ABSTRACT

The removal of natural organic matter (NOM) is one of the main challenges facing water utilities in both the UK and the US. As a consequence of changes in land management and an increased carbon loss from solids, a greater amount of accumulated organics is now being flushed into the aquatic environment during increased surface run-off events such as snowmelt or heavy rainfall. Furthermore, whilst traditional treatment with trivalent coagulants has proven a successful strategy in the past, operational problems are now being reported during periods of elevated organic levels in the water. These include the formation of fragile flocs, a greater particulate carryover onto downstream processes and increased disinfection by product (DBP) formation.

Resin adsorption techniques were employed to fractionate the water samples into their hydrophobic and hydrophilic components. This, coupled with raw water monitoring, revealed that NOM composition and characteristics can vary, even if the total organic concentrations appear stable. In particular, hydrophobic NOM fractions contribute the majority of the charge compared to the hydrophilic fractions, and therefore exert a greater impact on coagulation conditions. Comparison across different source waters, seasons, at varying experimental scales and under varying coagulation conditions, revealed that zeta potential monitoring during coagulation takes into account the changing electrical property of the water, and in general, maintaining a value between $-10 < \zeta < +3$ mV will result in low and stable residuals. A similar operational zeta potential range exists for clarification processes, although the zeta potential value at the positive threshold is influenced by the hydrophobic NOM content, such that the range is extended as the specific UV absorbance (SUVA) value of the raw water decreases. Whereas the hydrophilic concentration was found to control the achievable dissolved organic carbon (DOC) residual, attributed to a negligible charge density and poor coagulant-interactions. Consequently, the key finding of this study is that raw water characterisation coupled with zeta potential monitoring will provide a straightforward guide to the mechanistic understanding of treating NOM rich waters.
ACKNOWLEDGEMENTS

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<td>American Water Works Association Research Foundation</td>
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<td>CCC</td>
<td>Colloid Charge Capacity</td>
</tr>
<tr>
<td>Da</td>
<td>Daltons</td>
</tr>
<tr>
<td>DAF</td>
<td>Dissolved Air Flotation</td>
</tr>
<tr>
<td>DBP</td>
<td>Disinfection By-Product</td>
</tr>
<tr>
<td>DI</td>
<td>De-Ionised</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
</tr>
<tr>
<td>DWI</td>
<td>Drinking Water Inspectorate</td>
</tr>
<tr>
<td>DVLO</td>
<td>Derjaguin Verwey Landau Overbeek</td>
</tr>
<tr>
<td>EOM</td>
<td>Extracellular Organic Matter</td>
</tr>
<tr>
<td>FA</td>
<td>Fulvic Acid</td>
</tr>
<tr>
<td>FAF</td>
<td>Fulvic Acid Fraction</td>
</tr>
<tr>
<td>FCWTF</td>
<td>Fort Collins Water Treatment Facility</td>
</tr>
<tr>
<td>HA</td>
<td>Humic Acid</td>
</tr>
<tr>
<td>HAA</td>
<td>Halo Acetic Acid</td>
</tr>
<tr>
<td>HAF</td>
<td>Humic Acid Fraction</td>
</tr>
<tr>
<td>HPI</td>
<td>Hydrophilic</td>
</tr>
<tr>
<td>HPO</td>
<td>Hydrophobic</td>
</tr>
<tr>
<td>HPINA</td>
<td>Hydrophilic Non Adsorbed</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>HPSEC</td>
<td>High Performance Size Exclusion Chromatography</td>
</tr>
<tr>
<td>IEP</td>
<td>Iso-Electric Point</td>
</tr>
<tr>
<td>MIEX®</td>
<td>Magnetic Ion Exchange Resin</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td>NOM</td>
<td>Natural Organic Matter</td>
</tr>
<tr>
<td>NTU</td>
<td>Nephelometric Turbidity Units</td>
</tr>
<tr>
<td>polyDADMAC</td>
<td>Polydiallyldimethylammonium chloride</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle Size Distribution</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions Per Minute</td>
</tr>
<tr>
<td>SUVA</td>
<td>Specific Ultraviolet Absorbance</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>THM</td>
<td>Trihalomethane</td>
</tr>
<tr>
<td>THMFP</td>
<td>Trihalomethane Formation Potential</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>UV$_{254}$</td>
<td>Ultraviolet Absorbance at 254 nm</td>
</tr>
<tr>
<td>WHO</td>
<td>World Heath Organisation</td>
</tr>
<tr>
<td>WTF</td>
<td>Water Treatment Facility</td>
</tr>
<tr>
<td>WTW</td>
<td>Water Treatment Works</td>
</tr>
</tbody>
</table>
## Abbreviations and Notation

### Notation

- $\gamma$  
  Floc size exponent
- $\gamma'$  
  Floc size exponent
- $d$  
  Floc diameter ($\mu$m)
- $d_{50}$  
  50 percentile equivalent diameter floc size ($\mu$m)
- $D_f$  
  Fractal dimension
- $G$  
  Velocity gradient ($S^{-1}$)
- $v_t$  
  Terminal settling velocity ($\mu$m.s$^{-1}$)
- $\zeta$  
  Zeta potential (mV)
1 Introduction

1.1 Project background

Natural waters throughout the world contain natural organic matter (NOM) as a result of the interactions between the hydrological cycle and both the biosphere and geosphere. The diversity of subsequent interactions is dependent on the surrounding environmental and biogeochemical cycles which result in a highly heterogeneous mixture of organic compounds that vary both temporally and spatially with regards to acidity, molecular weight and charge density (Collins et al., 1986; Edzwald, 1993; Owen et al., 1993; Carlson et al., 1994; Vuorio et al., 1998; Scott et al., 2001; Goslan et al., 2002). Changes in land management, such as the disturbance of peat or vegetation damage can lead to increased decomposition and the production of loosely bound organic material (Niskavaara et al., 1997; Worrall & Burt, 2005). Furthermore, recent research has also revealed a significant increase in organic carbon loss from solids which has been linked to climate change (Bellamy et al., 2005). The accumulated organics are then flushed into the aquatic environment during increased surface run-off events such as heavy rainfall or snowmelt (Goslan et al., 2002; Hurst et al., 2004).

Traditional treatment with trivalent coagulants has proven a successful strategy for the removal of NOM in the past, driven by charge neutralization for colloidal material and charge complexation / precipitation for soluble compounds with additional removal occurring due to adsorption on to precipitated flocs and metal hydroxides (Randtke, 1988). Accordingly, optimisation of the coagulation process occurs under acidic conditions between the iso-electric point (IEP) of the coagulant and the NOM; pH 4.5-5.5 for iron based system and pH 5-6 for aluminium based coagulants (Amirtharajah and O’Melia, 1990). However, in the last decade, rapid changes in organic levels have generated significant operational difficulties for both UK and US water utilities during certain periods of the year, resulting in inadequate NOM removal, the formation of fragile flocs and increased particulate carryover onto downstream processes such as filtration. Furthermore, insufficient NOM removal can also lead to the production of potentially carcinogenic disinfection by products (DBP), formed when residual organics react with chlorine during disinfection (Singer, 1999).
DBP concentrations are strictly regulated by organisations such as the World Health Organisation (WHO), the Drinking Water Inspectorate (DWI) and the United States Environmental Protection Agency (USEPA).

The aim of this work is to investigate the changing nature of the NOM during these periods and assess this in terms of the impact on coagulation performance and the charge balance of the system. Furthermore, by linking these changes to zeta potential measurements it is hoped that a set of guidelines can be devised to aid operations and provide a robust level of performance when coagulating elevated organic content waters.

1.2 Motivation for work

The work presented in this thesis forms part of American Water Works Association Research Foundation (AwwaRF) tailored collaboration investigating the ‘Treatment of elevated organic content waters’.

This study is focussed on three case study sites, all subject to rapidly changing organic concentration during certain periods of the year. All three waters are typically characterised as low alkalinity, high DOC and low turbidity sources (Table 1.1). The main case study source was located at the Albert Reservoir, Halifax, Yorkshire, UK, and has also been the subject of a number of characterisation and optimisation studies (Goslan, 2003; Fearing, 2004, Jarvis, 2004), whereas the second UK case study source was taken from Bamford, Derbyshire. Both UK sites were situated on moorland catchments and experience elevated organics following periods of heavy rainfall, of particular significance during the autumn months. The third case study source was the Poudre river, taken from the Fort Collins Water Treatment Facility (FCWTF), Colorado, USA, which experiences changes in organic concentration due to spring snow melts between April and June.
Table 1.1: Source water characteristics

<table>
<thead>
<tr>
<th>Source</th>
<th>UV&lt;sub&gt;254&lt;/sub&gt; (abs)</th>
<th>DOC (mg.L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Turbidity (NTU)</th>
<th>pH</th>
<th>SUVA (m&lt;sup&gt;-1&lt;/sup&gt;.L.mg&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Alkalinity (mg.L&lt;sup&gt;-1&lt;/sup&gt; as CaCO&lt;sub&gt;3&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albert</td>
<td>36.9-63.6</td>
<td>4.3-15.0</td>
<td>3.7-10.9</td>
<td>5.5-6.5</td>
<td>3.8-7.4</td>
<td>&lt;20.0</td>
</tr>
<tr>
<td>Bamford</td>
<td>36.7-45.9</td>
<td>4.5-10.2</td>
<td>1.4-4.2</td>
<td>5.5-6.5</td>
<td>3.6-8.7</td>
<td>&lt;20.0</td>
</tr>
<tr>
<td>FCWTF</td>
<td>9.9-22.5</td>
<td>2.0-7.4</td>
<td>0.5-19.6</td>
<td>7.0-7.6</td>
<td>2.1-3.2</td>
<td>16.3-35.0*</td>
</tr>
</tbody>
</table>

*Maintained within 25-35 mg.L<sup>-1</sup> range during experiments through the addition of lime.

Previous raw water monitoring at Albert reservoir has highlighted the seasonal variability in organic levels with reported DOC concentrations of up to 15 mg L<sup>-1</sup> (Figure 1.1). Consequently, elevated organics not only pose a problem in terms of the variation in coagulation conditions and subsequent removal, but also the increased costs associated with the rise in coagulant dose. However, effective monitoring and characterisation of the NOM fractional make-up during these periods should enable a better understanding of the changes occurring in the system during these periods of elevated organics. Furthermore, relating these changes to zeta potential should provide an improved insight regarding the interactions between NOM and coagulants, and lead to the development of a more mechanistic approach to optimising the coagulation process.
Figure 1.1: Raw water DOC concentrations for Albert reservoir Jan-01 to May-03.

1.3 Project aims and objectives

The main aim of this thesis was to investigate the application of zeta potential monitoring in order to optimise the coagulation process for natural water sources subject to a rapidly changing elevated organic content. In order to achieve this, particular emphasis was placed on the following:

1. Seasonal variations in NOM composition and character.
2. Impact of NOM character on NOM-coagulant interactions.
3. The relationship between coagulation performance and zeta potential.
4. Impact on downstream process operating properties.
In order to achieve these objectives, the experimental work plan focused on the following areas:

1. Raw water monitoring of mountain and moorland catchment sources involving the bulk water measurements (DOC and UV$_{254}$) and fractionation experiments.
2. Charge density determination of raw water and NOM fraction samples, followed by iso-electric point determination of a range of NOM-coagulant combinations.
3. Coagulation performance was investigated at both bench (jar tests) and pilot scales, and subsequently compared with full-scale data.
4. Floc diagnostic techniques were employed to investigate the impact on parameters such as floc strength, size and settling.

1.4 Thesis plan

The thesis is presented in paper format. All papers were written by the first author, Emma Sharp, and edited by Dr Bruce Jefferson (supervisor). All experimental work was undertaken by the first author, with the exception of the floc photos and diagnostic data, featured in figures 3(C).7 and 8 which were generated by Peter Jarvis. In addition, jar test experiments, featured in paper 5, were undertaken by Max Mergen under the supervision of Emma Sharp.

The main objective of each paper, and how they interconnect within the thesis, is detailed in Table 1.2 and Figure 1.2. The initial paper is a literature review which discusses the application of zeta potential as a potential process control parameter during water treatment. (Chapter 2 – submitted: Sharp, E.L., Henderson, R., Parsons, S.A. and Jefferson. B. The role of zeta potential in water treatment processes, Critical Reviews in Environmental Science and Technology).

The technical content of the thesis is incorporated into Chapters 3-7. Chapter 3 investigates the character of the NOM in terms of charge properties and how this influences the interactions between coagulants and NOM. The first paper is based on samples taken from Albert reservoir and looks at the influence of NOM character on the interactions with ferric sulphate. This paper was published in: Sharp, E.L.,
Parsons, S.A. and Jefferson, B. (IN PRESS) Seasonal variations in natural organic matter and its impact on coagulation in water treatment. Science of the Total Environment. The second paper is also based on samples obtained from Albert reservoir, although the main focus of this paper is the differences in NOM-coagulant interactions when coagulating with either iron or aluminium. This was published in: Sharp, E.L., Parsons, S.A. and Jefferson, B. (IN PRESS). The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts. Environmental Pollution. The final paper in this chapter is concerned with the identification of the main NOM fraction characteristics and their proportional impact on the coagulation process. This paper was submitted: Sharp, E.L., Jarvis, P., Parsons, S.A. and Jefferson, B. Impact of fractional character on the coagulation of NOM, Colloids and Surfaces A: Physicochemical and Engineering Aspects.

Chapter 4 looks at bench scale coagulation and investigates the application of zeta potential measurements for maintaining a robust operation. The first paper examines the impact of varying NOM composition and character on removal when coagulating with iron. This work is based on samples collected from the two UK moorland water sources, Albert reservoir and Bamford, during the autumn winter period. (submitted: Sharp, E.L., Mergen, M.R.D., Parsons, S.A. and Jefferson, B. Evaluation of zeta potential for determining optimum coagulation conditions for sources with varying NOM. Journal of Water Supply: Research and Technology- AQUA). The second paper compares the performance of a traditional coagulant, ferric sulphate, with a highly charged novel coagulant. This paper has been published: Sharp, E.L., Parsons, S.A. and Jefferson, B. The effects of changing NOM composition and characteristics on coagulation performance, optimisation and control. Water Science and Technology: Water Supply, 4(4), 95-102.

Chapter 5 looks at both the effect of increasing scale and source water variation on the relationship between coagulation performance and zeta potential. The first paper discusses the link between coagulation performance and zeta potential at pilot scale, comparing a moorland (Albert reservoir) and snowmelt water source when coagulating with either iron or aluminium. This paper was published in: Sharp, E.L., Banks, J., Billica, J.A., Gertig, K.R., Henderson, R., Parsons, S.A., Wilson, D. and

Chapter 6 investigates the use of zeta potential as an optimisation tool, for a number of natural and synthetic systems, in terms of both coagulation and clarification performance, in order to devise a set of operational guidelines. This paper has been submitted: Sharp, E.L., Edwards, M.E., Jarvis, P., Parsons, S.A. and Jefferson, B. Linking source water characteristics to treatment using zeta potential measurements: A mechanistic approach to coagulation. Water Research.

Chapter 7 examines the impact of zeta potential on floc properties in order to determine whether zeta potential or carbon:coagulant ratio is the most dominant factor in determining optimal treatment performance. This paper has been submitted: Sharp, E.L., Jarvis, P., Parsons, S.A. and Jefferson, B. The impact of zeta potential on the physical properties of NOM flocs. Environmental Science and Technology.

The combined findings of all the papers are then discussed in Chapter 8. In addition, although each paper investigates specific impacts on the coagulation process, all the source waters featured were characterised in terms of their NOM composition and character. Consequently, this represents both a common theme throughout the thesis and the opportunity to link any findings back to the initial source water characteristics.
### Table 1.2: Main objectives of each paper.

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Paper</th>
<th>Main Objective</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chapter 2</td>
<td>Paper 1</td>
<td>Literature review: Zeta potential in water treatment processes</td>
</tr>
<tr>
<td>Chapter 3.1</td>
<td>Paper 2</td>
<td>NOM:Fe interactions.</td>
</tr>
<tr>
<td>Chapter 3.2</td>
<td>Paper 3</td>
<td>NOM:Coagulant interactions, iron and aluminium.</td>
</tr>
<tr>
<td>Chapter 3.3</td>
<td>Paper 4</td>
<td>NOM Fraction:Coagulant interactions and removal.</td>
</tr>
<tr>
<td>Chapter 4.1</td>
<td>Paper 5</td>
<td>Bench scale coagulation: Varying raw water characteristics.</td>
</tr>
<tr>
<td>Chapter 4.2</td>
<td>Paper 6</td>
<td>Bench scale coagulation: Zirconium and iron.</td>
</tr>
<tr>
<td>Chapter 5.1</td>
<td>Paper 7</td>
<td>Pilot scale coagulation: Moorland vs snowmelt, Fe and Al.</td>
</tr>
<tr>
<td>Chapter 5.2</td>
<td>Paper 8</td>
<td>Pilot scale coagulation: Varying raw water characteristics.</td>
</tr>
<tr>
<td>Chapter 5.3</td>
<td>Paper 9</td>
<td>Coagulation overview: Linking character to treatment.</td>
</tr>
<tr>
<td>Chapter 6</td>
<td>Paper 10</td>
<td>Coagulation and clarification: Influence of organics.</td>
</tr>
<tr>
<td>Chapter 7</td>
<td>Paper 11</td>
<td>Floc properties and removal.</td>
</tr>
</tbody>
</table>

---

**Figure 1.2:** How each paper interconnects within the thesis.

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Page 8
1.5 References


CHAPTER 2

LITERATURE REVIEW

2 The role of zeta potential in water treatment processes

Submitted to: Critical Reviews in Environmental Science and Technology.
2 The role of zeta potential in water treatment processes

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Abstract

Physical water treatment processes involved in the removal of natural contaminants, such as algae, natural organic matter (NOM) and particulate matter, operate based on differences in size, density and charge. Hence, the role of zeta potential is key, as it indicates the surface potential of the colloidal system and is commonly related to the stability of the colloidal materials under any given set of water characteristics, with natural colloids in water acquiring a zeta potential between -5 mV and -40 mV. Traditional approaches to coagulation diagnostics focus on the impact of coagulant dose and pH, although this review demonstrates that zeta potential can be used to optimise coagulation and downstream separation processes, irrespective of exact pH dose combination employed, provided the zeta potential remains within the threshold values set for each process. The exact location of these boundaries appears to be dependent on the contaminant load. Nevertheless, as the majority of water utilities tend to operate coagulation and clarification processes within the zeta potential range -15 mV <ζ>-8 mV, this review has highlighted the benefit of zeta potential monitoring for a range of treatment options.

Keywords

Algae, Coagulation, Natural organic matter (NOM), Water treatment, Zeta potential.
2.1 Introduction

The nature of contaminants in natural waters varies with both source and season, with three of the most common being natural organic matter (NOM), algae and inorganic colloids such as clays. In general, these are removed successfully by coagulation and flocculation, followed by a particle separation stage during water treatment. All the processes involved separate the contaminants based on differences in their size, density and charge. The role of charge is key in understanding why two surfaces combine, as similar signed charges produce a repulsion which can hinder or prohibit aggregation of the two surfaces if the magnitude is sufficient. This can involve two like particles (coagulation), a bubble and a particle (dissolved air flotation or DAF) or a media grain and a particle (filtration). Consequently, measurement of the charges involved can provide significant insight into process optimisation.

The application of charge measurement for the diagnosis and control of water and wastewater treatment processes is not new, nor has the basic understanding of how charge controls performance changed considerably over the years. Zeta potential indicates the surface potential of the colloidal system and is commonly related to the stability of the colloidal materials under any given set of water characteristics. Hence, any zeta potential near zero indicates the minimal electrical repulsion and so increases the likelihood of capture (Hunter, 2001). However, robustness of the instruments and changes in the water environment which generate process compliance issues, have led to an increased application of charge measurement in the water industry.

The aim of this paper is to review the role of zeta potential within the water treatment process, with particular emphasis on the main source water contaminants such as NOM, algae and inorganic colloids. Hence, by linking raw water characteristics to process optimisation using zeta potential measurements, it is hoped that a set of guidelines can be devised to aid operations and provide a robust level of performance for a range of treatment options.
2.2 Background

2.2.1 Charged surfaces

All particles in water carry a surface charge, which is almost invariably negative (Dentel, 1991). Furthermore, it is the charge on the surface of a particle that influences the ions in the surrounding water, attracting ions of an opposite charge (counter-ions) and repelling ions of the same charge (co-ions). The distribution of these ions together with the effects of thermal motion produces what is termed a “double layer” which maintains overall electro neutrality. An idealised schematic reveals the two distinct regions of the electron double layer (Figure 2.1). The first is an inner region (The Stern Layer) which includes adsorbed ions and the second is a region made up of ions distributed according to the balance of electric and thermal forces (The Diffuse Region). The extent or thickness of the double layer (1/k) is characterised by the distance required to reduce the potential by 1/e, where k is the Debye-Hückel parameter and e is the electron charge (Qu and Li, 2000). This is determined by the concentration and valency of the ions in solution, such that particles are stabilised when their double layers are expanded and the net particle charge is not equal to zero (McCarthy and Zachara, 1989).

![Figure 2.1: Schematic of the electric double layer.](image-url)
2.2.2 Measurement principles

Direct measurement of the charge on the surface is currently not possible and, in the context of this review, probably not of any significance. A more important characteristic of the double layer is the plane of shear. This is the boundary of a hypothetical static liquid film around the particle. Any movement of the particle causes the particle and its liquid film to move, such that the shear plane represents the interface between the portion of the double layer that remains connected to the particle and the portion which remains stationary as the particle moved. In fact, the relative charge on a particle can be inferred by measuring properties that arise as a function of separating the mobile part of the double layer from the particle (Table 2.1). In each case either the particle or the water is kept stationary and the other phase moved. The movement may be generated by applying a voltage, in which case the velocity of motion is measured, or mechanically when the resultant electric field is measured. The two most common techniques are zeta potential and streaming current. Details of the application and evaluation of streaming current detectors have been published elsewhere (Barron et al., 1992; de Haas, 1996; Briley and Knappe, 2002), and so this review will concentrate on the application of surface electrical character on the treatment process in terms of zeta potential measurements.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrophoresis</td>
<td>The movement of a charged particle relative to a stationary liquid caused by a known applied voltage</td>
</tr>
<tr>
<td>Electro osmosis</td>
<td>The movement of water relative to a stationary charge particle by an applied voltage</td>
</tr>
<tr>
<td>Streaming potential</td>
<td>The electric field created by the movement of water along a stationary charged surface</td>
</tr>
<tr>
<td>Sedimentation potential</td>
<td>The electric field created when a charged particle moves relative to stationary liquid</td>
</tr>
</tbody>
</table>
2.3. Zeta potential

2.3.1 Typical values

Most natural colloids in water acquire a zeta potential between -5 and -40 mV, as shown by the values for a range of particulate materials (Table 2.2). With the majority of particles in water this is achieved through one of the following charge mechanisms: acceptance or donation of electrons, the reaction of surface groups with solutes or imperfections resulting in the substitution of atoms (Letterman et al., 1999; Hunter, 2001). Consequently, many surfaces exhibit a changing zeta potential with pH (Figure 2.2). In relation to the principle surfaces of interest to the water industry, three types of response are possible: changes over acidic pHs, changes over basic pHs and changes over all pHs. In general, the zeta potential of organic contaminants, such as NOM or algae, exhibit negative zeta potentials at a pH greater than 4 (Beckett and Le, 1990; Liu et al., 1999; Zhang and Bai, 2002; Jefferson et al., 2004). Whereas basic particulates, such as calcium carbonate, do not exhibit a negative zeta potential until the pH has exceeded 8 (Bob and Walker, 2001). The zeta potential of non ionic particulates, such as hydrophilic organic material with surface confined acidic groups, is likely to exhibit charge reversal as the bulk water shifts from acidic to alkaline at approximately 7, depending on the system (Sharp et al., 2005a).

