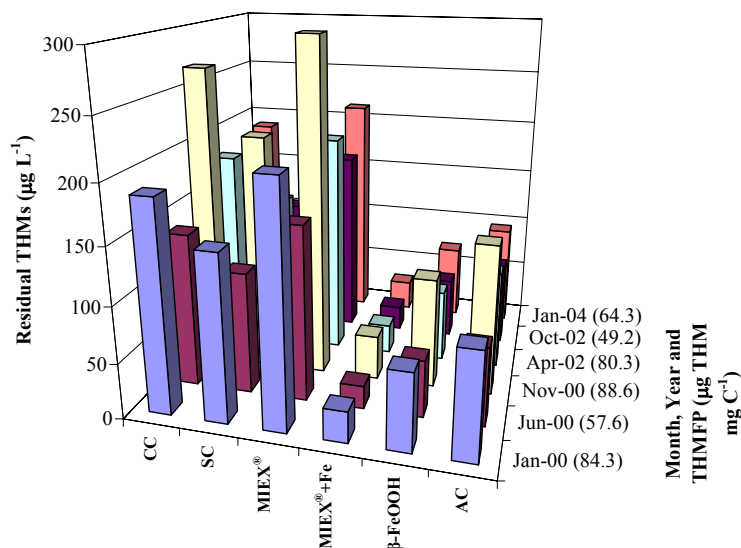


Figure 5.54 Predicted residual THMs for proposed processes and their effect on seasonal changes (cc-conventional coagulation, sc-staged coagulation)

5.5.4 Size removal

The next parameter to be considered is the performance of the processes over three defined MW ranges. Ferric coagulation is highly effective for the removal of high (> 5000 Da) and mid (2000 – 5000 Da) MW ranges (100% for both) and less effective for the removal of the low (< 2000 Da) MW material (~50%). Staged coagulation showed no improvement in the UV₂₅₄ removal of the bulk water compared to conventional coagulation and as HPSEC is determined by UV₂₅₄ absorbance MW removals was not measured. The low MW material is the major component of the HPI-NA fraction, which is the largest fraction in the treated water and is the most recalcitrant fraction to treatment (Bolto *et al.*, 1999; Croué *et al.*, 1993) and can also be highly reactive in terms of THMFP (Goslan *et al.*, 2002). Therefore the removal of the low MW material is important in the control of THMs for a WTW. The use of MIEX[®] alone for the treatment of Albert raw water showed that there was no removal of the high MW material but ~95% removal of the mid MW compounds and 65% removal of the low

MW material. With this in mind the combination of MIEX[®] and coagulation would in theory be an effective overall treatment solution for this water and as expected the results showed that there was excellent removals (>97%) for both the high and mid MW material and ~70% for the low MW material. Both β -FeOOH and AC proved to be effective for the removal of the high and mid MW ranges (~100% for both) and gave the best overall removal (86% and 94% respectively) of the low MW compounds (Figure 5.55). (As stated previously the MW distribution is determined by the elution of UV₂₅₄ absorbing material and does not take into account DOC, hence the use of MW data can not be used for absolute removals of organics and is the reason why higher removals are seen here compared to those seen for DOC and THMs.)