In terms of capture mechanisms operating within water treatment, zeta potential values indicate that both bubbles (flotation) and sand (filtration) are also likely to generate a negative surface charge at the pH of natural waters. For instance, bubbles have a reported iso-electric point (IEP) of 2 (Kubota and Jameson, 1993; Han and et al., 2001) with slightly higher values reported for sand and silica at an IEP of 2-3 (Fairhurst et al., 1995; Stephan and Chase, 2002). Consequently, this indicates that pHs should be reduced in order to reduce the electrostatic repulsion between collector and particulate and improve removal.
### Table 2.2: Typical values of Zeta Potential.

<table>
<thead>
<tr>
<th>Material</th>
<th>IEP</th>
<th>Standard numbers</th>
<th>Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural Organic Matter (NOM)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw water</td>
<td>NOM</td>
<td>-9.5*</td>
<td>George Town NOM</td>
<td>Deshiikan et al., 1998</td>
</tr>
<tr>
<td>Humic</td>
<td>1.8</td>
<td>c-40</td>
<td>Commercial humic acid</td>
<td>Zhang and Bai, 2002</td>
</tr>
<tr>
<td>Humic</td>
<td>-</td>
<td>c-30</td>
<td>Commercial humic acid, deionised water</td>
<td>Duan et al., 2002</td>
</tr>
<tr>
<td>Fulvic</td>
<td>&lt;3</td>
<td>-12</td>
<td>Suwannee river fulvic acid</td>
<td>Chandrakanth et al, 1996</td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>3.5-5</td>
<td>+4, 0</td>
<td>Albert fractionated water</td>
<td>Jefferson et al, 2004</td>
</tr>
<tr>
<td><strong>Particulates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>Calcium carbonate</td>
<td>Bob and Walker, 2001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>-55</td>
<td>7</td>
<td>Kaolinite</td>
<td>Specht et al., 2000</td>
</tr>
<tr>
<td>9</td>
<td>c-40</td>
<td>10</td>
<td>Activated alumina</td>
<td>Fairhurst et al., 1995</td>
</tr>
<tr>
<td>3</td>
<td>c-60</td>
<td>9</td>
<td>Silica</td>
<td>Fairhurst et al., 1995</td>
</tr>
<tr>
<td>6.5</td>
<td>c-30</td>
<td>10</td>
<td>Titanium dioxide</td>
<td>Fairhurst et al., 1995</td>
</tr>
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<td>2.5</td>
<td>c-23</td>
<td>4</td>
<td>Kaolin</td>
<td>Zhang and Bai, 2002</td>
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<td></td>
<td>c-35</td>
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<td></td>
</tr>
<tr>
<td>c2</td>
<td>-28</td>
<td>4</td>
<td>Kaolin, lake water</td>
<td>Han and Kim, 2001</td>
</tr>
<tr>
<td></td>
<td>-40</td>
<td>7</td>
<td>conditions (0.0001 M)</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>-2.4*</td>
<td>7</td>
<td>Oil, ionic strength = 5x10^{-4}</td>
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</tr>
<tr>
<td></td>
<td>+0.4*</td>
<td>4</td>
<td>M, n-hexadecane</td>
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</tr>
<tr>
<td><strong>Microbiological contaminants</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>-27.5</td>
<td>4</td>
<td>BK algae</td>
<td>Malik et al., 2002</td>
</tr>
<tr>
<td>3.5</td>
<td>c-40</td>
<td>7</td>
<td>Nocardia cells</td>
<td>Sadowski, 2001</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>Algal cells</td>
<td>Liu et al., 1999</td>
</tr>
<tr>
<td>&lt;2</td>
<td>-18</td>
<td>4</td>
<td>Selenastrum capricontum, NaClO₄ = 10^{-1.5} M</td>
<td>Huang et al, 1999</td>
</tr>
<tr>
<td></td>
<td>-22.5</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c2</td>
<td>-20</td>
<td>4</td>
<td>Ionic strength 0.0001M (Lake water)</td>
<td>Han and Kim, 2001</td>
</tr>
<tr>
<td></td>
<td>-20</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>-7</td>
<td>4</td>
<td>Scenedesmus quadricauda</td>
<td>Chen et al, 1998</td>
</tr>
<tr>
<td></td>
<td>-22</td>
<td>7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>c-1*</td>
<td>6.7</td>
<td>Cryptosporidum oocysts</td>
<td>Dai and Hozalski, 2002</td>
</tr>
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</table>
### Table 2.2 continued:

<table>
<thead>
<tr>
<th>Variety</th>
<th>Zeta potential</th>
<th>Conductivity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryptosporidium oocysts coated with natural organic matter</td>
<td>+4*</td>
<td>6.7</td>
<td>Dai and Hozalski, 2002</td>
</tr>
<tr>
<td>Cryptosporidium oocysts</td>
<td>2.18</td>
<td>-</td>
<td>Drozd and Schwartzbrod, 1996</td>
</tr>
<tr>
<td>Cryptosporidium oocysts, conductivity = 400 µS (raw water)</td>
<td>-38</td>
<td>7</td>
<td>Hsu and Hwang, 2002</td>
</tr>
<tr>
<td>Giardia cysts, conductivity = 400 µS (raw water)</td>
<td>-28</td>
<td>4</td>
<td>Okada et al, 1990</td>
</tr>
<tr>
<td>Giardia cysts, conductivity = 400 µS (raw water)</td>
<td>-55</td>
<td>7</td>
<td>Hsu and Hwang, 2002</td>
</tr>
<tr>
<td>Rivers and Reservoirs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yarra, Au</td>
<td>-1.8 x10^{-8}</td>
<td>7.5</td>
<td>Beckett and Le, 1990</td>
</tr>
<tr>
<td>Magela creek, Au</td>
<td>-2.5 x10^{-8}</td>
<td>6</td>
<td>Beckett and Le, 1990</td>
</tr>
<tr>
<td>Media</td>
<td>-40 8</td>
<td>8</td>
<td>Han and Kim, 2001</td>
</tr>
<tr>
<td>Crushed white quartz, ionic strength = 5x10^{-4} M,</td>
<td>-3.5*</td>
<td>7</td>
<td>Soma and Papadopoulos, 1995</td>
</tr>
<tr>
<td>Crushed white quartz, ionic strength = 5x10^{-4} M,</td>
<td>-2.8*</td>
<td>4</td>
<td>Soma and Papadopoulos, 1995</td>
</tr>
<tr>
<td>Sandstone, 1.0 M NaCl</td>
<td>-10</td>
<td>4</td>
<td>Stephan and Chase, 2002</td>
</tr>
<tr>
<td>Sandstone, 1.0 M NaCl</td>
<td>-15</td>
<td>7</td>
<td>Stephan and Chase, 2002</td>
</tr>
<tr>
<td>Amorphous silica (Syton HT50) 0.1 µm</td>
<td>-7</td>
<td>4</td>
<td>Fairhurst et al, 1995</td>
</tr>
<tr>
<td>Amorphous silica (Syton HT50) 0.1 µm</td>
<td>-21</td>
<td>7</td>
<td>Fairhurst et al, 1995</td>
</tr>
<tr>
<td>Bubbles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measured in new system</td>
<td>-7.8</td>
<td>4</td>
<td>Han and Dockko, 2003</td>
</tr>
<tr>
<td>Measured by modified electrophoretic cell</td>
<td>-26</td>
<td>8</td>
<td>Kubota and Jameson, 1993</td>
</tr>
<tr>
<td>Measured by modified electrophoretic cell</td>
<td>-20</td>
<td>4</td>
<td>Kubota and Jameson, 1993</td>
</tr>
<tr>
<td>Measured by modified electrophoretic cell</td>
<td>-40</td>
<td>7</td>
<td>Kubota and Jameson, 1993</td>
</tr>
</tbody>
</table>

*Electrophoretic mobility rather than zeta potential
2.3.2 Influence of source water characteristics

The major contaminants in natural waters, with reference to the current study, are NOM, algae and river particulates. At the pH of most natural waters, both Algae and NOM are likely to exhibit a negative surface charge (Chandrakanth et al., 1996; Malik et al., 2002). Parasites such as Cryptosporidium oocysts, which are present in most surface waters (Betancourt and Rose, 2004), also demonstrate similar surface charge properties, with a negative charge above pH 4 (Hsu and Hwang, 2002). Conversely, for mineral based particulate material surface charge characteristics are not so uniform and vary depending on the nature of the surface groups present and the purity of the system. For instance, silica based particles have an acidic IEP of approximately 3, attributed to the presence of acidic surface groups, compared to the more basic groups found on the alumina surface with a resultant IEP of 9 (Fairhurst et al., 1995).

2.3.2.1 NOM

NOM, ubiquitous in all surface water sources, is a highly heterogeneous mixture of anionic polyelectrolytes that vary with regards to acidity, molecular weight and charge density (Collins et al., 1986; Edzwald, 1993; Vuorio et al., 1998; Goslan et al., 2002). This organic mixture is also known to vary in terms of concentration and make-up due to the temporal and spatial variations that exist between sources (Owen...
et al., 1993; Carlson et al., 1994; Scott et al., 2001). In general, the zeta potential of organic systems is negative at ambient pHs, with values ranging from -12 mV to -40 mV (Chandrakanth et al., 1996; Duan et al., 2002). The negative charge is believed to arise from the dissociation of carboxylic functional groups on the surface of the NOM, with a pKa typically in the range of 3-6 (Chandrakanth et al., 1996; Duan and Gregory, 2003), with charge densities for humic substances having been reported in the range of 2-15 meq.g$^{-1}$DOC (Tiller and O’Melia, 1993; Kam and Gregory, 2001; Scott et al., 2001). However, NOM also contains hydrophilic material, which tends to be aliphatic, with surface confined acidic groups tending to less acidic, attributed to the electrostatic interactions of surface groups of the monolayer and a reduced permittivity at the surface (Schweiss et al., 2001). Hence, the charge density for the hydrophilic bases and neutrals is reportedly at least an order of magnitude lower than the hydrophobic NOM, resulting in a less negative zeta potential in ambient conditions. However, overall the hydrophobic NOM is thought to be the dominant fraction in terms of the raw water characteristics (Malcolm, 1985), and therefore most likely to influence the charge balance and coagulant demand of the water.

2.3.2.2 Particulates
Inorganic colloids and particulates constitute another mobile phase present in the majority of natural water systems, present as oxides or hydroxides of manganese, iron, aluminium or silica for example, in addition to clays. With regards to surface charge, many oxides are amphoteric such that colloidal clays have zeta potentials which vary over both acidic and basic pH ranges (Jefferson, 1997). In the case of kaolin particles in water, the surface charge develops as a result of chemisorption of water splitting into H$^+$ and OH$^-$ during adsorption to form a hydroxylated surface. Consequently, as the pH increases the OH$^-$ ions are adsorbed until they are in excess, resulting in a negative zeta potential (Huang et al., 1999). However, previous research has suggested that these bare colloidal surfaces are unlikely to exist for long in natural waters, due to the presence of organic material such as NOM. This readily adsorbs onto particulate material, often masking the physicochemical properties of the underlying solid whose behaviour, in terms of electrophoretic mobility, colloidal stability and transport, may then be dominated by the NOM (McDay et al., 1994; Buffle and Leppard, 1995; Pizarro et al., 1995; Chandrakanth and Amy, 1998). This is thought to occur through ligand exchange between carboxylic groups on the NOM.
and hydroxylated surface sites on the solids (Murphy et al., 1990). In general this modifies the particles surface charge, rendering it more negative with an increased particle stability (Tiller and O’Melia, 1993; Chandrananth et al., 1996; Zhang et al., 1998; Kretzschmar et al., 1998; Wilkinson et al., 1997), as the attraction of cations in a complex layer adjacent to the negatively charged humic surface, results in the formation of a diffuse double layer (Wall and Chopin, 2003). For instance, Bob and Walker (2001), observed an increase in stability by a factor of 50 when the humic acid concentration on latex particles was increased from 0.2 mg.l$^{-1}$ to 0.7 mg.l$^{-1}$. In fact, NOM has been shown to increase the negative surface charge when adsorbed onto a range of surfaces; Cryptosporidium oocysts (Dai and Hozalski, 2002); Amidine latex (Deshiikan et al., 1998) and Goethite (Tipping and Cooke, 1982). Furthermore, the negative charge associated with NOM is also thought to be important with regard to interactions and subsequent transportation of natural metal ions (Tipping, 1993).

The adsorption of humic acid onto inorganic colloids also occurs over a wide pH range, suggesting that in most natural aquatic systems a number of different mineral surfaces will be coated with humic substances, altering both the zeta potential and IEP (Table 2.3). Relatively acidic surfaces such as silica have less of a tendency to form complexes with the acidic functional group of humic acid, compared to the more basic hydroxyls of the activated alumina and bohemite (Fairhurst et al., 1995). This indicates that adsorption is hindered due to electrostatic repulsion when the zeta potential of both the mineral and organics was negative. The concentration of NOM is also a factor. For instance, Amal et al. (1992), looked at the effects of fulvic acid adsorption on zeta potential at a constant pH (3) on haematite. At low fulvic acid concentrations, the zeta potential remained essentially unchanged and the particle surface was relatively free of fulvic acid molecules. As the organic concentration is increased, the zeta potential decreases significantly until it reaches an equilibrium value, after which it remains constant. This was explained as both a physical and chemical phenomena, as electrostatic forces could not be wholly responsible for the adsorption, otherwise the zeta potential would remain at zero for increasing fulvic acid concentration. Instead the zeta potential reverses, indicating some specific chemical interaction.
Table 2.3: Influence of humic acid adsorption on inorganic colloid IEP (Adapted from Fairhurst et al., 1995).

<table>
<thead>
<tr>
<th>Particulate material</th>
<th>IEP (No HA)</th>
<th>IEP (HA added in mg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boehemite</td>
<td>9.5</td>
<td>4.2 (10)</td>
</tr>
<tr>
<td>Goethite</td>
<td>7</td>
<td>2 (10)</td>
</tr>
<tr>
<td>Silica</td>
<td>3</td>
<td>3 (10)</td>
</tr>
<tr>
<td>Haematite</td>
<td>8</td>
<td>3 (10)</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>6.5</td>
<td>5 (25)</td>
</tr>
<tr>
<td>Alumina</td>
<td>9</td>
<td>2.5 (25)</td>
</tr>
</tbody>
</table>

2.3.2.3 Algae

Algae, like NOM, is also ubiquitous in natural waters, although concentrations tend to vary considerably and as such are generally considered a seasonal issue (Henderson et al., 2005). Zeta potential values for algal particles demonstrate that the surface charge is typically electronegative for pH ranges 4 to 10, with similar values to NOM ranging between -10 and -35 mV (Ives, 1959; Liu et al., 1999; Chen et al., 1998; Huang et al., 1999; Phoochinda and White, 2003). Hence, the resultant suspension is likely to be stable at ambient pHs, due to steric effects produced when water is bound to the algal cell wall surface (Vlaski et al., 1997). The negative surface charge originates from the ionisation of functional groups on the algae cell wall surface, of which protein molecules (amino acids linked by peptide bonds) are a major component of the membrane CONH group (Huang et al., 1999). pKa values for the carboxyl groups of amino acids range from 1.7 to 3.0. Consequently, the IEP for a number of algal species have been reported between 1.5 and 3.5 (Table 2.2).

It is also interesting to note that the zeta potential value has been demonstrated to alter depending on the algal growth, hence lower coagulant doses are required to neutralise the surface charge generated during the stationary growth phase (Edzwald and Wingler, 1990). It has been suggested that this observation is due to an increase or decrease of extracellular organic matter (EOM), dependent on when during the growth phase the algae are sampled, which in turn generates a negative charge. For instance, the zeta potential of the diatom *Nitzschia* was -30 mV during the initial growth phase, -35 mV in the log growth phase and -28 mV in the stationary phase (Konno, 1993). This indicates that during the log growth phase, the diatom was extremely active and as a result produced a larger volume of algogenic substances, which then acted to increase the negative surface charge (Konno, 1993).
2.4 Application to water treatment processes

All physical separation processes rely on characteristics such as size, density and charge of the particles, for the latter to be removed. Consequently, a number of studies have used zeta potential to analyse performance across various stages of the water treatment process (Table 2.4). In each instance the removal efficiency increased as the magnitude of the zeta potential was reduced; resulting in optimum operational zeta potential ranges similar to those shown in Figure 2.3. In all cases, the existence of a range as opposed to a single value indicates that complete neutralization of the charge is not required, only that the barrier generated by electrostatic repulsion is minimized or removed. Nevertheless, previous research has demonstrated that the majority of water utilities tend to operate coagulation and clarification processes within the zeta potential range -15 mV <ζ>-8 mV, as demonstrated by Bourgeois et al. (2005) who carried out a survey of 11 different treatment works in the UK. This work indicates that many sites may be operating very close to the negative threshold values, depending on the contaminant load (Figure 2.4). Consequently, rapid changes in raw water characteristics, arising from snowmelt or heavy rainfall events, could shift the charge balance of the system before the coagulant dose has responded sufficiently (Sharp et al., 2005b). The impact of which is a shift in the operational zeta potential to outside the range, and a rapid deterioration in performance.
Figure 2.3: Zeta potential vs removal for (a) coagulation (b) sedimentation (c) flotation and (d) filtration processes.

\(^1\) Rebhun and Lurie, 1993; Childress et al., 1999, \(^2\) Rebhun and Lurie, 1993; Zhang et al., 1998; Henderson et al., 2005, \(^3\) Edzwald and Winkler, 1990; Han et al., 2001; Zouboulis et al., 2003, \(^4\) Parsons et al., 2005.
Figure 2.4: Average zeta potential profile through a water treatment works (Adapted from Bourgeois et al., 2005).
Table 2.4: Operational zeta potential windows for optimum water treatment performance.

<table>
<thead>
<tr>
<th>System</th>
<th>Coagulant/Collector</th>
<th>Process</th>
<th>Optimum removal (%)</th>
<th>Positive Threshold (mV)</th>
<th>Rate of decline (%.mV⁻¹)</th>
<th>Negative Threshold (mV)</th>
<th>Rate of decline (%.mV⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae</td>
<td>Chlorella vulgaris</td>
<td>Alum</td>
<td>Sedimentation &gt;60</td>
<td>+12</td>
<td>44</td>
<td>-12</td>
<td>18</td>
<td>Henderson et al., 2005</td>
</tr>
<tr>
<td>Algae</td>
<td>Cyclotella</td>
<td>Alum</td>
<td>Flotation &gt;80</td>
<td>-</td>
<td>-</td>
<td>-15 &lt;ζ&gt;-13</td>
<td>11-18</td>
<td>Edzwald and Wingler, 1990</td>
</tr>
<tr>
<td>Algae</td>
<td>Cyclotella</td>
<td>PAC</td>
<td>Flotation &gt;75</td>
<td>-</td>
<td>4</td>
<td>-13 &lt;ζ&gt;-10</td>
<td>8-10</td>
<td>Edzwald and Wingler, 1990</td>
</tr>
<tr>
<td>Kaolin</td>
<td>Alum</td>
<td>Sedimentation &gt;80</td>
<td>+5</td>
<td>9.3</td>
<td>-20</td>
<td>7</td>
<td>Henderson et al., 2005</td>
<td></td>
</tr>
<tr>
<td>Algae</td>
<td>Cyclotella</td>
<td>Alum</td>
<td>Flotation 60</td>
<td>+7</td>
<td>-</td>
<td>-4</td>
<td>5</td>
<td>Han et al., 2001</td>
</tr>
<tr>
<td>Algae</td>
<td>Cyclotella</td>
<td>Ferric</td>
<td>Coagulation 36</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>Childress et al., 1999</td>
</tr>
<tr>
<td>Algae</td>
<td>Cyclotella</td>
<td>Ferric</td>
<td>Coagulation 48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>Childress et al., 1999</td>
</tr>
<tr>
<td>Kaolin</td>
<td>Alum</td>
<td>Filtration &gt;98</td>
<td>+7</td>
<td>-</td>
<td>-4</td>
<td>5</td>
<td>Parsons et al., 2005</td>
<td></td>
</tr>
<tr>
<td>Organic</td>
<td>River water</td>
<td>Ferric</td>
<td>Coagulation 48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>Childress et al., 1999</td>
</tr>
<tr>
<td>Organic</td>
<td>State project water</td>
<td>Ferric</td>
<td>Coagulation 48</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>Childress et al., 1999</td>
</tr>
<tr>
<td>Organic*</td>
<td>Humic acid</td>
<td>Sedimentation &gt;60</td>
<td>+14</td>
<td>34</td>
<td>-13</td>
<td>37</td>
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</tr>
<tr>
<td>Organic</td>
<td>River water</td>
<td>PAC</td>
<td>Sedimentation &gt;80</td>
<td>+5</td>
<td>-</td>
<td>-12</td>
<td>8</td>
<td>Zhang et al., 1998</td>
</tr>
<tr>
<td>Organic</td>
<td>River water</td>
<td>Ferric</td>
<td>Sedimentation &gt;93</td>
<td>+17</td>
<td>10</td>
<td>-10</td>
<td>34</td>
<td>Edwards, 2002</td>
</tr>
<tr>
<td>Organic</td>
<td>River water + Humic acid</td>
<td>Ferric</td>
<td>Sedimentation &gt;93</td>
<td>+7</td>
<td>8</td>
<td>-10</td>
<td>52</td>
<td>Edwards, 2002</td>
</tr>
<tr>
<td>Organic</td>
<td>Humic acid</td>
<td>CTAB</td>
<td>Flotation &gt;80</td>
<td>+13</td>
<td>-</td>
<td>-15</td>
<td>4</td>
<td>Zouboulis et al., 2003</td>
</tr>
<tr>
<td>Organic</td>
<td>Moorland</td>
<td>Ferric</td>
<td>Filtration &gt;95</td>
<td>-</td>
<td>-</td>
<td>-10</td>
<td>-</td>
<td>Parsons et al., 2005</td>
</tr>
<tr>
<td>Organic</td>
<td>Snowmelt</td>
<td>Ferric</td>
<td>Filtration &gt;90</td>
<td>-</td>
<td>-</td>
<td>-10</td>
<td>10</td>
<td>Parsons et al., 2005</td>
</tr>
</tbody>
</table>

* converted from EPM using Henry’s equation (Hunter, 2001).
2.4.1 Coagulation and flocculation

2.4.1.1 Removal mechanisms

Coagulation is the process of chemically changing colloids, such that they are able to overcome the forces maintaining the stable suspension, promoting aggregation and the formation of larger particles. This is achieved through a number of destabilisation and precipitation mechanisms including surface charge modification, double layer compression, adsorption-charge neutralisation and inter particle bridging (Randtke, 1988; Crozes et al., 1995; Dennett et al., 1995; Duan and Gregory, 2003). However, coagulants can also induce removal in terms of precipitation mechanisms such as sweep flocculation, which involves the addition of high coagulant doses, increasing collision rates through the enmeshment of suspended particles (Montgomery, 1985). As a consequence, sweep flocculation is more tolerant of departures from optimum coagulant dose and less influenced by the resultant zeta potential.