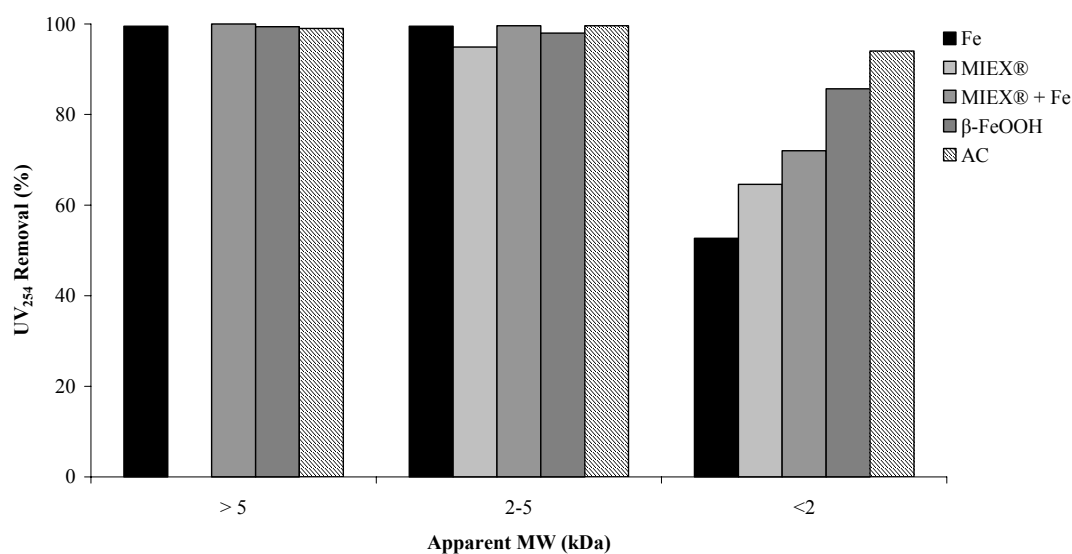


Figure 5.55 Comparison of removal efficiencies by the trialed processes on three defined MW ranges

5.5.5 Fraction removal

Finally the treatment processes were compared on the basis of DOC removal for the four isolated fractions (HAF, FAF, HPI-A and HPI-NA). UV₂₅₄ removal is not

considered here as the hydrophilic fractions have very low UV_{254} absorbance. Compared to conventional coagulation, staged coagulation achieves considerably higher removals for all the isolated fractions and in particular the hydrophilic fractions. Whilst removals with MIEX[®] are comparable to those achieved with conventional coagulation. The removal of HAF is less effective due to its high proportion of high MW material (> 5000 Da). The effect of the two adsorbents on the fractions was only determined for the hydrophilic fractions. The removals observed for HPI-A and HPI-NA with β -FeOOH are approximately 55% and 57% respectively, whilst the removals with AC are approximately 58% and 70% respectively. Conventional coagulation affords relatively low removals of the hydrophilic fractions (HPI-A and HPI-NA) compared to both staged coagulation and AC. However the removal efficiencies shown here are based on the removal of the individual fraction and does not take into account any synergistic effects that may be present in the unfractionated water (Figure 5.56).