Traditional approaches to coagulation diagnostics focus on the impact of coagulant dose and pH, as they represent the main operational variables (Duan and Gregory, 2003). Optimising the process for the removal of organic particles generally occurs under acidic conditions, this is typically around pH 4.5-5 for iron and pH 5-6 for aluminum based coagulants (Amirtharajah and O’Melia, 1990). The dominant mechanism for coagulation depends on the pH, coagulant dose and contaminant (Duan and Gregory, 2003). This was illustrated by Henderson (2004) who investigated the coagulation of algae and kaolin systems (Figure 2.5). This work revealed that the charge neutralisation zones (II) coincided with the lower coagulant doses of 4mg.l\(^{-1}\) and 6mg.l\(^{-1}\) for kaolin and algae respectively, with a narrower band observed for kaolin. Whereas at the higher coagulant doses, in excess of 60 mg.l\(^{-1}\)as alum when operating at pH 5, the sweep flocculation mechanism was found to dominate (IV). However, at higher pHs, the alum dose required for sweep flocculation was reduced, to 15 mg.l\(^{-1}\) and of 25 mg.l\(^{-1}\) alum at pH 7, for algae and kaolin respectively. The reduced coagulant dose was attributed to the fact that the number of ligands associated with the aluminium ion increased at higher pHs, ultimately leading to increased precipitation (Briley and Knappe, 2002), and is confirmed by standard dissociation diagrams for the coagulants (Duan and Gregory, 2003). In terms of algae removal, Vlaski et al. (1997) reported an improved performance when particles were destabilised at the lower pH of 6 under adsorption and charge neutralisation.
mechanisms with simultaneous sweep flocculation occurring, compared to the performance of sweep flocculation alone at a higher pH of 7.8. Duan and Gregory (2003) reported the existence of similar mechanisms in terms of NOM removal. Conversely, in terms of the removal of inorganic particles such as kaolin, removal has been optimised at a higher pH of 7 (Henderson, et al., 2005), where both charge neutralisation and sweep flocculation are thought to operate in combination (Duan and Gregory, 2003).

![Graph](image)

**Figure 2.5: Coagulation mechanism zones at pH 5 for (a) inorganic (Kaolin) and (b) organic (Algae). (Adapted from Henderson, 2004).**

I= Insufficient coagulant, II= Charge neutralisation, III= Restabilisation, IV= Sweep flocculation.

However, a traditional approach based on coagulation pH set points does not always allow the process to adequately respond to rapid changes in surface charge, providing a route for non-compliance. The incorporation of zeta potential in terms of monitoring and diagnostics would take into account the changing charge characteristics of the water. Furthermore, in reality, optimised charge conditions for both inorganic and
organic systems tend to occur over a range of zeta potential values, rather than specifically at the IEP of the system (Ratnaweera et al., 1999; Gregory and Carlson, 2003; Henderson et al., 2005), which would allow process operators time to respond and adapt to fluctuations in the charge load.

2.4.1.2 Charge control
The most widely used metal salts in water treatment are iron and aluminium salts (Fe$^{3+}$ and Al$^{3+}$) (Rebhun and Lurie, 1993). When a metal salt is added to water it hydrolyses, producing a series of cationic dissociation products, whose relative abundance varies with pH. The aim being to reduce the negative surface charge of the system. The negative charge of the contaminant is reduced or reversed through the addition of a cationic coagulant. This is demonstrated with the addition of either ferric chloride or alum to well dispersed kaolin in uncontrolled pH environments at an initial pH of 5.5 (Figure 2.6). However, the response curves of the two coagulants are very different due to the formation of different hydrolysis products. In the case of alum, cationic species predominate whilst ferric chloride produces a hydroxide precipitate which coats the particles and progressively controls the overall charge (Jefferson, 1997). Nevertheless, despite the observed reported improved removal with iron based coagulants compared with aluminium (Edzwald and Tobias, 1999; Bell-Ajy et al., 2000; Budd et al., 2004), based on a mass ratio basis, influence of charge ratio (meq.meq$^{-1}$) revealed a more consistent comparison, with an equivalent impact on the charge response for both a humic and a fulvic acid based systems (Figure 2.7).
Polymer use is another option for altering the surface charge, and also efficient in terms of dosage, leading to improved removal at one tenth of the dose compared to conventional coagulants (Vlaski et al., 1997). This is attributed to the fact that only small amounts of polymer may be required to form positive patches for charge
neutralisation which then works in combination with the polymer bridging mechanism (Petzold et al., 2003). The polymer can achieve this in a number of ways, depending on the characteristics of the polymer. For instance, the addition of the non-charged polymer extends the shear plane and hence reduces the zeta potential. The addition of a charged polymer affects the surface charge by adsorption, which can result in charge neutralisation and reversal, as demonstrated by Jameson (1999), who reduced the negative zeta potential of silica particles from -47 mV to the IEP through the addition of a cationic polymer. Whereas in the case of the anionic polymer, the magnitude of the negative charge is actually increased and so the net effect is less significant than that of the non-charged polymer, as demonstrated by Mpofu et al. (2003) who increased the negative zeta potential of a kaolin slurry from -32.5 mV to -7 mV and -30 mV using a non ionic and an anionic polymer respectively.

2.4.1.3 Operational window
The removal of dissolved organic species, such as NOM, following coagulation is independent of the solid liquid separation process (Malley, 1990; Malley and Edzwald, 1991). Nevertheless, zeta potential can still be employed to optimise removal, as despite variation between different systems, optimum removal has been shown to occur as the surface charge is minimised, regardless of the varying coagulation conditions (Figure 2.3a). Results demonstrate the existence of operational windows with respect to zeta potential, such that a certain level of removal is achieved. Zeta potential values at the boundary of the operational window represent a threshold which if exceeded will result in a reduction in removal. The zeta potential of each system can be manipulated through either coagulant dose or pH adjustment. In fact, research has shown that the exact combination is unimportant, provided the zeta potential remains within the threshold values. For instance, Figures 2.8 and 2.9 demonstrate using high performance size exclusion chromatograms (HPSEC) for both snowmelt and moorland water sources, that the residual organics remaining after treatment are similar when operating within the zeta potential range -10 mV to +3 mV (Sharp et al., 2005b). Refer to appendix for relationship between HPSEC elution time and molecular size.
With regards to organic based systems, one observed difference between algae and NOM is the time required to neutralise the surface charge. For instance, inert systems, even with organic coatings, demonstrate almost instantaneous changes in charge, whereas algae are living systems and respond to changes in environmental conditions. Clasen et al. (2000) reported a lag time of up to 7 minutes, when coagulating with 1 mg.l\(^{-1}\) aluminium before the charge stabilises.

However, zeta potential monitoring alone will not provide all the information required to operate the coagulation process. For instance, the removal of non or negligibly charged components, such as low molecular weight (MW) hydrophilic organic material which is less amenable to removal by conventional coagulation methods (Edwards, 1997; White et al., 1997; Krasner et al., 1994; Randtke, 1988; Owen et al., 1993), is unlikely to be optimised by zeta potential monitoring. Research undertaken on both moorland and snowmelt systems reported a variation in achievable DOC residual whilst operating within the optimum zeta potential range, this was then linked to the initial non charged fraction (HPINA) present in the raw water (Figures 2.10 and 2.11).
2.4.2 Sedimentation

The efficiency of the sedimentation process is largely dependent on the characteristics of the flocs formed during the coagulation and flocculation process. These are defined as highly porous, irregularly shaped and loosely bound aggregates (Kim et al., 2000). Furthermore, the role of zeta potential is in determining the extent to which electrostatics control the properties of the flocs. Hence, minimising the zeta potential reduces repulsive surface electrical charges, allowing the attractive forces between particles to dominate, and promoting the build up of a continuous network of particles in flocs (Gustafsson et al., 2003).

However, comparison of a number of different systems not only reveals the importance for minimising surface charge in order to improve performance, but also highlighted differences between the systems (Figure 2.3b). For instance, inorganic particles are less sensitive to the magnitude of the zeta potential and subsequent deterioration in performance, with optimum kaolin removal still achievable at a zeta potential of -20 mV, whereas, for both algae and NOM, removal decreased once the negative zeta potential had exceeded $-15 < \zeta < -10$ (Table 2.4). The presence of organics has also been shown to reduce the positive zeta potential threshold, from +17 mV to +7 mV with the addition of 5 mg.L$^{-1}$ of commercial humic acid solution (Edwards, 2002). The rate of deterioration is also important, as zeta potential can change with even a slight pH variation, as demonstrated by Gustafsson et al. (2003) who observed a decrease in the negative zeta potential from -25 mV to -30 mV of flocculated anatase suspensions, when the pH increased from 4.2 to 4.5. In terms of the different systems featured in this review, no clear trend was observed with regards
to performance deterioration rate, although the most rapid reduction rates in performance were reported for organic based systems (Table 2.4). Furthermore, Edwards (2002) reported that the reduction rate increased at the negative zeta potential threshold from 34 %.mV\(^{-1}\) to 52 %.mV\(^{-1}\) as the system was spiked with 5 mg.l\(^{-1}\) of humic acid. These differences in clarification performance of the systems and the influence of organics can be related in part to the strength of the bonds within the floc aggregates, which are dependent on both the magnitude and number of inter-particle bonds (Parker, 1972; Bache et al., 1997). Traditionally, flocs formed from the coagulation of NOM are considered weak and fragile, attributed to a lack of bridging bonds (Bache et al., 1997; Jarvis et al., 2005), hence the increased sensitivity of organic systems to zeta potential when compared to inorganic contaminants such as kaolin.

In terms of the operation of physical treatment processes, floc properties such as strength are fundamental. For instance, poor resistance to shear may lead to the exposure of newly fragmented surfaces, which may alter the surface charge of the floc aggregate and result in partial restabilisation (McCurdy et al., 2004). Furthermore, the occurrence of floc breakage and the formation of smaller particles could also result in lower removal efficiencies (Boller and Blaser, 1998). Operational experience has suggested that this can impact on downstream processes such as filtration, resulting in carryover onto the filters, greater particle loads, turbidity breakthrough and reduced filter run times. Nevertheless, although research has investigated the properties of flocs formed in different systems (Bache et al., 1997; Jarvis et al., 2005), little research has focussed on establishing a link between zeta potential and floc properties.

Although it has been demonstrated that performance can be optimised using zeta potential measurements, a number of authors have also indicated that pH not only affects the magnitude of the zeta potential but also the distribution of surface charge, resulting in improved performances at the higher pHs when the same zeta potential is maintained. For instance, Gregory and Carlson (2003) found improved sedimentation and filtration performance of NOM when coagulating with alum when the pH was increased from 6.1 to 7.4. This corresponded with an increase in alum dose from 26 mg.l\(^{-1}\) to 97 mg.l\(^{-1}\) in order to maintain a zeta potential of 1.0-1.2 mV, and resulted in a more consistent performance in terms of filter run times and particle counts. Settled
turbidities were also lower at the higher pH, 0.4 NTU compared to 1.0 NTU. Gray et al. (1997) attributed the improved flotation performance of oil in water emulsions at pH 7, compared to pH 5, to a reduction in electrostatic shielding, leading to increased floc sizes. In general, the improved performance has been related to a more even distribution of charge resulting in an increased number of successful collisions (Amal et al., 1992). Consequently, this would affect the physical separation processes and not necessarily the removal of dissolved material. This was demonstrated by Gregory and Carlson (2003), who did not observe an increase in total organic carbon (TOC) removal, which remained at 68% as the pH was increased from 6.1 to 7.4. These results were mirrored by Hundt and O’Melia (1988), who also achieved a constant 80% DOC fulvic acid removal for the pH range 6-8 when the alum doses were increased accordingly. Furthermore, in the majority of cases, a high pH process involving a high coagulant dose is not always a practical solution in terms of chemical feed costs and solids handling (Gregory and Carlson, 2003). Nevertheless, in general, the removal of particulate matter is less sensitive to zeta potential, generating a wider range for optimum removal. Consequently, optimising for DOC removal will also produce good turbidity removal (Dennett et al., 1995).

2.4.3 Flotation

Flotation is widely used in treatment of upland and algal waters, and relies on the attachment of air bubbles to flocculated particles to give an effective density less than water. In this process, the ability of the bubbles to adhere to the particles is a function of the combined zeta potentials of the particles and bubbles, Hence, as the product of the zeta potentials increases then the process efficiency will reduce due to an increase in electrostatic repulsion (Gray et al., 1997). The effect of the combination of particle and bubble charges has been confirmed by studies carried out by Han et al. (2001), using clay particles, Okada et al. (1988) using oil droplets and polyelectrolytes (Gray et al., 1997; Al-Shamrani et al., 2002).

A number of authors have attempted to utilise the relationship between zeta potential and good removal in flotation processes to generate a simple floatability criteria based model of hetero-coagulation (Rao, 1974; Okada, 1990). Consequently, maximum flotation has been shown to occur when the zeta potential of the particles is minimised (Figure 2.12). Once again, differences occur between organic and inorganic systems.
In this instance, the inorganic particles (kaolin) were more sensitive to the operational zeta potential, with a reduced removal once the negative zeta potential had exceeded \(-4 \text{ mV} < \zeta < +7 \text{ mV}\) (Han et al., 2001). Whereas for humic acid, optimum removal was achieved over a wider zeta potential range of \(-15 \text{ mV} < \zeta < +13 \text{ mV}\) (Zouboulis et al., 2003). This can be explained by the fact that the mechanism for flotation is such that bubble adhesion or attachment to particles requires a hydrophobic particle surface, whereas other particles have polar surface groups that bond with water rendering them hydrophilic and less likely to adhere (Edzwald, 1995). Consequently, as the humic acid surface is more hydrophobic, this would account for the increased zeta potential range for optimal flotation. The extension of zeta potential range to higher negative values, with regards to organic particles, has also been attributed to a higher coagulant dose, compared to inorganic particles such as kaolin, such that flocs can carry enough positive charges even if the overall mobility is negative (Roussy et al., 2005).

Figure 2.12: Turbidity removal vs. zeta potential during the flotation of a high turbidity water (Jefferson, 1997).

A number of authors have identified the fact that chemical pre-treatment is an essential requirement for high efficiency within a dissolved air flotation (DAF) unit (Al-Shamrani et al., 2002; Vlaski et al., 1997; Han et al., 2001), and that the demands on flocculation ahead of DAF treatment are very different from the traditional practices associated with clarification based on sedimentation (Bache and Rasool, 2001). According to Malley (1990), DAF removes particulate matter better than conventional gravity separation when comparing the NOM coagulation using alum.
Malley and Edzwald (1991) attributed this to differences in particle size, particle density, temperature and settling rate. Furthermore, the fact that a slight degree of hydrophobicity or contamination could influence flotation of some open floc structures does confirm that the floc characteristics can have an influence on the attachment mechanism (Gochin and Solari, 1983).

While charge neutralisation may indicate that optimum flotation conditions may have been approached, a number of other factors have also been shown to influence performance. For instance, Gray et al. (1997) found flotation performance of an oil in water emulsion improved from 96.5% to 99% when the median floc size increased from 13.5 µm to 24.2 µm. This corresponded with an increase in pH from 7 to 9. This was attributed in part to the existence of polymer bridging. However, an increased pH has also been shown to result in a more even distribution of charge which may account for increased removal (Amal et al., 1992).

While this review has demonstrated that optimal flotation performance has been linked to zeta potential measurements, no reported links have been found between zeta potential and the individual operational flotation parameters such as loading rate or solids fraction for example. A number of authors have investigated the impact of surface charge modification as a means of improving flotation performance by making the electrostatic force between collectors attractive as opposed to a repulsion force. For instance Chen et al. (1998) looked at removing the algae Scenedesmus quadricuad, with an IEP of 3.5 increasing to a zeta potential of -10 mV to -25 mV at pH 5. On the addition of 10 mg.l\(^{-1}\) chitosan, which is positively charged, the IEP shifted to pH 8, and the process was driven by the electrostatic interactions between the positively charged cell surfaces and the negatively charged collector. Similar results were achieved by Liu et al. (1999). Han and Dockko (2003), attempted to change the charge of the receptor, by making positively charged bubbles to improve flotation. This demonstrates that efficiency depends on both the particle surface charge (receptor) and the charge of the collector (bubble). In addition, it is the sign of the zeta potential which is more important than the magnitude. For example, with an anionic collector, flotation is possible below the IEP when the particles are positively charged and with a cationic collector above the IEP when the particles are negatively charged (Somasundaran and Krishnakumar, 1997).
2.4.4 Filtration

Filtration processes function by the attachment of particles onto media grains of materials such as anthracite and sand. Filtration media generally exhibit a negative charge (Table 2.4), with reported values for sandstone media of -10 mV and -15 mV at pH 4 and 7 respectively (Stephan and Chase, 2002). Hence, an electrostatic repulsive force component is likely to exist. Consequently, reduction of the zeta potential of the pollutant component enhances filtration by reducing the electrostatic repulsion between the pollutant and the media. The role of zeta potential here is in determining the ability of the particles to be captured. In principle, this is the same as flotation except that the media surfaces are fixed and not constantly removed, and as a consequence tend to exhibit a more consistent surface property over time.

The relationship between zeta potential, or electrophoretic mobility, and filtration performance has been reported using a number of parameters. In general results demonstrate optimal performance when the negative zeta potential does not exceed -10 mV (Figure 2.13). For instance, Tchobanoglous and Eliasson (1970) plotted grade efficiency curves, based not on particle size, but on electrophoretic mobility and found that particles with a lower mobility were more likely to be removed, and that a linear relationship existed between the two factors. Jegatheesan et al. (1997) also observed a relationship between filtration efficiency and zeta potential. They conducted filtration experiments on latex particles and haematite particles in the presence of fulvic acid and found that a larger adhesion force corresponded to an improved particle removal due to stronger attachment onto the filter media surface. Stephan and Chase (2002) reported the use of zeta potential as a possible measure of deep bed filtration performance, in terms of permeability loss in the migration of clay particles through sandstone media. They observed that permeability loss also increased as the zeta potential was minimised due to the capture of clay particles in the filtration media. Similarly, Vane and Zang (1997) looked at packed bed electro-osmotic permeability and suggested that rapid zeta potential analysis could be used to predict osmotic performance for expected site conditions as well as selecting electrolyte control strategies to optimise electro-kinetic soil remediation processes.
As with coagulation, the presence of organic contaminants can also adversely affect filtration performance through modification of the resultant zeta potential. For instance, Dai and Hozalski (2002) investigated the filtration of Cryptosporidium oocysts in the presence of NOM. Cryptosporidium oocysts possess a negligible surface charge at neutral pH, although when exposed to NOM the magnitude of the negative zeta potential is increased, in this case to -35 mV at pH 6.7. This resulted in a decrease in oocyst removal from 51± 6% to 14± 1%. Similarly, a 75% reduction in attachment efficiency was observed by Deshiikan et al. (1998), when 5 mg.l\(^{-1}\) of George Town NOM was added to sulphate latex particles, with almost no attachment at a concentration of 20 mg.l\(^{-1}\). In both cases the addition of NOM increased the electrostatic repulsion between particles and the filtration media, causing the decreased level of filtration efficiency. However, if the particles possess a positive charge, such that the suspension is stable, then stability can be reduced through the addition of the negatively charged NOM in by reducing the zeta potential. Jegatheesan et al. (1997), reduced the zeta potential of haematite particles (25 mg.l\(^{-1}\) Fe) from +35 mV to -0.5 mV by adding 0.75 mg.l\(^{-1}\) of fulvic acid. The corresponding adhesion force increased by 93%. Prasanthi et al. (1994) demonstrated that increasing the fulvic acid concentration beyond 1 mg.l\(^{-1}\) resulted in a charge reversal and at 4 mg.l\(^{-1}\) the magnitude of the negative zeta potential had increased to -35 mV, with the particles regaining stability and a reduction in filtration efficiency.
In general, results indicate that the zeta potential window is unaffected by operational variables and relates directly to the chemistry of the system. Consequently, optimum filtration efficiency tends to occur when the surface charge is minimised, as demonstrated for a number of particle types; Kaolin, Calcite and Quartz (Besra et al., 2000), NOM (Gregory and Carlson, 2003). However, although the zeta potential considerably influences filtration efficiency for the adsorptional mechanism of liquid purification, it has practically no influence on the efficiency for mechanical purification (Leitschks and Rammensee (1999). For instance, Jegatheesan et al. (1997), found that although optimal performance occurred when the surface charge was minimised, the change in zeta potential of the latex particles had less of an influence on filtration performance than with the haematite particles. This relates to the balance of weight and electrical forces. For instance, the larger latex particles, (0.8 µm) for example, were less affected, with a 25% reduction in adhesion force when the negative zeta potential was increased from -3.9 mV to -54.6 mV. Whereas, for the haematite particles, the adhesion force was reduced by 40% although the negative zeta potential only increased from -6.1 mV to -16.2 mV. Huang et al. (1999) looked at the effect of surface properties of both kaolin and algae on removal by depth filtration. They also concluded that larger particles will result in better collector efficiency, as for non-Brownian particles (greater than 1µm), such as algae and kaolin, transport is controlled by gravity, fluid drag and interception.

A number of authors have investigated the possibility of changing the surface charge in order to increase capture and filtration efficiency. Gimbel and Sontheimer (1980) changed the zeta potential of quartz particles by adding a polymer and demonstrated that the highest filtration efficiency corresponded to the point of zero zeta potential. Shaw et al. (2000), coated Ottawa sand with hydrous iron and aluminium oxides in order to reverse the zeta potential of the sand grains from negative to positive in order to increase removal of the negatively charged Cryptosporidium oocysts. The IEP increased from pH 3 to pH 8, and the subsequent oocyst removal increased from 72 to 95%. Zhang and Bai (2002), state that surface interactions play an important role in the removal of colloids and surface modification has potential application in water treatment. They coated glass beads to make zeta potential positive over pH range 4-10 and enhance humic acid adsorption or kaolin deposition, both of which had negative zeta potential over pH range 4-10.
In general, results imply that poor chemical pre-treatment, generating high zeta potentials, cannot be corrected for during filtration whereas poor operation of upstream clarification units as seen by increased turbidity onto the filter can, to a degree, be successfully managed by good filtration operation. The operational cost of poor upstream management is reduced filter run times as the bed becomes laden with material more quickly (Logsdon et al., 2003).

2.5 Conclusions

This review has highlighted the role of zeta potential as a universal indicator of performance for a range of different treatment processes. Previous research has suggested that this can be incorporated into operational strategies by following a simple flowsheet diagram (Figure 2.14). Furthermore, the fact that, in general, zeta potential is an effective indicator, irrespective of the coagulant dose and pH combination, offers a degree of flexibility for water utilities when operating during periods of rapidly changing raw water characteristics.

The overall picture indicates that organic surface layers dominate coagulation processes such that NOM and algae systems have similar responses when compared to inorganic contaminants, and will thus control coagulation if present in a turbidity based system. Hence, the exact boundaries of the operational window are dependent on the balance of forces involved. Furthermore, although zeta potential can be used to optimise the treatment processes, it cannot provide a definition of optimum in terms of the achievable residuals post treatment, such as DOC or turbidity. This is dependent on both the make-up of the water, in terms of non charged components, and the operational parameters which are likely to influence collision efficiency.

The future challenge is therefore to understand in more detail how the nature and concentration of the contaminant load and the operational parameters influence the zeta potential boundaries, and also the robustness and ease with which the system can remain within the operational charge boundaries set.
Figure 2.14: Flowsheet diagram (Adapted from Sharp et al., 2005b).

2.6. References


Chapter 2: Literature Review


Chapter 2: Literature Review


Chapter 2: Literature Review


CHAPTER 3
NOM-COAGULANT INTERACTIONS

3(A) Seasonal variations in Natural Organic Matter and its impact on coagulation in water treatment.

Published in: *Science of the Total Environment*, (IN PRESS).

3(B) The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts.

Published in: *Environmental Pollution*, (IN PRESS).

3(C) Impact of fractional character on the coagulation of NOM.

Submitted to: *Colloids and Surfaces A: Physicochemical and Engineering Aspects.*
3(A) Seasonal variations in Natural Organic Matter and its impact on coagulation in water treatment.

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Abstract

In the past decade, a number of UK and US water utilities have been experiencing operational difficulties connected with the increased dissolved organic carbon (DOC) levels during the autumn and winter periods. This has been observed as an increase in the production of disinfection by products (DBP), and a greater coagulant demand. Resin adsorption techniques were used to fractionate raw water and investigate the variation in surface charge and coagulant-humic interactions over a 36 month period. A change in the natural organic matter (NOM) composition throughout the year was observed, with the fulvic acid fraction (FAF) increasing from 36% in September to 61% in November. However, a reduction in treatment performance is not simply due to an increase in DOC concentrations (from 4.3 mg.l\(^{-1}\) to 14.5 mg.l\(^{-1}\)), but also a change in the charge density of the NOM. It was found that hydrophilic NOM fractions possess negligible charge density (<0.06 meq.g\(^{-1}\)DOC), and it is the hydrophobic NOM fractions, FAF in particular, that exert the greater dominance on coagulation control. The hydrophilic NOM fractions are less amenable to removal through conventional coagulation with metal salts, and are therefore likely to indicate the DOC residual remaining after treatment. Understanding the seasonal changes in NOM composition and character and their reactivity with coagulants should lead to a better optimisation of the coagulation process and a more consistent water quality.

Key Words

Charge density, Coagulation, Natural organic matter, Water treatment, Zeta potential
3(A).1 Introduction

The removal of natural organic matter (NOM) has become increasingly important in light of the potential for carcinogenic disinfection-by-products (DBP) to form if organic carbon is insufficiently removed. Consequently, recent legislation around the world calls for the strict control of DBP’s (Gibbons and Laha, 1999). NOM is generally described as a poorly defined mix of organic substances with variable properties in terms of acidity, molecular weight (MW) and molecular structure (Goslan et al., 2002). Functionally, the organic material is predominantly phenolic and carboxylic in nature, but also contains alcohol, purine, amine and ketone groups (Dennett et al., 1995) and is often described as a weak anionic polymer.

Current options for dissolved organic carbon (DOC) removal include membrane filtration (80-99 % removal) (Amy and Cho, 1999; Pikkarainen et al., 2004), Ion exchange/adsorption (60-80 % removal) (Fu and Symons, 1990; Summers and Roberts, 1998), Ozonation/biodegradation (25-75 % removal) (Goel et al., 1995; Graham, 1999) and coagulation with cationic additives (10-60 % removal) (Croué et al., 1993b; Edzwald 1993; Volk et al., 2000). Whilst high removal efficiencies are possible with processes such as membranes and activated carbon they remain expensive and generally require pretreatment. Consequently, current preference is to coagulate with metal additives such as alum and ferric salts coupled to a downstream physical separation process such as sedimentation or dissolved air flotation.

The mechanisms of coagulation with regard to NOM removal are charge neutralization for colloidal material and charge complexation/precipitation for soluble compounds with additional removal occurring due to adsorption on to precipitated flocs and metal hydroxides (Randtke, 1988). Accordingly, optimisation of the coagulation process occurs under acidic conditions between the iso-electric point (IEP) of the coagulant and the NOM; pH 4.5-5.5 for iron based system and pH 5-6 for aluminium based coagulants (Amirtharajah and O’Melia, 1990).

Comparison of reported schemes reveals DOC removals between 10 and 99 % (Figure 3(A).1) with both a spatial and temporal variability. Whilst in general no clear trend exists to demonstrate a link between coagulant type, pH, dose and DOC removal, the
majority of the case studies reporting high DOC removals were associated with ferric coagulants (Fearing, 2004). Investigation of the observed differences between the schemes suggests that both the concentration and character of the organics change, especially in terms of MW, solubility, hydrophobicity, charge density and functional group composition (Edzwald, 1993; Korshin et al., 1997; Schlautman and Morgan, 1994; Vuorio et al., 1998). Mechanistic appraisals have demonstrated that coagulants preferentially remove hydrophobic material but are relatively poor at removing hydrophilic, low molecular weight organics (Fearing et al., 2004b). However, removal of each component part is not consistent over time even at a single site suggesting changes to the character of the individual fractions.

![Figure 3(A).1: Comparison of percentage DOC removal by aluminium and iron based coagulants (Fearing, 2004).](image)

Given that the coagulation of NOM is predominately charge related for both soluble and colloidal material then the electrical character of the NOM is likely to be a key parameter in describing the process. Characterisation in this regard relates to either surface potential (expressed as zeta potential or electrophoretic mobility) or the total surface charge (measured as colloidal charge or charge density) (Ratnaweera et al., 1999). Zeta potential indicates the surface potential of the colloidal system and is commonly related to the stability of the colloidal materials under any given set of water characteristics. However, it does not necessarily provide a proportional indication of the amount of coagulants required for destabilization. In contrast, the total surface charge of the raw water is proportional to the theoretical coagulant
demand providing a charge neutralisation mechanism prevails. Previous attempts to link the coagulation of NOM to the charge character of the water have found that optimum doses occurred at a range of zeta potentials between -8 and +8 mV depending on the water source and the pH of coagulation (Ratnaweera et al., 1999). Hence indicating that complete neutralization of the charge is not required, only that the barrier generated by electrostatic repulsion is minimized or removed. The aim of the current paper is to investigate the character of NOM in terms of its charge properties and how this influences the interactions between coagulants and NOM.

3(A).2 Materials and Methods

3(A).2.1 Works overview
The raw water investigated in the current study was sampled from a moorland water works in the north of England and is typically characterized as a low turbidity (3.7-7.0 NTU), low alkalinity (20 mg.l⁻¹ CaCO₃), high colour (44-160 Hazens), high DOC (4.3-14.5 mg.l⁻¹) water. The treatment works contains coagulation with ferric sulphate, dissolved air flotation and deep bed filtration prior to chlorination and is mainly designed to control DOC and metal ions in the water. Samples were taken at various periods from the inlet channel from the reservoir.

3(A).2.2 Apparatus
The turbidity of the samples was measured using a HACH2100 turbidity meter (Camlab, UK). A Shimadzu 5000A TOC analyzer was used for determining the DOC content. UV-Abs (m⁻¹) at a wavelength of 254nm was measured using a Jenway 6505 UV/Vis spectrophotometer. All samples were passed through a Fischer Scientific MF200 1µm glass microfibre filter paper before both UV and DOC analyses. The zeta potential was measured with a zetasizer 2000HSA (Malvern Instruments, UK). The coagulation and flocculation experiments were undertaken using a Phipps and Bird PB-900 six paddle jar tester.

3(A).2.3 Reagents
The coagulant used was ferric sulphate (Ferripol xl, EA West). The cationic polymer polydiallyldimethylammoniumchloride (polyDADMAC), with a MW of 100,000-200,000, was obtained from Sigma-Aldrich as a 20 wt% aqueous solution. This was
then diluted to a 0.1% solution with the charge density calculated to be 6.2 meq.g\(^{-1}\) from the manufacturer’s information.

### 3(A).2.4 Procedure

Raw water samples, obtained from between November 2000 and September 2003, were fractionated by XAD resin adsorption techniques into hydrophobic (HPO) and hydrophilic (HPI) components using a method adapted from Malcolm and MacCarthy (1992) and previously used on samples from the same water source (Goslan et al., 2002). The hydrophobic fractions were then separated further by reducing the pH to 1 and precipitating the humic acid fraction (HAF) fraction, with fulvic acid fraction (FAF) remaining in the supernatant. The non-adsorbed fraction was categorised as hydrophilic non adsorbed (HPINA). Detailed descriptions of the methods used can be found in Goslan et al. (2002).

Charge density was determined by an adjusted form of the method used by Kam and Gregory (2001), which monitored the change in charge as a function of polyDADMAC dose and was shown to produce a clearer end point determination than traditional ion titration methods. Varying amounts of 0.1% poly DADMAC were added to a 100 mL solution of deionised water with 2.5 mg of the appropriate NOM fraction adjusted to pH 7 with NaOH. The hydrophilic fractions were analysed at lower concentrations and with a more dilute polyDADMAC source due to availability issues.

The NOM-coagulant interactions were investigated by adding 20mg of sodium hydrogen carbonate to one litre of de-ionised water containing the required amount of NOM fraction and a magnetic stirrer bar. The beaker was then placed on a magnetic stirrer and 2mg of required coagulant, as the metal, was added in order to achieve the required NOM: coagulant ratio. Portions of the solution were then removed and adjusted to varying pHs between 2 and 9 and the resulting zeta potential recorded. The increase in ionic strength as a result of a reduction to pH 2 did not influence the zeta potential. In addition, the zeta potential of the original solutions were also measured over a two hour time period and also remained stable.
With regards to the coagulation-flocculation experiments only one jar was used at any one time. Raw water samples were stored at 5°C prior to jar testing and subsequent jar testing was undertaken at room temperature (20°C). The initial rapid mix was for 2 minutes at 200 rpm whilst adding the required dose of coagulant. NaOH was then added, until reaching the required coagulation pH, whilst stirring for an additional 1.5 minutes, also at 200 rpm. The jars were then stirred for 15 minutes at 30 rpm and left to settle for an additional 20 minutes before taking the samples, which were extracted from the centre of the jar. The zeta potential was initially measured at varying stages of the jar test procedure from the end of the rapid mix to the final settlement, and was found to show no significant variation. The zeta potential was measured with a zetasizer at 25°C. The zetasizer yields estimates and standard deviations of the zeta potential directly, and all measurements were conducted in triplicate. The general accuracy of the zetasizer was determined using standard solutions (Malvern Instruments, UK.)

3(A).3 Results and Discussion

3(A).3.1 Seasonal trends and variations
The DOC of the raw water decreased across the monitoring period, October 2002 to September 2003, with a high of 14.5 mg.l⁻¹ in December 2002 to a low of 4.3 mg.l⁻¹ in September 2003 (Figure 3(A).2). Over this period, the specific UV absorbance (SUVA) appeared insensitive to the change in organic levels with an average value of 6.1 (± 2.3 m⁻¹.l.mg⁻¹DOC) suggesting the water was predominately hydrophobic in character.
Figure 3(A).2: Annual DOC and zeta potential, for raw water samples taken between October 2002 and September 2003.

Fractionation of the raw water confirmed this with up to 80% of the organic matter being associated with the fulvic and humic acid fractions (Figure 3(A).3). Throughout the sampling period the DOC concentration of the hydrophilic (combined) and humic acid fractions remained relatively stable at 2.5 ± 0.5 mg.l⁻¹ and 2.2 ± 0.5 mg.l⁻¹ respectively. In contrast, the FAF demonstrated greater variability, in terms of total DOC, with a concentration of 4.4 ± 1.4 mg.l⁻¹ throughout the sampling period (Figure 3(A).4). The variation in fulvic acid concentration was the major component of change in the fractional make up of the water. To illustrate, in November 2000, the relative contribution of each fraction to the total DOC of the water was 61, 18 and 21% for the FAF, HAF and hydrophilic fractions respectively. Whereas, in September 2003, the relative fractions were 36% for FAF, 32% for HAF and 32% for the hydrophilic fractions; demonstrating a much lower contribution from the FAF fraction.
Comparison with published data reveals similar levels and variation in DOC across different seasons for river and lake systems from both Europe (Ratnaweera et al., 1999) and the United States of America (Aiken et al., 2004). For instance, the DOC from an intake from the Santa Ana river varied between a low of 2.2 mg.L⁻¹ and a
high of c9 mg.l$^{-1}$ between June 2000 and May 2002 (Aiken et al., 2004). Fractionation of waters from different sources and locations reports much greater variability than observed in the current study. Analysis from around 100 different surface source waters indicated that typically about 56% of the material is hydrophobic in character (Leenheer and Huffman, 1976). Similarly Croué et al., (1993a,b), reported that water taken from the Apremount reservoir was composed of 51 % hydrophobic and is higher than the 38 % reported for the Colorado river in September 2000 (Aiken et al., 2004). The range of values (68-79%) in the current study are similar to values reported for highly coloured waters in Canada, Scandinavia and Russia where the hydrophobic content typically varies between 60 and 80 % of the total DOC (Malcolm, 1985). The observed differences are consistent with the view that as the DOC of a water increases the majority of the additional organic matter is likely to be hydrophobic in character (Malcolm, 1985) and hence high DOC waters tend to be more hydrophobic in character. The observed variations throughout the year are often explained in relation to a microbially driven mechanism of DOC release (Scott et al., 2001). The microbes within the soil matrices are more active during the warmer, relatively drier period in the summer/early autumn but the impact of this is not seen at the treatment works until sufficient rainfall/snow melt occurs to flush the released materials into the intake system. After which time the soil becomes colder and more water laden and aerobic microbial activity significantly decreases.

Charge density measurements of the raw water fractions in the current study revealed the majority of the total colloidal charge to exist in the hydrophobic fractions. For instance, in relation to water fractionated from samples collected in April 2002, the charge densities of the individual fractions were 6.8, 4.2 and 0.006 meq.g$^{-1}$ DOC for the HAF, FAF and HPIA fractions respectively (Figure 3(A).5). Kam and Gregory (2001) reported a value of 5-5.6 meq.g$^{-1}$DOC for commercial humic acid and similar values have been reported elsewhere with humic and fulvic waters typically exhibiting charge densities between 5-15 meq.g$^{-1}$DOC (Table 3(A).1). The charge density of the hydrophilics was very low such that the levels for the HPINA fraction was below the level of detection. Edzwald (1993) reported similar findings for both hydrophilic bases and neutrals and found that the acid fraction was at least an order of magnitude smaller than the hydrophobic fractions; compared to 2-3 orders of magnitude lower in the current study.
Conversion of the charge densities to charge concentration reveals that whilst the HAF fraction has the highest charge density the largest proportion of the total load comes from the FAF fraction. To illustrate, in the case of the water collected in April 2002, the total charge of the individual fractions was $0.013, 0.026$ and $0.08 \times 10^{-3}$ meq.g$^{-1}$ for the HAF, FAF and HPIA samples respectively. To establish how much impact variation in the FAF fraction may have on the total charge, the charge density of the FAF fraction was monitored throughout the sampling period (Figure 3(A).6). The charge density varied between $2.5$ meq.g$^{-1}$DOC in September 2003 to $4.2$ meq.g$^{-1}$DOC in October 2002 representing a variation of 60 % compared to the maximum recorded value. Combining the change in charge density and DOC concentration for the same period reveals that the total charge of the FAF fraction varied between $0.006$ and $0.022$ meq.l$^{-1}$ throughout the sampling period. Collins et al., (1986) used potentiometric titration to determine the carboxylic acidity of the hydrophobic organic matter for a number of raw waters and fulvic acid components. For example, for the Grasse River and Floridan aquifer samples, the hydrophobic fraction contributed a charge of $0.035$ meq.l$^{-1}$ and $0.030$ meq.l$^{-1}$ respectively. The differences in carboxylic acidity or charge density will therefore influence the coagulant demand and the water treatment process as a higher charge is associated with the larger MW fractions (Collins et al., 1986; Ratnaweera et al., 1999).
Table 3(A).1: Previously determined humic substance charge densities.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Method</th>
<th>Charge density (meq.g(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fulvic acid</td>
<td>Potentiometric titration</td>
<td>13.5 ±1.4 (hydrophobic carboxylic acidity)</td>
<td>Collins et al., 1986.</td>
</tr>
<tr>
<td>Grasse river water</td>
<td>Potentiometric titration</td>
<td>8.0 ±1.2 (hydrophobic carboxylic acidity)</td>
<td>Collins et al., 1986.</td>
</tr>
<tr>
<td>Humic and fulvic acids</td>
<td>pH titration</td>
<td>5-10</td>
<td>Tipping, 1993</td>
</tr>
<tr>
<td>Fulvic acids</td>
<td>Colloid titration</td>
<td>10-15</td>
<td>Edzwald, 1993</td>
</tr>
<tr>
<td>Humic acids</td>
<td>Colloid titration</td>
<td>5-10</td>
<td>Edzwald, 1993</td>
</tr>
<tr>
<td>Organic carbon</td>
<td>Alkametric titration</td>
<td>12 (at max charge density)</td>
<td>Tiller and O’Melia, 1993</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.1 at pH 4</td>
<td></td>
</tr>
<tr>
<td>Humic acid</td>
<td>Colloid titration</td>
<td>5-5.6</td>
<td>Kam and Gregory, 2001</td>
</tr>
<tr>
<td>Humic acid</td>
<td>Colloid titration</td>
<td>1.5 ± 0.04</td>
<td>Mikkelsen, 2003</td>
</tr>
</tbody>
</table>

Figure 3(A).6: Variation in FAF charge density.
In relation to the specific colloidal charge, the zeta potential of the raw water was -15 ± 4 mV throughout the sampling period. Alteration of the pH of the water revealed a stable zeta potential value between pH levels of 4 and 8 and an iso-electric point (IEP) of 1.7-2.2. Within the study, both the raw water zeta potential and its pH profile remained fairly constant irrespective of changes in DOC or fractional make up. The results indicate that the charge of the colloids within the raw water can be characterised by an acidic dissociation site model (Hunter, 1981). This is expected as the main functional groups identified within the structures of NOM are predominately carboxylic and phenolic groups with a pKa in the range of 3-6 and 8-10 respectively (Edwards et al., 1996; Gu et al., 1995; Kretzschmar and Sticher, 1997; Tiller and O’Melia, 1993). The stable response to pH until a value of around 4 indicates that for the current water source the carboxylic groups are likely to dominate the charge response of the water.

Comparative studies, varying the pH between 1 and 9 for the individual fractions extracted from April 2002 raw water, revealed a clear difference between hydrophobic and hydrophilic fractions (Figure 3(A).7). The two hydrophobic fractions have similar profiles to the raw water such that the zeta potential values above pH 4 were -13 ± 3.7 mV, -17 ± 0.3 mV, and -25 ± 2.2 mV for the FAF, raw water and HAF respectively. In contrast, the zeta potential of the hydrophilic fraction decreased consistently across all the pH values tested. For instance, the zeta potential of the HPIA and HPINA fractions decreased from 2.1 ± 0.2 mV at pH 2 for both fractions to -4 ± 3.2 mV and -7 ± 2 mV at pH 9 for the HPIA and HPINA fractions respectively (Figure 3(A).7). The corresponding IEP of all the fractions was 1.5, 1.6, 1.7, 4 and 4.7 for HAF, FAF, raw water, HPIA and HPINA respectively. Previous work on the charge of NOM fractions has shown that the pKa of the FAF fraction to be around 2 ± 0.3 and can be attributed to the carboxyl groups (Leenheer et al., 1995a; 1995b). Whereas the hydrophilic fractions are composed of weaker acidic groups with correspondingly much higher values for their IEP. Comparing the different fractions to the raw waters shows as expected that the hydrophobic materials dominate the specific colloidal charge character of the water.
3(A).3.2 NOM-Coagulant interactions

The interactions between the NOM samples and coagulant ($M^+$) were monitored through changes in the IEP of the sample at various DOC to coagulant mass ratios. The IEP of the systems decrease as the DOC:$M^+$ ratio increases in all cases. To illustrate, in relation to the December 2002 water, the IEP of the systems decreased from 8 to 2.7 as the DOC:Fe ratio increased from 0 to 2.4 (Figure 3(A).8). The exact relationship between DOC:$M^+$ ratio and IEP was different for each sampling period and ranged between the extremes of December 2002 and September 2003. To demonstrate, to achieve an IEP of 4.4 in December 2002 required a DOC:Fe ratio of 1.2:1, whereas in September 2003 a lower ratio was required (2:1) in order to reach the same IEP (Figure 3(A).9). Importantly, the existence of a variation in the relationship between IEP and mass ratio between different water samples indicates that the changes must be due to character (Tseng et al., 2000) and can be explained in terms of the variation in total charge of the water from one period to the next. For example, at a dose ratio of 2:1 the IEP of the system was 3 in December 2002 and 4.4 in September 2003 indicating the samples in September 2003 were less influenced by the organic matter at the same mass ratio. The differences coincide with the
approximate minimum and maximum in the charge density of the FAF fraction described previously.

Calculation of the neutralizing charge provided by adding Ferric, based on speciation data (Jiang and Graham, 1998), reveals the coagulant charge density of the added ferric to be 35.5, 30.7, 12.6 and 1.7 meq.g\(^{-1}\)Fe at pH values of 4, 5, 6 and 7 respectively. The decrease in available charge as pH increases gives a clear indication why coagulation must proceed under acidic conditions; the charge neutralizing capacity of ferric is 20.8 times greater at pH 4 compared to pH 7. Comparison between mass and charge ratios under equivalent conditions reveals that at the IEP there is a broad agreement between the two. Importantly, the change of mass ratio at any given pH from one water sample to the next indicates that stoichiometric ratios are not appropriate for predicting dose requirements. Instead a simple charge density measurement appears to provide a more consistent indication of dose requirement.

![Diagram showing effect of coagulation pH on zeta potential for December 2002 raw water coagulated with iron to different DOC: coagulant ratios.]

*Figure 3(A).8: Effect of coagulation pH on zeta potential for December 2002 raw water coagulated with iron to different DOC: coagulant ratios.*
Chapter 3(A): NOM-Coagulant Interactions

The interactions of the individual NOM fractions with iron based coagulants were investigated further by increasing the concentrations of organics obtained from the April 2002 fractionation, dosed with 2 mg.l\(^{-1}\) (as metal) of coagulant (Figure 3(A).10). The FAF fraction results in the largest shift in IEP from pH 8 with no NOM present (i.e. ferric hydroxide) to pH 3 for a 2:1 FAF:Fe ratio. This was followed by the HAF and HPIA fractions at pH 3.8 and 4.8 respectively at the same mass ratio. The HPINA did shift the IEP although increasing the DOC concentration further did not have an additive effect. Therefore implying only a certain concentration of the HPINA combined with the iron which once exceeded did not affect the IEP of the system. Importantly, the FAF fraction appears to be critical in determining the resultant charge properties of the NOM-coagulant system and hence the dose requirements. Interestingly, complimentary work on floc structural properties has indicated that variation in the FAF component generates the greatest degree of change in the size and strength of the resultant flocs (Jefferson et al., 2004).
Reports in the literature suggest competitive interaction between coagulants and NOM are favoured towards larger MW, more hydrophobic, more highly charged components (Gu et al., 1995; Huang and Shiu, 1996) due to the combination of charge neutralization, complexation/precipitation and ligand exchange mechanisms which are thought to dominate NOM removal (McKnight et al., 1992). The current work agrees with that as the hydrophobic, rather than hydrophilic material, dominates the interactions between NOM and the metal coagulant. This is confirmed by studies that have examined DOC removal across different fractions where only hydrophobic fractions are significantly removed and hydrophilic non acids are almost completely not removed during coagulation (Fearing et al., 2004a). Further, recent comparisons between the coagulation of different source waters has revealed that the differences observed in the residual DOC correlate well with the difference in the initial level of hydrophilic fractions (Sharp et al., 2004). Consequently, the hydrophilic concentration in a water acts as a good indicator of the likely residual concentration achievable by coagulation.