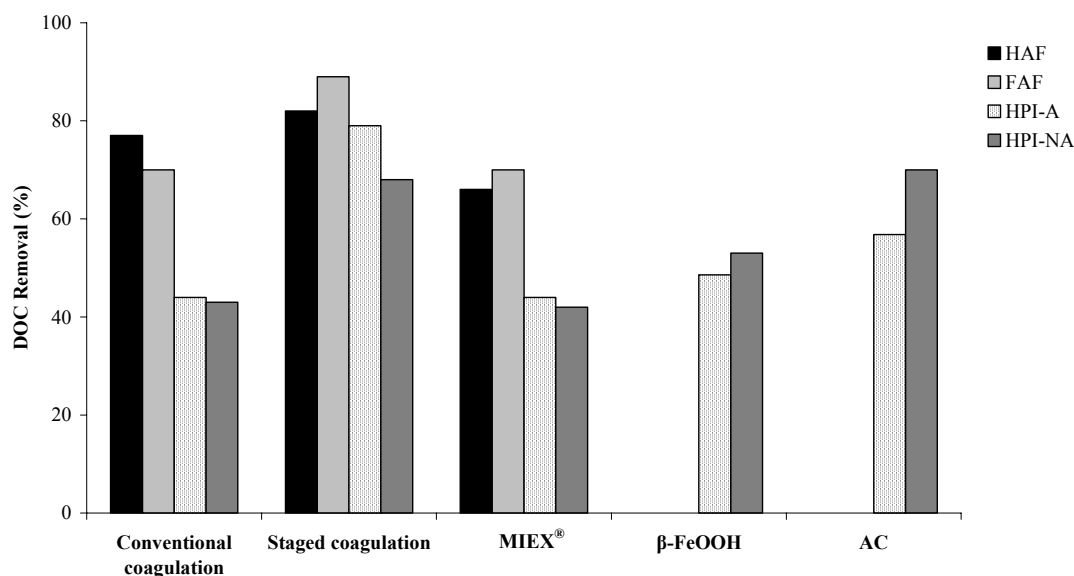


Figure 5.56 Comparison of the DOC removals for HAF, FAF, HPI-A and HPI-NA by the trialled processes

5.5.6 Summary

The effectiveness of the processes researched here compared to conventional ferric coagulation for the removal of bulk DOC, fractions and defined MW ranges is summarised in Table 5.14. If the water contains mainly high MW and hydrophobic material then it will be successfully treated by ferric coagulation. FAF though is an important contributor to the final THMFP and its removal needs to be maximised in order that the UK THM legislation is not breached. Conventional coagulation as seen earlier does not treat the low MW or HPI-NA fraction effectively; the use of MIEX[®] or adsorbents effectively removes this fraction which can also make a considerable contribution to the THMFP of the final water. The grounds by which the comparisons were made were based on removals of the parameter measured (DOC for bulk, HAF, FAF, HPI-A and HPI-NA, UV₂₅₄ for MW1, 2 and 3 and THM for THMs).

Table 5.14 Comparison of process effectiveness

Process	Bulk	MW1	MW2	MW3	HAF	FAF	HPI-A	HPI-NA	THMs
Fe coagulation	++	+++	+++	+	++	++	+	+	+
Staged coagulation	++	nt	nt	nt	++	+++	++	++	++
MIEX [®]	+	+	+++	++	++	++	+	+	+
MIEX [®] + Fe	++	+++	+++	++	nt	nt	nt	nt	+++
β-FeOOH	++	+++	+++	++	nt	nt	+	+	++
AC	++	+++	+++	+++	nt	nt	+	++	++

(+ = <65% removal; ++ = 65 – 90% removal and +++ = >90% removal)

MW1->5 kDa; MW2-2-5 kDa; MW3-<2 kDa

nt-not tested

All the proposed processes achieved a rating higher than that for conventional coagulation with the exception of MIEX[®] alone, which would never normally be used

without a post treatment as MIEX[®] was only designed for the treatment of DOC and not turbidity. The AC process is the most effective process, but likely to be expensive and therefore only suitable when the coagulated water had a high THMFP. The use of β -FeOOH is also questionable due to the high doses required to treat the water (2.5 g L⁻¹). It would therefore appear that staged coagulation or a combination of MIEX[®] with a reduced coagulant dose would be the most favourable. The particular process used would then depend on the driver forcing the WTW to adapt. The staged coagulation offers a possibility of improved filterability of the flocs formed whilst affording a slight increase in the reduction of THMs. MIEX[®] plus coagulation on the other hand reduces the THMs significantly and is particularly robust to variations in the raw water.

In addition to identifying treatment options in this thesis a comparison of each of the processes was made and a rating of each process was made by saying whether each process afforded better, worse or the same removal compared to conventional coagulation for each parameter (Table 5.15). The MIEX[®] treatment alone was not compared as it is not a likely option on its own and would always be used with a turbidity removal process such as coagulation or microfiltration.