The comparison between humic and fulvic acids is less clear as they are both hydrophobic and have MW distributions that overlap considerably. To illustrate, in the case of the water reported in the current study, high performance size exclusion chromatograms (HPSEC) of the HAF and FAF had a distribution between 5.27 and
11.2 minutes and 6.50 and 11.2 minutes respectively, showing an overlap across the 0.5-5kDa range (Goslan, 2003). Reports in the literature discuss the issue in relation to the principle removal pathways for the two components. HAF is thought to be removed through a combination of charge neutralization (for colloids), complexation/precipitation and ligand exchange adsorption (Huang and Shiu, 1996). Whereas FAF is thought to be principally removed through an adsorption pathway (McKnight et al., 1992). Evidence for this has been shown by recording pH changes due to the exchange of OH\(^-\) groups as the adsorption process proceeds (Gu et al., 1995). The situation is further complicated as evidence suggests adsorption follows a two stage sequence of fast followed by slow adsorption during which competitive displacement occurs where high absorption affinity compounds replace low affinity ones (Avnea and Koopal, 1999). Replacement is thought to be aided as residual charge on the adsorbed molecules repel each other and reduce the affinity of large MW compounds thus enabling smaller MW material to adsorb shifting the balance of molecules bound to the floc.

However, it should be noted that most of the reported work has involved synthetic solutions of known chemistry or preformed adsorption sites. Consequently interpretation to the current situation of polydispersed NOM solutions and their interaction to added coagulants is unclear and ultimately the exact hierarchy is unknown. Whilst the exact explanation of the observed interactions is unclear it does however provide a useful guide to understand differences in observed removal patterns and the properties of the resultant flocs. Given that optimum removal occurs over a range of zeta potentials around the zero value (Parsons et al., 2004) the concentration and character of the FAF fraction is likely to control the dose requirements to maintain the system within the appropriate range. Also the balance of hydrophobic to hydrophilic compounds will control the optimised residual concentration. This is demonstrated by a case study reported by Sharp et al., (2004), which showed that the residual DOC was minimised between zeta potential values of +5 mV and -10 mV for a mountain water source affected by elevated organic levels during the spring snowmelt run-off. Comparison with other source waters showed similar zeta potential ranges but different residual levels. The difference in residual concentration correlated well with the difference in initial hydrophilic content of the source waters. Therefore, optimising the coagulation process based on charge is likely
to result in improved hydrophobic NOM removal, although the same level of success may not be observed with the hydrophilic fractions.

3(A).4 Conclusions

Results from this investigation show that it is not simply the increased organic concentration, but also the change in composition and character which creates a greater coagulant demand. The hydrophobic NOM fractions (HAF and FAF) have a significantly higher charge density than the hydrophilic NOM fractions. Hence, the negligible charge density of HPINA fraction may explain the reduced interaction with iron and the poor removal of this fraction with conventional coagulation methods. The largest proportion of the total charge comes from the FAF fraction, which also exerts the greatest influence on coagulation conditions. The charge density of the FAF fraction has also shown some variation throughout the sampling period. However, due to the heterogeneous mix of compounds it is still difficult to make conclusive statements with regards to the differences between HAF and FAF. In general, without some form of charge monitoring many of the hidden changes discussed in this paper could go unnoticed, especially if the process is simply controlled on UV$_{254}$ levels and pH, thus operating far from optimum.

3(A).5 References


3(B) The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts.

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Abstract

The removal of natural organic matter (NOM) is one of the main challenges facing water utilities in both the UK and the US. Whilst traditional treatment with trivalent coagulants has proven a successful strategy in the past, operational problems are now being reported during periods of elevated organic levels in the water. Characterisation of the pollutants in terms of polarity, molecular weight and charge, provides a method to understand the impact of the observed temporal and spatial variations in terms of a mechanistic parameter relevant to the treatment processes. Results from this study demonstrate that it is not simply the increased organic concentration, but also the change in NOM composition and character, which influences the impact on the treatment processes. Consequently, monitoring of these parameters provides an insight into how to manage the impact caused by environmental changes to the catchments.

Key Words

Coagulation, Charge density, Natural organic matter, Water treatment, Zeta potential.
3(B).1 Introduction

The removal of natural organic matter (NOM) is one of the main challenges facing water utilities in both the UK and the US, especially for low alkalinity, low turbidity source waters delivered from moorland or mountain catchments. Changes in land management, such as the disturbance of peat or vegetation damage, can lead to increased decomposition and the production of loosely bound NOM (Worrall and Burt, 2005). The accumulated organics are then flushed into the aquatic environment as a result of increased surface run-off, such as a rainfall event or snowmelt run-off (Hurst et al., 2004).

Whilst traditional treatment with trivalent coagulants has proven a successful strategy in the past, operational problems are now being reported during these periods of elevated organics, the impact of which has been observed as an increase in the production of potentially carcinogenic disinfection by products (DBP), formed when residual organics react with chlorine during water treatment.

NOM is defined as a highly heterogeneous mixture of organic compounds which are known to vary both spatially and temporally in terms of molecular weight (MW), solubility, hydrophobicity, charge density and functional group composition (Edzwald, 1993; Owen et al., 1993; Korshin et al., 1997; Scott et al., 2001). However, whilst broad spatial variations in the nature of organics are reasonably well understood, the variations in temporal change at a particular site are more uncertain. For example, reported variations in the removal of organics of between 10 and 99% (Fearing, 2004), which are not consistent over time, even for a single site, are most likely to be associated with changes in NOM character.

NOM contains compounds over a broad spectrum of MW, although it is the larger MW humic substances, absorbing visible light and giving the water its characteristic brown colouration, which contribute significantly to the overall charge load of the water. Charge densities for the hydrophobic NOM fractions are in the region of 5-15 meq.g$^{-1}$ of dissolved organic carbon (DOC), compared to the hydrophilic NOM fractions for which the contribution is an order of magnitude less (Edzwald, 1993;
Tipping, 1993; Collins et al., 1986). Consequently, the impact of varying NOM fraction make-up is to alter the coagulant demand of the system.

Coagulation is believed to involve a combination of charge neutralization, complexation/precipitation and ligand exchange mechanisms (McKnight et al., 1992; Randtke, 1988). Furthermore, optimisation of the coagulation process occurs under acidic conditions between the iso-electric point (IEP) of the coagulant and the NOM, corresponding to pH 4.5-5.5 for an iron based system and pH 5-6 for aluminium based coagulants (Amirtharajah and O’Melia, 1990). Previous attempts to link the coagulation of NOM to the electrical character of the water have looked at defining a range of zeta potentials, varying between -8 and +8 mV depending on the system involved, within which residual concentrations are both low and stable (Gregory and Carlson, 2003; Ratnaweera et al., 1999). Furthermore, the definition of a range also suggests that complete neutralization of the charge is not required, only that the barrier generated by electrostatic repulsion is minimized or removed.

Aluminium and iron salts are widely used for coagulation in drinking water treatment. They act to destabilize and remove both colloidal and dissolved impurities, such as DOC, through the production of cationic hydrolysis products. However, despite their similarities, the affinity of each coagulant for different impurities is known to vary. For example, with regards to DOC removal, a number of authors have reported improved performance with iron salts compared with alum (Edzwald and Tobison, 1999; Bell-Ajy et al., 2000). It has been suggested that this is due to the fact that alum based coagulants are more selective and iron can remove more DOC at higher doses, especially when treating elevated levels of organics (Budd et al., 2004; Kastl et al., 2004). Coagulation with iron salts has also been shown to produce flocs that are both larger and more numerous than those formed with alum, therefore increasing the likelihood of collisions and subsequent removal (Ratnaweera et al., 1999; Jarvis et al., 2005).

The aim of the current work is to understand the impact of observed temporal and spatial variations in NOM composition and character, and to investigate the impact of this in relation to observed differences when coagulating NOM with either iron or aluminium.
3(B).2 Materials and Methods

3(B).2.1 Works overview
The raw water investigated in the current study is taken from Albert Water Treatment Works (WTW), a moorland water works in the north of England. Albert WTW treats water which has drained down through the peat catchment system before reaching Albert reservoir, ultimately producing a highly coloured organic rich water for the majority of the year (44-160 Hazens). Other raw water characteristics include low turbidity (3.7-7.0 NTU), low alkalinity (20 mg.l⁻¹ CaCO₃), and high DOC (4.3-14.5 mg.l⁻¹). Samples were taken at various periods from the inlet channel to the reservoir.

3(B).2.2 Apparatus
The turbidity of the samples was measured using a HACH2100 turbidity meter (Camlab, UK). A Shimadzu 5000A TOC analyzer was used for determining the DOC content. UV-Abs (l.m⁻¹) at a wavelength of 254nm was measured using a Jenway 6505 UV/Vis spectrophotometer. All samples were passed through a Fischer Scientific MF200 1µm glass microfibre filter paper before both UV and DOC analyses. The zeta potential was measured with a zetasizer 2000HSA (Malvern Instruments, UK). The coagulation and flocculation experiments were undertaken using a Phipps and Bird PB-900 six paddle jar tester.

3(B).2.3 Reagents
The coagulants under investigation were: Ferric Sulphate (Ferripol xl, EA West) and Aluminium Sulphate (Kemwater, UK). Charge density measurements were determined using the cationic polymer polydiallyldimethylammoniumchloride (polyDADMAC), with a MW of 100,000-200,000, obtained from Sigma-Aldrich as a 20 wt% aqueous solution.

3(B).2.4 Procedure
Raw water samples were fractionated by XAD resin adsorption techniques into hydrophobic (HPO) and hydrophilic (HPI) components using a method adapted from Malcolm and MacCarthy (1992). Detailed descriptions of the methods used can be found in Goslan et al., (2002), where the procedure has also been undertaken using Albert raw water.
Charge density was determined by an adjusted form of the method used by Kam and Gregory (2001), which monitored the change in charge as a function of polyDADMAC dose and was shown to produce a clearer end point determination than traditional ion titration methods. This method has been used previously with Albert water samples (Sharp et al., 2004).

Raw water samples were stored at 5°C prior to jar testing, which was undertaken at room temperature (20°C) using a previously published standard method (Sharp et al., 2004), involving a 3.5 minute rapid mix at 200 RPM, a 15 minute 30RPM flocculation stage and 20 minute settlement period.

The NOM-coagulant interactions were investigated by adding 20mg of sodium hydrogen carbonate to one litre of de-ionised water containing the required amount of NOM fraction and a magnetic stirrer bar. The beaker was then placed on a magnetic stirrer and 2mg of required coagulant, as the metal, was added in order to achieve the required NOM:Coagulant ratio. Portions of the solution were then removed and adjusted to varying pHs between 2 and 9, with NaOH and HCl, and the resulting zeta potential recorded. The increase in ionic strength as a result of a reduction to pH 2 did not influence the zeta potential. In addition, the zeta potential of the original solutions were also measured over a two hour time period and also remained stable.

3(B).3 Results and Discussion

3(B).3.1 Seasonal trends and variations

The DOC of the raw water samples varied across the period of investigation from a low of 6.6 mg.l⁻¹ in September 2003 to a high of 13.3 mg.l⁻¹ in August 2004. (Figure 3(B).1). Over the temporal period of the investigation, the specific UV absorbance (SUVA) appeared insensitive to the change in organic levels with an average value of 5.1 (± 1.1 m⁻¹.l.mg⁻¹DOC) with the value suggesting the water was predominately hydrophobic in character (Edzwald and Tobiason, 1999). Fractionation of the raw water confirmed this, with between 59% and 75% of the organic matter being associated with the fulvic and humic acid fractions (Figure 3(B).1). Previous research at Albert has shown the fulvic acid fraction (FAF) concentration to be the most variable, whereas the humic acid fraction (HAF) and hydrophilic fractions remained
relatively stable (Sharp et al., 2005a), and this was the case for the majority of the sampling period during this investigation. For instance, the hydrophilic concentration (hydrophilic acid (HPIA) and hydrophilic non adsorbed (HPINA) combined) was 2.4 ± 0.4 mg.l⁻¹ and the HAF fraction concentration was 2.0 ± 0.6 mg.l⁻¹. In contrast, the FAF fraction demonstrated greater variability, in terms of absolute values, at 3.9 ± 1.3 mg.l⁻¹. However, the sample taken in August 2004 followed a heavy rain incident and the concentrations were 4.9 mg.l⁻¹, 2.9 mg.l⁻¹ and 5.4 mg.l⁻¹, for HAF, FAF and the combined hydrophilic fractions respectively. The impact of this was to significantly increase the hydrophilic content of the water from 25-33% to 41%.

![Figure 3(B).1: NOM fraction contribution expressed as mg.l⁻¹DOC. Humic acid fraction (HAF), Fulvic acid fraction (FAF), Hydrophilic acid (HPIA) and Hydrophilic non adsorbed (HPINA).](image)

Variations in organic composition and character within this study are similar to those published elsewhere (Owen et al., 1993; Ratnaweera et al., 1999), which have concluded that the observed differences are often consistent with the view that as the DOC of a water increases the majority of the additional organic matter is likely to be hydrophobic in character (Malcolm, 1985). However, results obtained during this investigation highlight that during certain periods, particularly following initial periods of heavy rainfall, there is not only an increase in hydrophobic material but also an additional increase in the hydrophilic content of the water. Similar findings
have been reported by Scott et al., (1998), who also looked at the seasonal variations in NOM obtained from a UK upland peat catchment system. During a four year study, they observed variations in the hydrophilic content of the water ranging between 20 and 80%, with the dissolved organic matter increasing in hydrophilicity during the summer months. The observed variations throughout the year are often explained in relation to a microbially driven mechanism of DOC release (Scott et al., 2001). The microbes within the soil matrices are more active during warmer, relatively drier periods in the summer/early autumn, but the impact of this is not seen at the treatment works until the organic matter enters the aquatic environment during the first rainfall (Hurst et al., 2004). In terms of NOM composition during this period, Scott et al., (1998) concluded that the initial increases in hydrophilic content were attributed to its relative ease of dissolution, whereas the hydrophobic material is leached more slowly resulting in a more gradual increase and increased variation.

In relation to the electrical character of the individual fractions, charge density measurements of the raw water fractions in the current study revealed the majority of the total colloidal charge to exist in the hydrophobic material. For instance, the charge densities of the individual fractions were $5.1 \pm 1.3$, $3.6 \pm 0.7$ and $1.0 \pm 0.6$ meq.g$^{-1}$ DOC for the HAF, FAF and HPIA fractions respectively (Figure 3(B).2). In comparison, Kam and Gregory (2001) reported a value of 5-5.6 meq.g$^{-1}$DO for commercial humic acid, and similar values have been reported elsewhere, with humic and fulvic waters typically exhibiting charge densities between 5-15 meq.g$^{-1}$DOC (Collins et al., 1986; Edzwald, 1993; Tipping, 1993). The charge density of the Hydrophilics was very low, such that the levels for the non adsorbed fraction (HPINA) was below the level of detection. Edzwald (1993) also reported similar findings for both hydrophilic bases and neutrals and found that the charge density of the hydrophilic acid fraction was at least an order of magnitude less than the hydrophobic fractions, as seen in the present investigation.

Conversion of the charge densities to charge concentration revealed that the majority of the charge load comes from the hydrophobic fractions. For instance, the charge load from the hydrophobic fractions for April 2002, January 2004 and August 2004 was calculated to be 0.0266 meq.l$^{-1}$, 0.0263 meq l$^{-1}$, and 0.0280 meq.l$^{-1}$ respectively. Collins et al., (1986) obtained similar values for a number of raw waters and fulvic
acid components using potentiometric titration to determine the carboxylic acidity of the hydrophobic organic matter. With regards to the hydrophilic charge load, determined for the current investigation, the value was significantly less with $0.054 \times 10^{-3}$ meq.l$^{-1}$, $0.0043$ meq.l$^{-1}$ and $0.0035$ meq.l$^{-1}$ for the same samples (April 2002, January 2004 and August 2004). Consequently, the differences in carboxylic acidity or charge density between the fractions are likely to influence the coagulant demand during the water treatment process, as a higher charge is associated with the larger MW fractions (Collins et al., 1986). However, the charge load from the hydrophilic fractions did vary significantly and therefore cannot always be discounted, as shown by the August 2004 sample in which it contributed 11% to the total fraction charge load.

![Figure 3(B).2: The impact of NOM fraction on charge density (mean of all samples).](image)

High performance size exclusion chromatography (HPSEC) analysis provides a useful indication of the molecular size of the organic material, with the larger molecules eluted from the column first. In this case, HPSEC traces of the HPIA fraction clearly demonstrate its variability, with respect to both molecular size and UV$_{254}$ absorbance (Figure 3(B).3). January and August 2004 samples show the existence of a primary peak, eluted at approximately 7 minutes and corresponding to a molecular size of approximately 5 kilo Daltons (Goslan, 2003), which was not present in the April 2002 sample. The area under the graph also increased by 278% in August 2004 compared
to the April 2002 sample when the corresponding HPIA charge load increased by approximately 2 orders of magnitude. Consequently, the fact that the charge load originating from each fraction has also been shown to vary demonstrates that coagulant demand cannot be calculated for a particular water based solely on bulk parameters, such as DOC concentration, or NOM fraction make-up.

![HPSEC traces of the HPIA fraction isolated from April 2002, January 2004 and August 2004 raw water samples.](image)

Figure 3(B).3: HPSEC traces of the HPIA fraction isolated from April 2002, January 2004 and August 2004 raw water samples.

Over the pH range of natural waters, pH 5-9, the zeta potential of the raw water was \(-15 \pm 4\) mV throughout the sampling period, with a corresponding IEP of 1.7-2.2 (Figure 3(B).4). These results indicate that the specific colloidal charge of the raw water can be characterised by an acidic dissociation site model (Hunter, 1981). This is expected, as the main functional groups identified within the structures of NOM are predominately carboxylic and phenolic groups with pKas in the range of 3-6 and 8-10 respectively (Gu et al., 1995; Edwards et al., 1996). The stable response of the raw water to a pH shift between 4 and 8 indicates that in this case the carboxylic groups are likely to dominate the charge response of the water.

Similar experiments undertaken with the individual NOM fractions, isolated from April 2002 raw water samples and varying the pH between 1 and 9, revealed a clear difference between hydrophobic and hydrophilic fractions (Figure 3(B).4). The two hydrophobic fractions have similar profiles to the raw water, such that the zeta potential values at a pH greater than 4 were \(-13 \pm 3.7\) mV, \(-17 \pm 0.3\) mV, and \(-25 \pm 2.2\) mV for the FAF, raw water and HAF respectively. In contrast, the zeta potential of
the hydrophilic fractions decreased consistently across all the pH values tested. For instance, the zeta potential of the HPIA and HPINA fractions decreased from 2.1 ± 0.2 mV at pH 2 for both fractions to -4 ± 3.2 mV and -7 ± 2 mV at pH 9 for the HPIA and HPINA fractions respectively (Figure 3(B).4). The corresponding IEP of all the fractions was 1.5, 1.6, 1.7, 4 and 4.7 for HAF, FAF, raw water, HPIA and HPINA respectively. Previous work on the charge of NOM fractions has shown that the pKa of the FAF fraction to be around 2 ± 0.3 and can be attributed to the carboxyl groups (Leenheer et al., 1995a; 1995b), whereas the hydrophilic fractions are composed of weaker acidic groups with correspondingly much higher values for their IEP. Comparing the different fractions to the raw waters shows, as expected, that the hydrophobic materials dominate the specific colloidal charge character of the water.

![Figure 3(B).4: Zeta potential of April 2002 NOM fractions with varying pH.](image)

**3(B).3.2 NOM-Coagulant interactions**

The interactions between the NOM samples and coagulant (M⁺) were monitored through changes in the IEP of the sample at various DOC to coagulant mass ratios. The initial IEP of the coagulants were 8 and 8.5 for iron and aluminium respectively, and were in general agreement with previously reported values (Van Benschoten and Edzwald, 1990). The IEP of the system subsequently decreased in all cases as the DOC:M⁺ (mg.mg⁻¹) ratio increased. To illustrate, in relation to the September 2003 raw water samples, the IEP of the systems decreased from 8 to 4.4 as the DOC:Fe
ratio increased from 0 to 2 (Figure 3(B).5). The influence, in terms of mass ratio, was slightly less for aluminium, shifting the IEP from 8.5 to 6 for the same DOC:Al ratio increase.

![Figure 3(B).5: pH of zero charge and DOC:coagulant ratios for September 2002 raw water.](image)

Calculation of the neutralizing charge of the coagulants, based on speciation data (Jiang and Graham, 1998), reveals the coagulant charge density of the added iron to be 35.5, 30.7 and 12.6 meq.g\(^{-1}\)Fe at pH values of 4, 5 and 6 respectively, compared to 104.5, 45.8 and 12.5 meq.g\(^{-1}\)Al at the same pH's. Hence the charge neutralizing capacity for both coagulants was greater at pH 4 compared to pH 6, by a factor of 8 and 3 for alum and iron respectively although at pH 6, the neutralizing capacity for both aluminium and iron was almost identical.

The interactions between the individual NOM fractions and coagulant (M\(^+\)) were also monitored through changes in the IEP of the sample, at various DOC to coagulant mass ratios (Figure 3(B).6). Results for both coagulants revealed the FAF fraction produced the largest shift in IEP, although the influence was greater when coagulating with iron compared to aluminium. For instance, with iron the IEP changed from pH 8 with no NOM present (i.e. ferric hydroxide) to pH 3 for a 2:1 FAF:Fe ratio and for aluminium the IEP shifted from pH 8.5 to pH 5.3 for the same change in ratio. Similar results were observed for the HAF fraction as the IEP changed to pH 3.8 and 5.8 for
iron and aluminium respectively, at a 2:1 DOC:M$^+$ ratio. The effect of the HPIA fraction on the IEP was less pronounced, as demonstrated with iron, with a reduction in IEP from pH 8.0 to pH 4.8 for the 2:1 DOC:Fe ratio. The HPINA did shift the IEP in both cases, although increasing the DOC concentration further did not have an additive effect. This implies that only a certain concentration of the HPINA combined with the coagulant, which once exceeded did not affect the IEP of the system. Hence this reduced NOM-coagulant interaction may be due to the fact that at the coagulation pH of normal operation (5-7), the hydrophilic fractions (HPIA and HPINA) possess a negligible or slightly positive charge. Consequently, leading to the associated poor removal, with reported values as low as 16% (Fearing et al., 2004).
Despite the observed differences in IEP between iron and aluminium, based on a mass ratio basis, subsequent examination of the influence of charge ratio (meq.meq\(^{-1}\)), revealed a more consistent comparison (Figure 3(B).7). For instance, combining the results for both aluminium and iron with FAF produced a regression line \((R^2 = 0.98)\), such that an increase in charge ratio of approximately 0.04 meq.meq\(^{-1}\) would result in a reduction in the IEP of one pH unit. The influence of the HAF fraction was slightly less but of a similar magnitude to FAF, with an increase in charge ratio of 0.07 meq.meq\(^{-1}\) required to reduce the IEP by one \((R^2 = 0.89)\). For the HPIA fraction, the
influence on the IEP was significantly reduced, with an increase in charge ratio of 1.35 meq.meq\(^{-1}\) required to reduce the IEP by 1. Consequently, it is the hydrophobic fractions which appear to be critical in determining the resultant charge properties of the NOM-coagulant system and hence the subsequent coagulant dose requirements. This is in agreement with previous research, which suggests that competitive interaction between coagulants and NOM are favoured towards larger MW, more hydrophobic, more highly charged components (Gu et al., 1995; Huang and Shiu, 1996) due to the combination of charge neutralization, complexation/precipitation and ligand exchange mechanisms which are thought to dominate NOM removal (McKnight et al., 1992). This would also explain the fact that differences observed in the residual DOC correlate well with the difference in the initial level of hydrophilic material (Sharp et al., 2005b).

Differences in NOM-coagulant interactions, for both aluminium and iron, appear to be minimal in terms of the IEP when based on a charge ratio. Previous research, investigating the coagulation of a mountain source water, has clearly demonstrated the possibility of optimising the process based on zeta potential measurements, revealing a similar profile for both aluminium and iron based coagulants (Sharp et al., 2005b), with optimum DOC residuals achieved when the zeta potential was minimised (Figure 3(B).8). However, the main observed difference was that approximately 0.5 mg.l\(^{-1}\)
more DOC removal was possible with iron, which is in broad agreement with other authors (Edzwald and Tobaison, 1999; Bell-Ajay et al., 2000; Budd et al., 2004).

![Zeta vs. removal for iron and aluminium salts (Sharp et al. 2005b).](image)

**Figure 3(B).8: Zeta vs. removal for iron and aluminium salts (Sharp et al. 2005b).**

The exact understanding of the way both aluminium and iron coagulants operate in relation to NOM removal is far from complete. However, if the differences do not originate from electrical interactions such as charge, then they may be controlled by the affinity of each coagulant to a particular surface, or to a particular functional group. In this respect, ferric ions, for example, have a higher affinity for carboxylic groups (Leja, 1982), which may result in increased DOC removal when coagulating with iron.

The results from this study demonstrate that the impact of variations in NOM composition on the downstream coagulation process, caused by changes in the catchment, can be both understood and controlled. Hence, with current trends forecasting an increase in DOC concentrations for peat catchment systems in particular (Scott et al., 1998), an increased understanding of both the system and the mechanisms involved is vital, especially as the potential consequences are likely to impact dramatically on the water industry with regards to water quality parameters such as DBP formation. However, characterization methods highlighted here, such as fractionation and charge density, coupled with surface charge measurements during the coagulation process, could provide that vital link. In fact, comparisons across
different source waters, seasons and chemical solutions reveal the potential of this proactive strategy in achieving a more robust operation during these problem periods (Parsons et al., 2005).

3(B).4 Conclusions

Results from this investigation show that it is not simply the increased organic concentration, but also the change in composition and character which creates a greater coagulant demand. The hydrophobic NOM fractions have a significantly higher charge density than the hydrophilic NOM fractions, whereas the negligible charge density of the HPINA fraction may explain the reduced interaction with iron and the poor removal of this fraction with conventional coagulation methods. Comparison of iron and aluminium based NOM systems demonstrate that the observed differences in terms of DOC removal may not be associated with the electrical character of the system, but with the affinity of each coagulant for a particular surface or system. Consequently, monitoring of parameters, such as NOM fraction make-up and associated surface charge, could provide valuable insight into how to manage the impact caused by environmental changes to catchments.
3(B).5 References


3(C) Impact of fractional character on the coagulation of NOM.

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Abstract

The current work investigates how the natural organic matter (NOM) fraction make-up of the raw water influences coagulation performance. Four characteristic organic fractions were separated based on their hydrophobicity. Results revealed that the hydrophilic non adsorbed fraction (HPINA) was least amenable to removal by conventional coagulation, attributed to a negligible charge density. Whereas the fulvic acid fraction (FAF) most readily resembled the bulk raw water operational characteristics in relation to coagulation, such as floc size, strength, settling velocity, iso-electric point (IEP), generating small compact flocs and exerting the most influence on the charge balance of the system. The most notable exception is in relation to removal. A lower FAF removal was observed compared to the raw water, attributed in part to co-operation effects, as although studying isolated NOM fractions does provide some benefits, some of the synergistic effects may be lost. However, results demonstrate that simple fractionation, in terms of the hydrophobic/hydrophilic balance of the water, could provide a fast and effective method for improved understanding of coagulation performance.

Keywords

Charge density, Coagulation, Flocs, Fractionation, Natural organic matter.
3(C).1 Introduction

Natural organic matter (NOM), is ubiquitous in natural waters and represents one of the major pollutants in low alkalinity, low turbidity source waters typically associated with moorland and mountain catchments. NOM is a highly heterogeneous, poorly defined mix of organic substances that vary both spatially and temporally in terms of acidity, molecular weight (MW), molecular structure and charge density (Edzwald, 1993; Scott et al., 2001; Goslan et al., 2002; Sharp et al., 2005). Functionally, the organic material is predominantly phenolic and carboxylic in nature, but also contains alcohol, purine, amine and ketone groups and is often described as a weak anionic polymer (Dennett et al., 1995). Traditional approaches in the literature to characterize NOM into its components have used a wide range of analytical techniques. For instance, resin and mineral adsorption separate the organics on the basis of polarity (Malcolm and MaCarthy, 1992; Meier et al., 1999), whereas membrane separation gives an idea of the molecular size of the material (Wershaw and Aiken, 1985). Goslan et al. (2002) employed XAD resin techniques to investigate the reactivity of the individual NOM with chlorine. This is important as although NOM itself is relatively harmless, if not removed sufficiently it can lead to the formation of potentially carcinogenic disinfection by products (DBP), such as trihalomethanes (THM), formed during the disinfection process (Singer et al., 1999). The humic fraction in particular, is generally regarded as the main THM precursor (Croué et al., 1993; Krasner et al., 1996; Goslan et al., 2002).

In the past decade, a number of UK and US water utilities have been experiencing operational difficulties coinciding with elevated organic levels often associated with increased surface run-off events such as snowmelt or heavy rainfall (Parsons et al., 2005). The increased surface run-off promotes the transport of any accumulated organics into the aquatic environment, rapidly influencing the NOM fraction make-up of the source water. This flush is likely to contain a high proportion of higher MW, hydrophobic material, with an increased colloidal charge density, therefore resulting in a significant increase in the charge density of the raw water and associated coagulant demand (Edzwald, 1993; Carlson et al., 1994; Green, 1997). However, previous studies have also highlighted the increased hydrophilic content, of moorland waters in particular, associated with heavy rainfall events and the subsequent first
flush (Scott et al., 2001). This is significant, as removal of hydrophilic, low molecular weight organics, through conventional coagulation methods, is known to be poor (Randtke, 1988; Edwards, 1997; Chow et al., 2000; Fearing et al., 2004). The presence of NOM has also been reported to produce fragile flocs (Bache et al., 1997; Jarvis et al., 2005). Operational experience has suggested that pronounced floc breakage during solid liquid separation phases can also impact on downstream processes such as filtration, resulting in carryover onto the filters, greater particle loads, turbidity breakthrough and reduced filter run times.

As the coagulation of NOM is related to charge, previous research has reported a link between optimal performance and zeta potential, a measurement employed to measure the charge character of colloids and particles, with optimum doses having occurred at a range of zeta potentials between -8 and +8 mV depending on the water source and the pH of coagulation (Ratnaweera et al., 1999; Gregory and Carlson, 2003; Sharp et al., 2005). However, although the coagulation of NOM has been researched extensively, little research has focused on the role of the individual NOM fractions and their operational impact on the coagulation process, in terms of both floc properties and removal. Consequently, the aim of this research was to identify the main characteristics of the different NOM fractions. Furthermore, linking the findings back to the raw water characteristics will therefore ultimately determine the value of such characterisation and analytical techniques. In addition, by understanding the impact of varying NOM composition and character on the coagulation process, this should promote the development of source management and treatment strategies to ensure a more robust level of treatment during periods of elevated organics.

3(C).2 Materials and Methods

3(C).2.1 Sampling
The raw water investigated in the current study was sampled from Albert Water Treatment Works (WTW), a moorland water works in the north of England, situated in Halifax. Sampling took place during a 36 month period from April 2002 until October 2004, with the water source typically characterised as a low turbidity (3.7-7.0 NTU), low alkalinity (20 mg.l\(^{-1}\) CaCO\(_3\)), high colour (44-160 Hazens) and high DOC (6.6-13.3 mg.l\(^{-1}\)) source.
3(C).2.2 Apparatus
The turbidity of the samples was measured using a HACH2100 turbidity meter (Camlab, UK). A Shimadzu 5000A TOC analyzer was used for determining the DOC content. High performance size exclusion chromatography (HPSEC) analysis was undertaken using a high performance liquid chromatography (HPLC) device (Shimadzu VP series, Shimadzu, Milton Keynes, UK). All samples were passed through a Fisher Scientific MF200 1µm glass microfibre filter paper before both DOC and HPSEC analyses. The surface charge was measured with a zetasizer (Malvern Instruments, UK) at 25°C. The coagulation and flocculation experiments were undertaken using a Phipps and Bird PB-900 six paddle jar tester. Dynamic floc size was measured during growth and breakage of flocs using a laser diffraction instrument (Malvern mastersizer 2000, Malvern Instruments, UK). Floc images were captured using a CV M90 colour close-coupled device (CCD) camera (JAI UK Ltd, UK). Image analysis software (Image Pro Plus, Media Cybernetics, Maryland, USA) was used to determine the floc settling velocity.

3(C).2.3 Characterisation
Raw water samples were fractionated by XAD resin adsorption techniques into hydrophobic (HPOA) and hydrophilic (HPIA) components using a method adapted from Malcolm and MacCarthy (1992). Detailed descriptions of the methods used can be found in Goslan et al. (2002).

Charge densities were determined through an adjusted form of the method used by Kam and Gregory (2001), which monitored the change in charge as a function of polyDADMAC dose. Detailed descriptions of the methods used can be found in Sharp et al. (2005).

3(C).2.4 NOM-Coagulant interactions
The NOM coagulant interactions were investigated by adding varying concentrations of coagulant to the NOM fraction or raw water sample in order to achieve the required NOM:coagulant mass ratio. Portions of the solution were then removed and adjusted
to varying pHs between 2 and 9 and the resulting zeta potential recorded in order to determine the IEP for each system as detailed in Sharp et al. (2005).

Raw water and NOM samples were stored at 5°C prior to coagulation jar testing, which was subsequently undertaken at room temperature (20°C) and involved a 1.5 minute rapid mix at 200 RPM, a 15 minute 30RPM flocculation stage and 20 minute settlement period. The rapid mix period was shorter than the 3.5 minutes stated in previous papers (2 and 3). However, a reduction in the rapid mix period to 1.5 minutes was not found to impact on either the coagulation zeta potential or subsequent removal values.

3(C).2.5 Floc diagnostics
Floc size, breakage and floc settling experiments were performed using the same experimental set-up as Jarvis et al. (2003). Coagulation tests were undertaken using a jar tester as before, however, following the slow stir phase, the effect of increased shear was investigated by increasing the rpm on the jar tester for a further 15 minutes. Separate experiments were undertaken in triplicate for an rpm of 30, 40, 50, 75, 100 and 200.

The settling column apparatus consisted of a central settling column enclosed by a water bath to avoid thermal currents disrupting floc settlement. Floc aggregates were introduced into the settling column via a tapered entry port and images were captured to determine the floc settling velocity.

3(C).3 Results and Discussion
3(C).3.1 Characterisation
The DOC concentration of the raw water varied across the period of investigation, with a low of 6.6 mg.l\(^{-1}\) in September 2003 to a high of 13.3 mg.l\(^{-1}\) in August 2004 following a period of intense rainfall (Figure 3(C).1). This is in agreement with previous work, revealing a link between periods of high precipitation and increased DOC levels (Riise, 1999). Characterisation data revealed that the raw water was predominantly hydrophobic in nature (53-76%). These values are in agreement with previously published work undertaken by Owen et al. (1993), which states that the
hydrophobic acids constitute the largest proportion of NOM at approximately 50% of the DOC concentration. Whereas Malcolm (1985), reported a slightly higher range of 60-80%.

Fractionation data at Albert, however, demonstrated that the contribution from the four NOM fractions was not observed to change proportionally with the variation in DOC over the whole sampling period. For instance, the fulvic acid fraction (FAF), in general, constituted the greatest proportion of DOC and also exhibited the most variation (39 ± 12%), closely followed by the humic acid fraction (HAF) (27 ± 8%). Whereas the hydrophilic fractions contributed to a lesser degree and also exhibited much less variation at 15 ± 6% and 18 ± 6% for the hydrophilic acid (HPIA) and hydrophilic non adsorbed (HPINA) fractions respectively. Comparison with results obtained from mountain surface water, during the snowmelt run-off period when the DOC increased from 4.4 to 7.4 mg.l\(^{-1}\), revealed a similar variation. The hydrophobic fractions contributed 58 ± 8% and 11 ± 16% (3.3 ± 0.7 mg.l\(^{-1}\) and 0.8 ± 1.2 mg.l\(^{-1}\)) for FAF and HAF respectively, whereas the hydrophilic fraction concentrations remained relatively constant at 0.6 ± 0.08 mg.l\(^{-1}\) and 1.1 ± 0.16 mg.l\(^{-1}\) for HPIA and HPINA respectively (Parsons et al., 2005). Comparison with previously published data employing a similar fractionation method to analyse river, lake and swamp water sources, also demonstrated the majority of the DOC was present as FAF (54-68%), with the HAF contributing to a lesser extent (14-29%) (Ma et al., 2001).
Given that the coagulation of NOM is predominately charge derived for both soluble and colloidal material, then the electrical character of the NOM is likely to be a key parameter in describing the process (Edzwald, 1993; Sharp et al., 2005). Comparative studies, varying the pH between 1 and 9 for the individual fractions extracted from April 2002 raw water, revealed a clear difference between the colloidal components of the hydrophobic and hydrophilic fractions (Figure 3(C).2). Comparison with the profile of the raw water suggests that the zeta potential of the water is controlled by the hydrophobic fractions, FAF in particular, under all but very acidic conditions. For instance, the two hydrophobic fractions have similar profiles to the raw water such that the zeta potential values post pH 4 were $-13 \pm 3.7$ mV, $-17 \pm 0.3$ mV, and $-25 \pm 2.2$ mV for the FAF, raw water and HAF respectively. In contrast, the zeta potential of the hydrophilic fraction decreased consistently across all the pH values tested. For instance, the zeta potential of the HPIA and HPINA fractions decreased from $2.1 \pm 0.2$ mV at pH 2 for both fractions to $-4 \pm 3.2$ mV and $-7 \pm 2$ mV at pH 9 for the HPIA and HPINA fractions respectively (Figure 3(C).2). The corresponding IEP of all the fractions was 1.5, 1.6, 1.7, 4 and 4.7 for HAF, FAF, raw water, HPIA and HPINA respectively. Previous work on the charge of NOM fractions has shown the pKa of the FAF fraction to be around $2 \pm 0.3$ and can be attributed to the carboxyl groups.
(Leenheer et al., 1995a; 1995b). Whereas the hydrophilic fractions are composed of weaker acidic groups with correspondingly much higher values for their IEP.

![Zeta potential of NOM fractions and raw water with varying pH.](image)

Figure 3(C).2: Zeta potential of NOM fractions and raw water with varying pH.

Charge density measurements of the raw water fractions in the current study revealed the majority of the total colloidal charge to exist in the hydrophobic fractions. For instance, the charge densities of the individual fractions were $3.6 \pm 0.6$, $5.1 \pm 1.3$ and $1.0 \pm 0.6$ meq.g$^{-1}$DOC for the HAF, FAF and HPIA fractions respectively, whereas the charge density of the HPINA fraction was below the level of detection. An identical method was used to determine charge densities of NOM fractions derived from both mountainous and moorland water sources, with comparable values observed (Sharp et al., 2005b). Similar values have also been reported elsewhere with humic and fulvic waters typically exhibiting charge densities between 5-15 meq.g$^{-1}$DOC, whereas the hydrophilic acids are often an order of magnitude lower (Kam and Gregory, 2001; Edzwald, 1993; Tipping, 1993; Collins et al., 1986).

Conversion of the charge densities to charge load, and ultimately coagulant demand, reveals that the hydrophilic fractions contribute a maximum of 11 % of the total charge load, therefore the majority of the coagulant demand is likely to be generated from the hydrophobic fractions. This is in agreement with the raw water data. For instance, the raw water charge density in January 2004 was $2.7$ meq.g$^{-1}$ DOC, increasing to $3.7$ meq.g$^{-1}$DOC in August as the DOC increased from 8.3 to 13.3 mg.l$^{-1}$. This corresponds to an increase in hydrophobic fraction content from 5.9 to 7.8 mg.l$^{-1}$. 
Similar results have been observed for other water sources. For example, the hydrophobic content of the Poudre river, Fort Collins, increased from 2.8 to 5.5 mg.l\(^{-1}\) and the charge density increased from 2.0 to 3.9 meq.g\(^{-1}\)DOC (Sharp \textit{et al.}, 2005). The implication of this is that the charge character of raw water, and hence the coagulant demand, is controlled by the changes in the hydrophobic fraction content and characteristics.

3(C).3.2 NOM-Coagulant interactions

The interactions between the NOM samples and coagulant (M\(^{+}\)) were monitored through changes in the IEP of the precipitated sample at various DOC to coagulant mass ratios (Figure 3(C).3). The FAF fraction results in the largest shift in IEP from pH 8 with no NOM present (i.e. ferric hydroxide) to pH 3 for a 2:1 FAF:Fe ratio. This was followed by the HAF and HPIA fractions at pH 3.8 and 4.8 respectively at the same mass ratio. The HPINA did shift the IEP although increasing the DOC concentration further did not have an additive effect. Therefore implying only a certain concentration of the HPINA combined with the iron which once exceeded did not affect the IEP of the system. Importantly, the FAF fraction appears to be critical in determining the resultant charge properties of the NOM-coagulant system and hence the dose requirements and coagulation conditions for the raw water.

![Figure 3(C).3: pH of zero charge for the for raw water and NOM fractions coagulated with varying doses of iron.](image-url)
Chapter 3(C): NOM-Coagulant Interactions

3(C).3.3 Removal

Analysis of the performance, when coagulating the raw water, revealed a clear relationship between zeta potential and residual organic concentration, in terms of DOC and UV$_{254}$ absorbance (Figure 3(C).4). Furthermore, inspection of HPSEC traces of post coagulation residual organics, revealed that the main residual was in the sub 3000 Dalton (Da) size range indicating that the coagulation process is far more effective at removing the larger MW compounds. Previous comparisons, across different source waters, and seasons, have lead to the identification of an operational zeta potential window (-10 and +3 mV), within which the residual DOC is optimised and stable (Sharp et al., 2005). Comparison of the coagulation of NOM fraction components, present at concentrations in existence in the raw water, revealed that removal of the hydrophobic fractions is most influenced by the magnitude of the zeta potential. The UV and DOC residual increased gradually, in a similar fashion to the raw water profile, as the magnitude of the negative zeta potential increased. However, with regards to magnitude of the positive zeta potential, the range was extended for the HAF fraction with a removal of 70% possible at a zeta potential of 12.5 mV, whereas only 35% was possible for the FAF fraction. This compares well with the work of Zouboulis et al. (2003), who were also able to achieve a significant humic acid removal of 92% at a zeta value of 12.6 mV, therefore suggesting a lower energy barrier is present with regards to coagulation of this fraction.

Removal data for the individual NOM fractions confirmed the effectiveness of conventional coagulation for the hydrophobic fractions, with 84% and 64% removal for HAF and FAF respectively. Whereas the maximum achievable removals for the hydrophilic fractions were 14% and 17%, for the HPIA and HPINA fractions respectively. Initial NOM fraction concentrations mirrored that of the raw water in the January 2004 samples, which contained 14%, 57%, 12% and 14% of HAF, FAF, HPIA and HPINA respectively. The principle observation is therefore reduction in FAF removal, when compared to the raw water sample. Previously reported work at Albert WTW, involving the fractionation of treated water, revealed high removals of DOC for HAF and FAF, of 98% and 89% respectively (Fearing, 2004). These results are also comparable to those published by Croué et al. (1993), where 87% removal was achieved for the HAF fraction. Reported removals for the low MW DOC is significantly lower, with values between 8 and 30% (Fearing, 2004; Krasner et al.)
1994). However, when Fearing (2004) coagulated fractions isolated from Albert WTW, a reduced removal was reported, of 66% and 70% for HAF and FAF respectively, therefore indicating the likelihood of co-operative mechanisms when coagulating the raw water.

With regard to the hydrophilic fractions, although up to 97% UV removal was possible, no significant change in DOC removal was observed across the whole zeta potential range. Although limited removal of 14 to 17% was achieved as the total DOC removal was greater than the hydrophobic content of the water (White et al., 1997). Previous investigations into the differences in the achievable residual DOC have demonstrated a clear relationship between the raw water HPINA concentration and the total residual DOC, indicating the majority of the residual is contained within the HPINA fraction (Sharp et al., 2005). Consequently, the impact is such that the concentration and character of the FAF fraction is likely to control the coagulation conditions and the operational zeta potential envelope, whereas the hydrophilic fractions are likely to influence the achievable residual following treatment.
Figure 3(C).4: Impact of zeta potential for NOM fractions and raw water (Jan-04) in terms of (a) DOC residual and (b) UV absorbance.

3(C).3.4 Floc properties

Floc growth follows a classical pattern composed of a short induction period followed by a rapid growth phase until the steady state floc size is reached within 5-10 minutes (Figure 3(C).5). Comparison of the steady state floc size revealed that the raw water FAF fraction produced flocs of a significantly smaller size compared to the other fractions. This is illustrated by the median volumetric diameter ($d_{50}$) of each fraction at 723 ±33 μm, 532 ±5 μm, 759 ±25 μm, 668 ±31 μm, 448 ±12 μm for HAF, FAF, HPIA, HPINA and the raw water respectively. Results also revealed that whilst the ultimate size changed depending on the NOM fraction, the growth rate remained within the range 103-131 μm.min⁻¹. Once the flocs had reached a steady state size, they were then exposed to levels of increased shear. Analysis of the profile revealed a classical response such that the steady state floc size was reduced with increasing
shear. Consequently, the gradient of the slope can be used as an indication of floc strength. For instance, the gradient of the slope was -0.64, -0.75, -0.74 and -0.82 for the FAF, HAF, HPIA and HPINA fractions respectively (Figure 3(C).6). Whereas the raw water profile was most similar to the FAF fraction, with a slope of -0.52, therefore highlighting the dominance of this fraction with respect to raw water coagulation.

![Figure 3(C).5: Floc breakage results for the HPINA fraction](image_url)

*Figure 3(C).5: Floc breakage results for the HPINA fraction*
The settling rates also revealed significant differences between the fractions (Figure 3(C).7). For example, the settling rate of a 1000 µm floc was 1497 µm.s\(^{-1}\), 710 µm.s\(^{-1}\), 1152 µm.s\(^{-1}\) and 1385 µm.s\(^{-1}\) for the HAF, FAF, HPIA and HPINA fractions respectively. This compares to previously reported values of 867 µm.s\(^{-1}\) for the raw water at a similar dose ratio (Jarvis et al., 2005). The gradient of the straight line relationship, obtained when plotting the equivalent floc diameter (µm) against settling rate (µm.s\(^{-1}\)) on a log-log scale, can be used as an indication of changes in floc structure between the fractions. This is most commonly defined through calculation of the fractal dimension (\(D_f\)), which is related to floc diameter (\(d\)) and the terminal settling velocity (\(v_t\)) by:

\[
v_t \propto d^{D_f - 1}
\]

A log-log plot of settling velocity against floc diameter yields a straight line with a slope of \(D_f - 1\). Model two reduced axis regression was used to calculate the slopes of the line through the data, as both variables were random and not controlled. This revealed a reasonable linear correlation for all the data (Figure 3(C).7), with corresponding \(D_f\) values of 1.78, 2.24, 1.90, 1.88 and 2.10 for HAF, FAF, HPIA, HPINA and the raw water respectively. This demonstrated that the FAF fraction...
produced the most compact flocs and is in agreement with the fact that fulvic acids have the largest apparent surface area and the narrowest microporosity (Alvarez-Puebla et al., 2005) with removal largely achieved through adsorption (McKnight et al., 1992). The most open flocs were generated from the HAF fraction, which is thought to adsorb both electrostatically and chemically through ligand exchange mechanisms and may give rise to the larger and more open structure (Au et al., 1999). Interestingly, the two ends of the spectrum are generated from the two hydrophobic fractions, indicating that the different mechanisms have a potentially significant impact on floc structure.