Table 5.15 Comparative rating for each proposed process

Process	Parameter		
	DOC	UV ₂₅₄	THMs
Staged coagulation	same	same	better
MIEX [®] + Fe	same	same	better
β -FeOOH	same	same	better
AC	same	same	better

The implications of applying any of the proposed processes to WTW will result in an annual reduction or increase of chemical usage. There will also be cost implications of retrofitting any of the processes. Here the estimated reduction in coagulant and/or increase in other material have been assessed (Table 5.16). The assessment was based on the following assumptions:

- inlet flow rate = 40000 m³ d⁻¹;
- inlet DOC = 10 mg L⁻¹;
- conventional coagulant dose = 10 mg L⁻¹ as Fe;
- DOC removal by conventional coagulation = 85%; and
- loading rates for β -FeOOH and AC = 200 mg DOC g⁻¹ and 100 mg DOC g⁻¹ respectively.

Table 5.16 Additional chemical and equipment requirements for proposed processes

Treatment Process	Coagulant usage (tonnes yr ⁻¹)	Additional chemicals (tonnes yr ⁻¹)	Additional equipment
Conventional coagulation	1080	-	-
Staged coagulation	1080	-	1 flash mixer
MIEX [®] + Fe	541	500 m ³ yr ⁻¹	MIEX [®] plant, MIEX [®] resin replacement costs, concentrated NOM disposal
β -FeOOH	1080	110	Contactors and clarifier
AC	1080	219	Contactors and clarifier

5.5.6.1 Bulk vs. fractions

The isolation of the hydrophobic (HAF and FAF) and hydrophilic (HPI-A and HPI-NA) material has been found to be beneficial when optimising treatment. Fractionation allows the parts of the organics that are most reactive to chlorine and therefore the

drivers for the formation of THMs in the treated water to be identified. This in turn allows treatment processes to be tailored for the removal of these fractions and hence improve the overall quality of the treated water. For Albert raw water, FAF and HPI-NA have been seen to be particularly reactive with chlorine and as such need to be specifically targeted. By using a combination of MIEX[®] and coagulation or a post coagulation adsorption process the concentration of the HPI-NA and hence the reactivity of the treated water could be reduced. However the downsides of fractionation are that the methodology used is slow (1 month) and is not a realistic method for WTW operators to use as a rapid analysis. Determination of the MW distribution by HPSEC analysis is a significantly more rapid method (30 minutes) that could easily be determined and can give the operators useful information in terms of the removal of specific MW ranges. However as previously stated only UV₂₅₄ absorbing compounds are detected and many hydrophilic compounds are not UV₂₅₄ active. However the combination of MW distribution and fractionation carried out periodically combined with bulk water parameters can enable an operator to determine when the water quality is deteriorating and make any necessary treatment changes.

6 Conclusions

6.1 Introduction

Determining the removal of NOM from humic rich waters has generally relied on the measurement of bulk parameters as an indicator of the effectiveness of the treatment process. This has led to many WTWs failing to meet regulations for the concentration of THMs in the final water even though bulk parameters such as colour are reduced significantly. Literature has shown that isolation of the NOM into hydrophobic and hydrophilic material can help identify the parts of the water that are more reactive to treatment with chlorine. Similarly a rapid separation technique (HPSEC) can split the NOM into MW ranges which can also be linked to DBP formation. A study of the literature showed that whilst many researchers had optimised treatment processes on these bulk parameters few had used separation techniques to determine their effectiveness. Also most research has focussed on the treatment of different water sources to give a wide range of results. Here a combination of bulk, fraction and MW range parameters were used on the same water during different times of the year and water sources with differing characteristics in order that existing processes and new treatments can be used for the removal of the THM precursors. This led to three treatment processes being proposed for the treatment of NOM which were optimised on bulk, fraction and size parameters.

6.2 Bulk water removal

The removal of DOC, UV₂₅₄ and THMs from raw Albert water showed that varying successes were achieved for the trialled processes (Section 5.2.2). MIEX[®] combined with ferric coagulation significantly reduced the loading demand for the coagulant

leading to a reduction in the coagulant required. This was coupled with a significant reduction in the residual THMs. The adsorbent trials showed that a polishing stage, post coagulation, could remove more of the hydrophilic material which has been seen to have a high THMFP during the autumn (Goslan *et al.*, 2002).