![Figure 3(C).7: Settling rate profiles for the individual fractions generated from the April 2002 water and coagulated with iron at the optimum dose.](image)

Environmental Scanning Electron Microscope (ESEM) images of the flocs generated from the individual fractions also revealed a difference in structural composition between the hydrophobic and hydrophilic fractions (Figure 3(C).8). The hydrophobic fractions were characterised by solid internal structures with a relatively smooth edge.
structure. This compared to the hydrophilic fractions which were characterised by more open internal structures with extensive edge morphology.

![Image](image1.png)
(a) HAF

![Image](image2.png)
(b) FAF

![Image](image3.png)
(c) HPIA

![Image](image4.png)
(d) HPINA

**Figure 3(C).8:** Environmental Scanning Electron Microscope (ESEM) images from the individual fractions generated from the April 2002 water coagulated with iron at the optimum dose.

### 3(C).4 Discussion

Results from this investigation reveal that with regard to the majority of parameters, the FAF fraction most readily resembles the raw water (Table 3(C).1). The most notable exception is in relation to removal. Investigations that fractionate raw water before and after treatment, as a monitoring tool for consistent coagulation, demonstrate similar levels of removal between HAF and FAF fractions. When evaluating the removal of the different NOM fractions it is easy to make distinctions with regards to hydrophobicity, whereas the comparison between humic and fulvic acids is less clear as they are both hydrophobic and have MW distributions that overlap considerably. The differences shown in the present study indicate co-operation effects may be important, and in agreement with previous studies, have shown the HAF fraction to be more amenable to removal by coagulation than the FAF fraction (Fearing, 2004). This has been attributed in part to the fact that humic acids
are more aromatic than fulvic acids, therefore rendering them more hydrophobic (Scott et al., 2001). In addition, fulvic acids have been shown to exhibit a greater dependence on pH compared to humic acid, in terms of adsorption onto metal oxide surfaces, which may explain the reduced operational range for FAF in terms of zeta potential (Davis and Gloor, 1981).

Significant removal of both the HAF and FAF fractions dictates that the majority of the organic material contained in the floc structures is likely to be hydrophobic. Floc diagnostics have also revealed significant differences with regards to the two hydrophobic fractions. Hence, offering some explanation as to why the resultant floc properties during coagulation, and subsequent removal, of the raw water organics are comparatively similar to those of the FAF fraction. Coagulating FAF resulted in the production of small more compact flocs, whereas the flocs produced by HAF were larger. Such differences, with regards to floc properties and subsequent removal, can both be related to the removal pathway. HAF is thought to be removed through a combination of charge neutralization (for colloids), whereas the removal of FAF, further influenced by the positive zeta potential values, is thought to be mainly through an adsorption pathway (McKnight et al., 1992). Evidence for this has been shown by recording pH changes due to the exchange of OH$^-$ groups as the adsorption process proceeds (Gu et al., 1995). The situation is further complicated as evidence suggests adsorption follows a two stage sequence of fast followed by slow adsorption during which competitive displacement occurs where high absorption affinity compounds replace low affinity ones (Avnea and Koopal, 1999). Replacement is thought to be aided as residual charge on the adsorbed molecules repel each other and reduce the affinity of large MW compounds thus enabling smaller MW material to adsorb shifting the balance of molecules bound to the floc.

In general, although studying the isolated NOM fractions can provide operationally defined samples for examination of NOM behaviour, the synergistic effects are often lost (Hwang et al., 2001). Hence, as a direct result of the isolation process, many interactions are disrupted and changes in the chemical structure of the compounds themselves may result (Aiken, 1988), and the relative reactivity may be different from the raw water (Peuravuori and Pihlaja, 1997). The advantage of using bulk raw water
samples is that the NOM present is in an unaltered state, with the disadvantage being that the effect of specific NOM fractions cannot be identified or understood.

The work presented in this paper suggests that in relation to understanding the treatment of NOM, a sensible level of separation is between the hydrophobic and the hydrophilic material. The hydrophobic material dominates the relationship between NOM and the metal coagulant, whereas the hydrophilic content relates to the residual remaining after treatment and the potential need for additional treatment.

Table 3(C).1: Fraction ranking.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ranking</th>
<th>Closest match to raw water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration</td>
<td>FAF&gt;HAF&gt;HPIA&gt;HPINA</td>
<td>FAF</td>
</tr>
<tr>
<td>Charge density</td>
<td>HAF&gt;FAF&gt;HPIA&gt;HPINA</td>
<td>FAF</td>
</tr>
<tr>
<td>Removal</td>
<td>HAF&gt;FAF&gt;HPIA&gt;HPINA</td>
<td>HAF</td>
</tr>
<tr>
<td>Floc size</td>
<td>HPIA&gt;HAF&gt;HPINA&gt;FAF</td>
<td>FAF</td>
</tr>
<tr>
<td>Growth rate</td>
<td>No significant difference</td>
<td>-</td>
</tr>
<tr>
<td>Breakage coefficient</td>
<td>FAF&gt;HAF&gt;HPIA&gt;HPINA</td>
<td>FAF</td>
</tr>
<tr>
<td>Settling rate</td>
<td>HAF&gt;HPINA&gt;HPIA&gt;FAF</td>
<td>FAF</td>
</tr>
<tr>
<td>Fractal dimension</td>
<td>FAF&gt;HPINA&gt;HPIA&gt;HAF</td>
<td>FAF</td>
</tr>
<tr>
<td>Zeta potential at pH 6 (IEP)</td>
<td>HAF&gt;FAF&gt;HPIA&gt;HPINA</td>
<td>FAF</td>
</tr>
<tr>
<td>THMFP*</td>
<td>FAF&gt;HPINA&gt;HAF&gt;HPINA</td>
<td>FAF</td>
</tr>
</tbody>
</table>

* THMFP of Albert raw water with a raw water DOC concentration of 10.2 mg.l$^{-1}$ (Goslan et al., 2002).

3(C).5 Conclusions

Using a range of techniques to investigate the role of the different fractions through varying stages of the coagulation process it has been possible to establish how the organic make up of raw water influences the physical properties of the flocculated suspension. The FAF fraction, although readily removed during conventional coagulation, also most readily resembles the raw water for the majority of operational parameters, generating smaller more compact flocs than the other fractions and dominating the charge response of the system. The lower MW material, such as the HPINA fraction is likely to influence the achievable residual post treatment, due to its poor removal during conventional coagulation. The combination of these two factors appears to be crucial in understanding how changes in the make up of the raw water...
influence treatability and should be included in any mechanistic approach to potable water treatment.

3(C).6 References


CHAPTER 4
BENCH SCALE COAGULATION

4(A) Evaluation of zeta potential for determining optimum coagulation conditions for sources with varying NOM.

Submitted to: Journal of Water Supply: Research and Technology-AQUA.

4(B) The effects of changing NOM composition and characteristics on coagulation performance, optimisation and control.

4(A) Evaluation of zeta potential for determining optimum coagulation conditions for sources with varying NOM.

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Abstract

Rapidly changing organic levels, following periods of rain during the autumn and winter months, are causing problems for UK water companies when trying to effectively optimise the coagulation process. A link between zeta potential and optimum coagulation performance has previously been identified. This work investigates this issue further by comparing two moorland UK water sources in the UK, Albert water treatment works (WTW) Halifax, Yorkshire and Bamford WTW, Derbyshire. Results indicate that optimising the coagulation process through zeta potential measurements is possible, despite the changing organic concentrations, providing the surface charge of the natural organic matter (NOM)-coagulant complexes is minimised. It has also been concluded that once the optimum zeta potential has been established and maintained, increasing the coagulant dose further does not result in an increased removal of organic material.

Keywords

4(A).1 Introduction

Natural waters throughout the world contain natural organic matter (NOM) as a result of the interactions between the hydrological cycle and both the biosphere and geosphere. The diversity of subsequent interactions is dependent on the surrounding environmental and biogeochemical cycles which result in a highly heterogeneous mixture of organic compounds that vary with regards to acidity, molecular weight and charge density (Collins et al., 1986; Edzwald, 1993; Vuorio et al., 1998; Goslan et al., 2002). Furthermore, the resulting heterogeneous organic mixture is also known to vary in terms of concentration and make-up due to the temporal and spatial variations that exist between sources (Owen et al., 1993; Carlson et al., 1994; Scott et al., 2001).

NOM is traditionally removed by coagulation with trivalent metal ions. The coagulation mechanisms, that are thought to prevail with regards to NOM removal, are charge neutralisation for colloidal material and charge complexation/precipitation for soluble compounds with additional removal occurring due to adsorption onto precipitated flocs and metal hydroxides (Randtke, 1988). Accordingly, optimisation of the coagulation is more favourable under acidic conditions which occur between the iso-electric point (IEP), the pH at which the particle is not charged, of the coagulant and the NOM; pH 4.5-5.5 for iron based coagulants and pH 5-6 for aluminium based coagulants (Amirtharajah and O’Melia, 1990). However, previous work has shown that the IEP, and hence coagulation conditions, are also influenced by both the nature and the concentration of the organics present (Sharp et al., 2004).

Changes in land management, such as the disturbance of peat or vegetation damage in moorland catchment areas, can lead to increased decomposition and the production of loosely bound organic material (Niskavaara et al., 1997; Worrall and Burt, 2005). The accumulated organics are then flushed into the aquatic environment during the first rainfall following a dry period (Goslan et al., 2002; Hurst et al., 2004). The flush contains a high proportion of hydrophobic material, giving an increased colloidal charge density, therefore resulting in a significant increase in the charge density of the raw water. The impact of this is to alter the charge response of the system at set coagulant dose rates such that the IEP may vary significantly. Green (1997) used a fluorescence polarisation colloid titration method and found that the colloid charge
capacity (CCC) increased from 2.0 to 2.5 meq.g\(^{-1}\)DOC during the 1993 spring snowmelt run-off at Fort Collins, Colorado. This was attributed to an increase in the hydrophobic content of the water, the charge density of which is at least an order of magnitude greater than the hydrophilic NOM fractions (Edzwald, 1993; Sharp \textit{et al.}, 2004).

The application of charge measurement for diagnosis and control is one option for achieving a more robust coagulation performance. Zeta potential indicates the effective surface charge of the colloidal system and is commonly related to the stability of the colloidal materials under any given set of water characteristics (Gregory and Carlson, 2003). However, although it is still unclear which NOM components contribute to the actual zeta potential value, measurements still provide a reproducible relationship which can be used to understand and optimize the coagulation process (Table 4(A).1). For instance, Ratnaweera \textit{et al.} (1999), found that zeta potentials at optimum coagulation doses of different sources of aquatic NOM varied from +8 to -10 mV depending on the water source and pH of coagulation. Hence indicating that complete neutralization of the charge is not required, only that the barrier generated by electrostatic repulsion is minimized or removed. This paper is concerned with investigating this concept further, using two UK moorland waters over a period of rapidly increasing organic levels, in order to assess the importance of zeta potential in maintaining a more robust operation despite varying:

- NOM fractional make-up and characteristics
- Coagulant dose, or DOC:coagulant ratio
- Water source
Table 4(A).1: Optimum zeta potential values identified by other authors.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Coagulant</th>
<th>Zeta potential</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae</td>
<td>Alum or PAC</td>
<td>~0 mV</td>
<td>Edzwald and Wingler, 1990</td>
</tr>
<tr>
<td>Cryptosporidium Oocysts</td>
<td>Alum</td>
<td>~0mV</td>
<td>Dai and Hozalski, 2002</td>
</tr>
<tr>
<td>NOM</td>
<td>Alum</td>
<td>-4 &lt;ζ&lt; +3 (pH 7.4)</td>
<td>Gregory and Carlson, 2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+1 &lt;ζ&lt; +3 (pH 6-6.7)</td>
<td></td>
</tr>
<tr>
<td>River water spiked with humic acid</td>
<td>Ferric chloride</td>
<td>-5mV</td>
<td>Edwards, 2002</td>
</tr>
<tr>
<td>Titanium dioxide colloid</td>
<td>Aluminium Nitrate</td>
<td>-14&lt; ζ &lt;+14</td>
<td>James et al., 1977</td>
</tr>
</tbody>
</table>

4(A).2 Materials and Methods

4(A).2.1 Sampling

The raw waters investigated in the current study were sampled from two moorland water works in the north of England, Albert Water Treatment Works (WTW), situated in Halifax, UK and Bamford WTW situated in Derbyshire, UK. Sampling took place during the period of September to December 2003. Both water sources are typically characterised as low turbidity (1.4-10.9 NTU), low alkalinity (20 mg.l$^{-1}$ CaCO$_3$), low conductivity (60µs.cm$^{-1}$) and high DOC (4.5-10.2 mg.l$^{-1}$) waters (Table 4(A).2).

Table 4(A).2: Source water characteristics.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Albert WTW</th>
<th>Bamford WTW</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>mg.l$^{-1}$</td>
<td>6.6 - 9.7</td>
<td>4.5 - 10.2</td>
</tr>
<tr>
<td>Hydrophobic content</td>
<td>%</td>
<td>63-67</td>
<td>58-76</td>
</tr>
<tr>
<td>UV-Abs</td>
<td>m$^{-1}$</td>
<td>45.0 - 63.6</td>
<td>36.7 - 45.9</td>
</tr>
<tr>
<td>SUVA</td>
<td>l.mg.m$^{-1}$</td>
<td>4.6-7.4</td>
<td>3.6-8.7</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>5.5 - 6.5</td>
<td>5.5 - 6.5</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>5.9 - 10.9</td>
<td>1.4 - 4.2</td>
</tr>
</tbody>
</table>

4(A).2.2 Apparatus

The turbidity of the samples was measured using a HACH2100 turbidity meter (Camlab, UK). A Shimadzu 5000A TOC analyzer was used for determining the DOC content. High performance size exclusion chromatography (HPSEC) analysis was
undertaken using a high performance liquid chromatography (HPLC) device (Shimadzu VP series, Shimadzu, Milton Keynes, UK). The method used was a TSK gel, GW3000SW column, 7.5mm internal diameter, 30cm in length. The guard column was also TSK, 7.5mm internal diameter and 7.5cm in length (Tsoh Biosep GmbH, Stuttgart, Germany). All samples were passed through a Fisher Scientific MF200 1μm glass microfibre filter paper before both DOC and HPSEC analyses. The zeta potential was measured with a zetasizer (Malvern Instruments, UK) at 20°C. The coagulation and flocculation experiments were undertaken using a Phipps and Bird PB-900 six paddle jar tester.

4(A).2.3 Reagents

The raw waters were coagulated with ferric sulphate (Ferripol XL, EA West) at a dose of either 5, 10 or 15 mg.l\(^{-1}\) as Fe (0.1-0.27 mMol Fe).

4(A).2.4 Procedure

Four raw water samples from both Albert and Bamford WTW, collected from September to December 2003, were fractionated using XAD resin adsorption techniques into their hydrophobic (HPO) and hydrophilic (HPI) components using a method adapted from Malcolm and MacCarthy (1992). An Amberlite XAD-7HP and Amberlite XAD-4 resin pair were used (Rohm and Haas, PA, USA). This method has been previously used on raw water collected from Albert WTW reservoir (Goslan et al., 2002; Fearing et al., 2004). The hydrophobic fractions were then separated further by reducing the pH to 1 and precipitating the humic acid fraction (HAF), with the fulvic acid fraction (FAF) remaining in the supernatant. The non-adsorbed fraction was categorised as hydrophilic non acid (HPINA), or non adsorbed fraction.

With regards to the coagulation-flocculation experiments only one jar was used at any one time. Raw water samples were stored at 5°C prior to jar testing and subsequent jar testing was undertaken at room temperature (20°C). The initial rapid mix was for 2 minutes at 200 RPM whilst adding the required dose of coagulant. NaOH was then added, until reaching the required coagulation pH, whilst stirring for an additional 1.5 minutes, also at 200 RPM. This order of chemical addition was chosen, as from experience this both produces the best results and matches full-scale operation at
Albert WTW. The jars were then stirred for 15 minutes at 30 RPM and left to settle for an additional 20 minutes before taking the samples, which were extracted from the centre of the jar. The zeta potential was measured with a zetasizer at 25°C. The zetasizer yields estimates and standard deviations of the zeta potential directly, and all measurements were conducted in triplicate. The general accuracy of the zetasizer was determined using standard solutions (Malvern Instruments, UK.) The zeta potential was initially measured at varying stages of the jar test procedure from the end of the rapid mix to the final settlement, and was found to show no significant variation.

4(A).3 Results and Discussion

4(A).3.1 Characterisation

The DOC concentrations of both raw waters increased across the period of investigation with a low of 6.6 mg.l\(^{-1}\) and 4.5 mg.l\(^{-1}\) in September 2003 to a high of 9.7 mg.l\(^{-1}\) and 10.2 mg.l\(^{-1}\) in December 2003, for Albert WTW and Bamford WTW respectively (Figure 4(A).1). The most significant increase in DOC for both sources was observed between September and October following the first period of heavy rainfall, at 40% and 53% for Albert WTW and Bamford WTW respectively. However, closer examination of results revealed that at Albert WTW the initial rise in DOC (2.6 mg.l\(^{-1}\)) was followed by a stable period when the DOC increase was only 0.1-0.4 mg.l\(^{-1}\) between October and December. At Bamford WTW, however, the DOC concentration continued to rise throughout the whole sampling period between 0.9 and 2.4 mg.l\(^{-1}\) each month.
Figure 4(A).1: (a) Albert and (b) Bamford NOM fraction make-up September-December. Humic acid fraction (HAF), Fulvic acid fraction (FAF), Hydrophilic acid (HPIA), Hydrophilic non adsorbed (HPINA).

HPSEC traces for both sites revealed a broad band of molecular sized material, characterised by two main peaks at c5.8 and c7.7 minutes with similar profiles for both Albert and Bamford raw water sources (Figure 4(A).2). Results from both sites revealed that the September rainfall event caused no shift in the position of the primary peak (c5.8 minutes), corresponding to an approximate molecular size greater than 5 kilo Daltons (kDa) (Pikkarainen et al., 2004). However, an increased absorbance of 23% was observed at Albert, as measured by the area under the curve,
compared to a 0.2% increase at Bamford. The total UV absorbance of both graphs did not change significantly, increasing by 7% and 2% for Albert and Bamford respectively. Although both values were 10-14% higher for Albert, attributed to the difference in UV measurements, 38.5-38.8 m$^{-1}$ and 48.7-63.6 m$^{-1}$ for Bamford and Albert respectively. In fact, the main difference for both sites, following the first flush, was the change in position of the secondary peak from an elution time of c7.7 minutes to c8.5 minutes, corresponding to an approximate decrease in molecular size from 4-5 kDa to 3-4 kDa. Subsequent HPSEC profiles for the months of November and December were also similar to the October sample.

![HPSEC plots](image)

**Figure 4(A).2: HPSEC plots of Albert and Bamford raw water, for both September and October 2003.**

HPSEC traces indicated a shift in NOM make-up following the first flush in September, whereas fractionating the NOM over the whole period demonstrated that the increase in DOC concentration was not observed to occur proportionally in all the fractions. Results revealed both an increase in hydrophilic and hydrophobic material at both Albert and Bamford during the period of September to October (Figure 4(A).1). Although the relative increases for both components were similar (1.1-1.3 mg.l$^{-1}$ for hydrophobic NOM and 1.1-1. mg.l$^{-1}$ for hydrophilic NOM), this reduced the overall proportion of hydrophobic material from 69% to 59% and from 67% to 62%, of the total DOC, for Albert and Bamford respectively. In the following period, October to December, the hydrophilic content was subsequently stabilised, whereas
the hydrophobic content continued to increase, the impact of which was to re-establish the hydrophobic:hydrophilic balance of the water prior to the flush phenomenon. Although both sources were affected by the changes in NOM fraction concentrations, Bamford appeared more stable with the overall hydrophobic content varying between 62 and 67%, compared to the variation at Albert of between 59% and 76%.

Previously reported fractionation data across different seasons for river and lake systems from both Europe (Ratnaweera et al., 1999) and the United States of America (Aiken et al., 2004), have concluded that the observed differences are often consistent with the view that as the DOC of a water increases the majority of the additional organic matter is likely to be hydrophobic in character (Malcolm, 1985). However, results obtained during this investigation highlight not only an increase in hydrophobic material but also an additional increase in the hydrophilic content of the water following initial periods of heavy rainfall. Similar findings, to the previous study, have been reported by Scott et al. (1998), who also looked at the seasonal variations in NOM obtained from a UK upland peat catchment system. During a four year study, they observed variations in the hydrophilic content of the water ranging between 20 and 80%, with the dissolved organic matter increasing in hydrophilicity during the summer months.

In relation to characterisation based on surface charge, the zeta potential of the raw water was -14.2 ± 1.7 mV and -16.1 ± 1.6 mV for Bamford and Albert respectively. In both cases, alteration of the pH of the raw water revealed a stable zeta potential value between pH 4 and 9 and an IEP of 2 (Figure 4(A).3). Results indicate that the charge of the colloids within the raw water can be characterised by an acidic dissociation model (Hunter, 1981). This is expected as the main functional groups identified within the structure of NOM are predominantly carboxylic and phenolic groups with a pKa in the range 3-6 and 8-10 respectively (Tiller and O’Melia, 1993; Gu et al., 1995; Edwards et al., 1996; Kretzschmar and Sticher, 1997).
Figure 4(A).3: Coagulation pH vs. zeta potential for September 2003 raw water samples from Bamford, coagulated with 5 and 15 mg.\text{L}^{-1} as Fe, and from Albert, coagulated with 5 mg.\text{L}^{-1} as Fe.

The interactions between NOM and ferric sulphate were monitored through changes in zeta potential with varying pH in order to establish the effect on the IEP of the system. For example, the IEP for a sample of Bamford water, coagulated with 5 mg.\text{L}^{-1} ferric sulphate (as Fe), was reached at pH 4.5. However, when the dose was increased to 15 mg.\text{L}^{-1} ferric sulphate (as Fe), this required an increase in pH to 5.5 in order to maintain the IEP. Hence the charge of the NOM-coagulant precipitate is dependent on both the mass ratio of NOM to metal ion, and the pH of the system (Jiang and Graham, 1998; Kam and Gregory, 2001; Duan and Gregory, 2003). When related to coagulant demand, the influence of pH corresponds to a mass ratio of Fe dose of 1.1 mg per mg DOC at pH 4.5, increasing to 3.3 mg per mg DOC at pH 5.5. The charge neutralising capacity of aluminium salts are also influenced by pH. For instance, Van Benschoten and Edzwald (1990) calculated an aluminium dose of 0.5 mg per mg of aquatic fulvic acid (FA) at pH 5.5, which then increased to 1 mg as Al per mg Aquatic FA at pH 7. Similarly, Tseng \textit{et al.} (2000), looked at treating snowmelt run-off water and concluded that 2.1 ± 0.1 mg.\text{L}^{-1} more alum was required for each additional mg of DOC. However, the relationship is not always one of simple stoichiometry and the relationship is also dependent on the character of the organics. For instance, coagulating both September water samples with 5 mg.\text{L}^{-1} ferric sulphate (as Fe)
required a pH of 5 and 4.5 for Albert and Bamford respectively, in order to reach the IEP. Albert raw water contained 2.1 mg.l$^{-1}$ more DOC than Bamford, hence if the relationship were one of simple stoichiometry, determined solely by the NOM concentration, then the IEP of the Albert sample would have been lower. In fact, it is more likely to be the NOM composition and character, rather that the total DOC concentration, which will determine the coagulant demand. Hydrophobic fractions, for instance, contribute the largest proportion of colloidal charge, at least one order of magnitude greater than the hydrophilic components (Edzwald, 1993; Sharp et al., 2004). Hence their increased presence will exert a greater coagulant demand required to minimise the surface charge and promote particle agglomeration. One added complication is that both character and composition of the individual NOM fractions have also been shown to vary both temporally and spatially (Owen et al., 1993; Sharp et al., 2004). Hence the differences in required coagulation conditions for Bamford and Albert in this case cannot be explained stoichiometrically in terms of NOM fraction make-up.