6.3 Seasonal effects

The changes in bulk and fraction parameters during different times of the year have been documented (Goslan *et al.*, 2002). The effect of these changing parameters on the treatability of the water has caused THM regulations to be breached. Here the processes evaluated provided a more robust treatment option. In particular the use of MIEX[®] combined with ferric coagulation appeared to be insensitive to variations in the quality of the raw water.

6.4 Effect of catchment on treatment with a combination of MIEX[®] and coagulation

MIEX[®] followed by ferric coagulation was trialled on a number of different water sources with varying bulk parameters such as DOC, UV₂₅₄ and reactivity. The results showed that the combined process again was less sensitive to changes in these parameters and improvements in bulk water parameter removals could be seen for all the waters tested using MIEX[®] and a significantly reduced coagulant dose.

6.5 Fraction removal

The optimisation of each proposed process on the removal of the isolated fractions showed that an improvement in terms of DOC removal could be made by staged

coagulation and MIEX[®] combined with ferric coagulation for all four of the isolated fractions. Similarly an improvement was also seen for the removal of the hydrophilic fractions (HPI-A and HPI-NA) by the use of β -FeOOH and AC. However these results were based on the removal of individual fractions and did not account for the synergistic effects likely to be seen in the bulk water. The benefits of fractionating water into isolated components allowed the most reactive fractions, with respect to DBP formation following chlorination, to be specifically targeted and hence reduce the overall THMFP of the treated water. This could be important during times when the water becomes increasingly difficult to treat and bulk parameters are remaining constant.

6.6 MW removal

The three defined MW ranges studied during this work were >5 kDa, 2-5 kDa and <2 kDa. The evaluation of the processes showed that the high and mid MW ranges (>5 kDa and 2-5 kDa) were well removed by all processes with the exception of MIEX[®] alone. The low MW range (<2 kDa) has previously proved to be the most recalcitrant to removal by conventional treatment (~50%) however, the use of MIEX[®] plus ferric coagulation and adsorption by β -FeOOH and AC showed an increase in removal ranging from ~70% to >90%.

6.7 Summary

The proposed processes all afforded an improvement in the treatment of NOM in humic rich waters. However depending on the particular driver faced by the WTW a number of different variations could be adopted. For WTWs with a filtration problem staged coagulation would give the best solution for little increase in cost. The removal of

THMs is best treated by a combination of MIEX[®] and conventional coagulation or adding an adsorption process following coagulation to ‘polish’ the water. The cost implications of each of these processes varies significantly however the likely reduction in current THM limits and the implementation of HAA standards in the future will require all WTWs to examine new processes and optimise current treatments if they are to meet these standards.

7 Further Work

The treatment of humic rich waters can lead to conventional processes being challenged. By understanding the character of the water in terms of organic and MW distribution a WTW can improve its overall treated water quality. However further research is needed in this area and should focus on such issues as:

1. fractionation can cause some adverse effects on the organic material within NOM and may change its structure and chemistry. During the fractionation procedure the water is first split into hydrophobic and hydrophilic material. The effect of the processes presented here on these parts of the water may be different to those seen for the individual fractions and offer an insight into the competition reactions that are likely to occur;
2. the mechanism for the staged coagulation and why it led to improved filterability is proposed here. Further research to verify the mechanism could be confirmed by studying the zeta potential following each coagulant addition;
3. evaluation of the effect of the adsorbents on coagulated water would give a more realistic idea of their effectiveness and pilot trials of the adsorption process to assess their scale up potential;
4. whilst the processes perform well in the laboratory their effect on downstream processes such as clarification and filtration should be examined; and

5. the analysis of the effectiveness by MW removal reported in this thesis was based on the elution UV₂₅₄ absorbing compounds from the HPSEC. This method does not take into account non UV₂₅₄ absorbing material. Therefore a DOC detector on the HPSEC would give a more complete MW distribution of the sample analysed.

8. References

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