4(A).3.2 Treatment

Analysis of the performance of the coagulation process revealed a clear relationship between the zeta potential and residual concentration of either DOC or turbidity. Results demonstrate the existence of operational windows with respect to zeta potential, such that the residual following treatment is minimised. The threshold values were determined by calculating the rate of change of the residual. The operational window for DOC removal, within which the DOC residual remained at 1.0 ± 0.2 mg.l$^{-1}$, was between zeta potential values of -10 mV and +3.5 mV (Figure 4(A).4). Whereas for turbidity removal, the operational window was wider on the negative side of the scale, with residual turbidities of less than 1 NTU still achievable at a zeta potential of -20 mV. Both ranges are of a similar magnitude to previously published work, with Gregory and Carlson (2003), having considered optimum alum doses for Total Organic Carbon (TOC) removal to be in the zeta potential range -4.0 ± 3 mV. Whereas Edwards (2002), also observed a more extended range for optimal turbidity removal following ferric coagulation of a river water, with a 1 NTU residual possible when operating at a zeta potential between -12.4 and +18 mV. The definition of a range, as opposed to a single value, suggests that in general, colloidal destabilisation occurs before complete neutralisation of surface charge (Ratnaweera et
al., 1999). With regards to the magnitude of the operational zeta potential windows, results suggest that it is the organic concentration which influences the coagulation conditions. Edwards (2002) recorded a narrower operational zeta potential window (-12.9 to +3.2 mV) when the raw water was spiked with 3.4 m.L$^{-1}$ of commercial humic acid. Although in general, if the process is optimised for DOC removal, the residual turbidity will naturally also be at a minimum (Edzwald, 1993; Dennett et al., 1995).

Profiles for both Bamford and Albert also lack symmetry. For instance, with increasing negative zeta potential values a gradual decline in performance was observed, corresponding to a negative gradient of 0.06, whereas for positive zeta potential values there was a much steeper reduction in performance at operational boundary. These observations suggest the importance of patchwork agglomeration where only partial neutralisation of the charge is required (Ratnaweera et al, 1999), whereas the large negative values that still provide optimal treatment suggest the potential importance of polymer bridging from the large MW material. Observed differences may also depend on the particular system involved. To illustrate, when coagulating Albert raw water at a zeta potential of -7.8 mV this resulted in a DOC removal of 85%. This then dropped to 68% when the magnitude of the negative zeta
potential was increased to -18.9 mV, corresponding to an approximate reduction in performance of 1.5% per mV. Zouboulis et al. (2003) reported a similar reduction in humic acid removal, using a commercial humic acid solution, for a similar increase in the magnitude of the negative zeta potential (-7.8 to -19.8 mV). In this case removal decreased from 94.7 % to 66.6% and corresponded to a 2.3% reduction per mV. However, when examining the profile with respect to a positive zeta potential, at a zeta value of 12.6 mV, Zouboulis et al. (2003), were still able to achieve 92% humic acid removal, whereas no significant or reliable removal was observed at either Albert or Bamford for a zeta potential greater than 5 mV.

Once operating the coagulation process within the operational window, with respect to zeta potential, the optimal residual concentrations are unaffected by an increase in coagulant dose providing the surface charge is maintained through pH adjustment. For instance, in the case of raw water samples from Albert in September 2003, coagulated with either 5 or 10 mg.l⁻¹ ferric sulphate as Fe, and the pH increased from 5.2 to 5.8 in order to maintain a constant zeta potential within the previously determined operational window (-10 mV and +3.5 mV). HPSEC chromatograms for both treated water samples were almost identical, thus demonstrating no additional removal or benefit with the increased coagulant dose (Figure 4(A).5). This has also been described by Krasner et al. (1994), who carried out jar tests on California State Project Water at incremented alum doses from 22 to 111 mg.l⁻¹. They also found that after a certain dose of 47 mg.l⁻¹, there was a plateauing of DOC removal. These results support the hypothesis that achieving the required zeta potential is more important than achieving a certain coagulant dose or pH.
Figure 4(A).5: HPSEC chromatograms of Albert raw water from September, coagulated with 5 and 10 mg.\textsuperscript{1} ferric sulphate as Fe and a resulting zeta potential of zero.

The relationship between zeta potential and residual DOC was unaffected by either the seasonal variations, source or changes in NOM composition over the period September to December 2003 (Figure 4(A).6). At Albert WTW for example, the DOC concentration rose from 6.6 to 9.7 mg.\textsuperscript{1} during the period of investigation. However, despite the increasing organic concentration in the raw water and increasing the coagulant dose from 15 to 24 mg.\textsuperscript{1} (as Fe) in order to maintain a 0.4:1 mgDOC:mg\textsuperscript{1}Fe ratio, the shape of the DOC residual profile with respect to zeta potential remained unaffected. In order to test the statistical significance of the operational zeta potential window identified from the experimental data, all results were divided into one of six operational bands with regards to zeta potential. The bands were as follows; <-15 mV, -5 to -10 mV, 0 to -5 mV, +3 to 0 mV and >+3 mV (Figure 4(A).7). Statistical analysis of the data was performed by first undertaking an F test, in order to determine if there were any significant difference in variance between the groups, followed by a series of T tests in order to determine whether the data sets were from the same distribution or significantly different. Statistical analyses confirmed the visual observations, such that in general, DOC residuals obtained within the operational zeta potential window (-10 to +3 mV) were not significantly different at a 95% confidence interval, whereas there was a significant difference when comparing these results with
those obtained when coagulating outside the operational window (Table 4(A).3). Additional t test analyses also revealed no significant difference, at the 95% confidence interval, with regards to seasonal variations, source or coagulant dose, when operating within the operational envelope (-10 to +3 mV).

![Zeta Potential vs. Rem. Performance](image)

**Figure 4(A).6:** Zeta potential vs. removal performance in terms of DOC residual for Albert raw water coagulated with ferric sulphate to a 0.4:1 DOC:Fe (mg:mg) ratio at pH's between 3 and 7.

![Average DOC Residuals](image)

**Figure 4(A).7:** Average DOC residuals according to zeta potential range, for all treated water samples.
Table 4(A).3: Statistical t test significance matrix.

<table>
<thead>
<tr>
<th>Zeta Potential Band</th>
<th>&lt;15 (mV)</th>
<th>-10 to -15 (mV)</th>
<th>-5 to -10 (mV)</th>
<th>0 to -5 (mV)</th>
<th>0 to +3 (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;-15 (mV)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-10 to -15 (mV)</td>
<td>SD</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-5 to -10 (mV)</td>
<td>SD</td>
<td>ND</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0 to -5 (mV)</td>
<td>SD</td>
<td>ND</td>
<td>ND</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>+3 to 0 (mV)</td>
<td>SD</td>
<td>ND</td>
<td>ND</td>
<td>SD</td>
<td>-</td>
</tr>
<tr>
<td>&gt;+3 (mV)</td>
<td>ND</td>
<td>SD</td>
<td>SD</td>
<td>SD</td>
<td>SD</td>
</tr>
</tbody>
</table>

SD- Significantly different at 95% Confidence interval
ND- No significant difference at 95% Confidence interval

As previously discussed, the NOM content of the water controls the critical coagulant concentration due to the high charge content, with the hydrophobic material contributing a greater proportion of the colloidal charge (Letterman et al., 1999; Sharp et al., 2004). However, the hydrophobic fraction is also the most amenable to removal by conventional coagulation with metal salts, whereas for NOM fractions with more hydrophilic tendencies, reported removals are poor (Randtke, 1988; Owen et al., 1993; Krasner et al., 1994; Edwards, 1997; White et al., 1997). Previous work at Albert, involving coagulation of the isolated HPINA fraction, has revealed limited removal of just 16% (Fearing et al., 2004). However, this phenomenon is not solely related to upland moorland UK waters, as Krasner et al. (1994), obtained similar results when blending two US waters, both with low MW DOC concentrations of 1.3-1.4 mg.1⁻¹, and found the residual after alum coagulation was 1.0-1.3 mg.1⁻¹ DOC, regardless of the blend. This corresponded to a removal of between 8 and 30% for the low MW DOC. One proposed explanation for the poor removal is attributed to the fact that at the coagulation pH of normal operation (5-7), the hydrophilic fractions (HPIA and HPINA) possess a negligible or slightly positive charge (Edzwald, 1993; Sharp et al., 2005). Consequently, increasing the coagulant dose further is less likely to promote any additional removal of this fraction. In fact, determination of the hydrophilic content can be used to provide a useful indicator for the achievable DOC residual once the coagulation process has been optimised.
Although few studies have been undertaken on fractionated organic matter, a number have reported removal in relation to specific UV absorbance (SUVA, m$^{-1}$.L mg$^{-1}$), which gives a relative indication of the hydrophobic content in water. It has been reported that a SUVA value of less than 2.5 indicates a more hydrophilic nature and subsequently leads to a poor removal performance, with values reported in the region of 11-30% (Fearing, 2004). However, with reference to this investigation, SUVA values varied between 3.6 and 7.4, therefore indicating the general hydrophobic nature of both water sources. In fact DOC removals were greater than 70% in all cases and SUVA values showed no correlation with the residual DOC values. Analysis of optimum achievable DOC residuals with respect to initial HPINA fraction concentrations did produce a more significant relationship which could be used to indicate coagulation performance. For instance, the HPINA fraction increased from 1.4 to 2.7 at Albert WTW, over the period September to December, and despite operating at optimum conditions the average DOC residual at optimum zeta potential increased from 0.9 to 1.9 mg.L$^{-1}$. However, when considering the DOC residual in terms of HPINA removal, the values were relatively similar with 27-35% removal. Similar results were observed at Bamford WTW, such that as the HPINA fraction increased from 1.1 to 1.8 mg.L$^{-1}$ in the raw water, the DOC residual increased by the
same amount from 0.9 to 1.6 mg.L\(^{-1}\). In both cases, operating within the operational zeta potential window revealed that the DOC residual was lower than the initial HPINA concentration, indicating that a certain degree of removal of this fraction is possible through conventional coagulation methods. This is also in agreement with White et al. (1997) who found that the total DOC removal was greater than the hydrophobic content of the water, indicating there is still a certain degree of hydrophilic NOM removal. Analysis of other waters reveals a similar relationship between the low MW non adsorbed fraction and achievable DOC residual, with the gradient of the regression line \((R^2 = 0.88)\) indicating the majority of the residual is contained within the HPINA fraction (Figure 4(A).8). Whilst the residual organics are likely to contain other material the results suggest the initial HPINA can serve as a useful guide to the likely achievable residual DOC by coagulation. This is, however, also dependent on both the source water characteristics at each location and the coagulant used, with ferric resulting in a lower residual compared to alum based coagulants (Edzwald and Tobaison, 1999; Bell-Ajy et al., 2000).

4(A).4 Conclusions

Results presented here have shown the relationship between zeta potential and residual concentration appears to be insensitive to seasonal variations, source and coagulation conditions. Consequently, optimising the coagulation process using zeta potential measurements should produce both a more robust performance, provided the following are considered:

- The coagulation zeta potential is maintained within -10 mV and +3 mV.
- Performance is more sensitive to changes at the positive zeta potential boundary.
- Optimising for DOC removal should also result in good turbidity removal.
- Coagulant demand may not always be identified through simple monitoring of bulk water parameters such as DOC or UV\(_{254}\).

The future challenge is therefore to understand robustness and the ease with which the system can remain within the operational charge boundaries set.
4(A).5 References


4(B) The effects of changing NOM composition and characteristics on coagulation performance, optimisation and control.

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Abstract

A number of water utilities have been experiencing operational difficulties during specific times of the year, associated with elevated levels of organics due to heavy rainfall or snow melt. Water samples were collected from Albert treatment works (Halifax, UK) and the natural organic matter (NOM) was characterised using XAD resin adsorption techniques. The addition of a cationic polyelectrolyte was employed to determine the charge density of the fractions. Results show that NOM fraction make-up changes throughout the year, with the fulvic acid fraction (FAF) showing the greatest increase during the autumn and winter period. The charge density of the FAF fraction also increases. The coagulation conditions for traditional coagulants, such as iron, are more affected by increased levels of organics than the highly charged novel coagulant also investigated, and the zeta potential range for optimum removal is narrower. Therefore, the conditions required for zero charge during coagulation varies with both raw water source and the coagulant type.

Keywords

Coagulation, Natural organic matter (NOM), Zeta potential, Water treatment.
4(B).1 Introduction

Process options for the treatment of water to remove organic matter are well established and understood and for the most part produce stable high quality product waters. However, a number of UK water utilities situated in northern England and Scotland, in addition to a number of US water companies with mountain catchments, are experiencing difficulties during specific times of the year associated with periods of elevated organics due to heavy rainfall or snow melt. During these periods of elevated organics, operational robustness is being reduced, especially in terms of dissolved organic carbon (DOC), trihalomethane formation potential (THMFP), colour and rapid gravity filter run time.

Surface charge is of particular importance for the majority of processes involved in water treatment, especially concerning the aggregation of particles during coagulation and flocculation, and capture by media filtration. Waters from moorland catchments (Yorkshire, UK) are characterised by low turbidities and high colour and as such coagulation is controlled by the concentration and character of the organics in the water. Natural organic matter (NOM) can be considered as a mixture of molecular weight anionic polyelectrolytes. The iso-electric point (IEP) of the raw water is generally between pH 1-2.5 and as such is normally negatively charged at the raw water pH. Coagulants such as ferric chloride or alum interact with the NOM by forming complexes with the positively charged hydrolysis products. Further interaction occurs as additional NOM adsorbs onto metal hydroxide precipitate and the NOM-coagulant complexes (O’Melia et al., 1999; Duan and Gregory, 2003). The understanding of these reactions and more importantly, the flocs that subsequently form, is complicated as the NOM has a dynamic character which alters according to changing condition within the catchment.

The aim of the study reported in this paper was to investigate the link between NOM seasonality, the charge of the NOM-coagulant complex and removal. In addition to iron, the use of a highly charged novel coagulant was also investigated. This coagulant has found its application in the leather processing industry, reacting with the carboxyl groups present on the animal skins, although its application to water treatment has never been previously documented.
4(B).2 Materials and Methods

Albert Water Treatment Works (WTW) is situated in Halifax, UK and the reservoir is fed by an upland peat catchment system. The raw water source has been the subject of various character, fractionation and reactivity studies (Jarvis et al., 2003; Goslan et al., 2002; Fearing et al., 2004). Seasonal variations in water quality at Albert WTW are shown below (Table 4(B).1).

*Table 4(B).1: Raw water quality at Albert WTW.*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Water quality (Summer)</th>
<th>Water quality (Autumn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>mg.l⁻¹</td>
<td>4.3-7.0</td>
<td>8.8-14.2</td>
</tr>
<tr>
<td>UV-Abs</td>
<td>l.m⁻¹</td>
<td>39.3-48.7</td>
<td>72.2-52.3</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>6.2-6.4</td>
<td>5.5-6.6</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>3.7-5.9</td>
<td>5.9-7.0</td>
</tr>
</tbody>
</table>

4(B).2.1 Apparatus

The turbidity of the samples was measured using a HACH2100 turbidity meter (Camlab, UK). A Shimadzu 5000A TOC analyzer was used for determining the DOC content. UV-Abs (l/m) at a wavelength of 254nm was measured using a Jenway 6505 UV/Vis spectrophotometer. All samples were passed through a Fischer Scientific MF200 1µm glass microfibre filter paper before both UV and DOC analyses. The zeta potential was measured with a zetasizer 2000HSA (Malvern Instruments, UK). The coagulation and flocculation experiments were undertaken using a Phipps and Bird PB-900 six paddle jar tester.

4(B).2.2 Reagents

The coagulants under investigation were: Ferric sulphate (*Ferripol xl, EA West*) and a highly charged novel coagulant (*patent pending*). The cationic polymer polydiallyldimethylammoniumchloride (PolyDADMAC), with a molecular weight (MW) of 100,000-200,000, was obtained from Sigma-Aldrich as a 20 wt% aqueous solution. This was then diluted to a 0.1% solution with the charge density calculated to be 6.2 meq.g⁻¹ from the manufacturer’s information. Details of the preparation of the novel coagulant are provided in Parsons and Jefferson (2004).
4(B).2.3 Procedure

Four raw water samples, collected from September to December 2003, were fractionated by XAD resin adsorption techniques into their hydrophobic (HPOA) and hydrophilic (HPIA) components using a method adapted from Malcolm and MacCarthy (1992). An Amberlite XAD-7HP and Amberlite XAD-4 resin pair were used (Rohm and Haas, PA, USA). This method has been previously used on raw water collected from Albert WTW reservoir (Fearing et al., 2004; Goslan et al., 2002). The hydrophobic fractions were then separated further by reducing the pH to 1 and precipitating the humic acid fraction (HAF), with FAF remaining in the supernatant. The non-adsorbed fraction was categorised as hydrophilic non adsorbed (HPINA).

The charge density of the NOM fractions was determined using the Malvern zetasizer and PolyDADMAC. A beaker containing 100ml of deionised water, 2.5mg of the appropriate NOM fraction and a magnetic stirrer bar were placed on a magnetic stirrer. Varying amounts of 0.1% PolyDADMAC were added to the beaker, with the pH adjusted to 7 with NaOH, and the zeta potential measured until the point of zero charge or iso-electric point (IEP) had been established.

With regards to the coagulation-flocculation experiments only one jar was used at any one time. Raw water samples were stored at 5°C prior to jar testing and subsequent jar testing was undertaken at room temperature (20°C). The initial rapid mix was for 2 minutes at 200 rpm whilst adding the required dose of coagulant. NaOH was then added, until reaching the required coagulation pH, whilst stirring for an additional 1.5 minutes, also at 200 rpm. The order of chemical addition was chosen, as from experience this both produces the best results and matches full-scale operation at Albert WTW. The jars were then stirred for 15 minutes at 30 rpm and left to settle for an additional 20 minutes before taking the samples, which were extracted from the centre of the jar. The surface charge was measured with a zetasizer at 20°C. The zetasizer yields estimates and standard deviations of the zeta potential directly, and all measurements were conducted in triplicate. The general accuracy of the zetasizer was determined using standard solutions (Malvern Instruments, UK.) The zeta potential was initially measured at varying stages of the jar test procedure from the end of the rapid mix to the final settlement, and was found to show no significant variation.
4(B).3 Results and Discussion

4(B).3.1 Changes in NOM composition and character
The raw water at Albert WTW is highly coloured with low turbidity (Table 1). Total DOC levels remained relatively stable at $9.4 \pm 0.3 \text{ mg.l}^{-1}$ across all the samples analysed with the exception of the sample collected in September 2003 which was considerably lower at $6.6 \text{ mg.l}^{-1}$ (Figure 4(B).1a). Fractionation of the raw water revealed that the make up of the water varied throughout the year even during periods of relatively stable total DOC. The water consisted of between 58 and 76 % hydrophobic material of which the fulvic component contributed between 27 and 46% (Figure 4(B).1b). From meteorological observations, the periods of high hydrophobic content follow periods of increased rainfall. Rainfall in the north increased from 17.6mm in August to 43.6mm for September, followed by an additional increase from 55.6mm in November to 79.1mm in December (Met Office, 2004).

The charge density was determined for NOM fractions taken from April 2002, a reference sample relating to previous work undertaken at Albert WTW (Goslan et al., 2002; Fearing et al., 2004), and showed the charge density of the hydrophobic fractions to be nearly two orders of magnitude greater than the hydrophilic fractions (Figure 4(B).2a). The charge density of the HAF fraction was 6.8 meq.g$^{-1}$ compared with 4.2 meq.g$^{-1}$ for the FAF fraction. Corresponding charge densities of 0.06 and <0.01 meq.g$^{-1}$ were measured for the HPIA and HPINA respectively. In fact the charge density of the HPINA fraction was so low that it remained effectively below the limit of detection of the method employed. The values from the current study are in broad agreement with those of Kam and Gregory (2001) at 5-5.6 meq. g$^{-1}$ for humic acid and Tipping (1993) at 5-10 meq.g$^{-1}$ for both humic and fulvic acids.

Measurement of the charge density of the fractions during different seasons revealed similar variability as with fractional make up (Figure 4(B).2b). To illustrate, the charge density of the FAF fraction decreased from 3.2 meq.g$^{-1}$ in Jun 03 progressively to 1.2 meq.g$^{-1}$ in Nov 03. This compares to a value of 4.2 meq.g$^{-1}$ as reported above and demonstrates that the charge density of the FAF fraction can vary by at least a factor of 3.5 due to seasonal effects. No correlation between DOC concentration, percentage contribution and charge density could be determined during the study.
indicating that the nature of the molecules within each fraction varies considerably throughout the year, making it very difficult to dose coagulant stoichiometrically based on the NOM fraction make-up.

Figure 4(B).1: NOM fraction contribution (a) as mg L⁻¹ DOC and (b) expressed as a percentage of the raw water.
4(B).3.2 Coagulation conditions for IEP

The zeta potential profiles demonstrate the impact of NOM concentration and character on the surface charge (Figure 4(B).3a). The IEP of the system shifts towards more basic conditions as the ratio of DOC to Fe decreases due to the greater influence of the coagulants on the net surface properties of the complex. For instance, with regard to the water collected in September 2003, the IEP shifted from pH 3.2 at a DOC:Fe ratio of 3 to a pH of 6 at a DOC:Fe ratio of 1. Consequently, at the pH of operation (pH 4.5) the water shifts from being relatively negatively charged to positively charged at the two DOC:Fe ratios described above. Comparison with water collected during December 2002 shows a more sensitive impact of DOC:Fe during the December samples. Unfortunately no charge density data was available for this period, although macroscopic changes in the water, such as a higher DOC and subsequent

Figure 4(B).2: The impact of (a) NOM fraction and (b) season on FAF charge density.
FAF concentration could be responsible for the increased sensitivity. Charge density data for FAF was available for October 2002, at 4.2 meq.g\(^{-1}\) and it is therefore likely that the value for December 2002 is in the same region.

The influence of coagulant was examined by conducting trials with a highly charged novel coagulant (Figure 4(B).3b). This has a charge density of 0.04 eq.g\(^{-1}\) and exists principally in its 4+ form across a broad range of pHs. Comparison of the September 03 water revealed that using the highly charged coagulant decreased the influence of the DOC:coagulant ratio on the i.e.p, based on a mass ratio. When converted to moles, for the 1:1 ratio, this equates to 0.1 moles of iron compared to only 0.07 moles of the novel coagulant.

![Figure 4(B).3: pH of zero charge plotted against DOC:coagulant ratio for (a) water samples collected from two different seasonal periods and dosed with iron and (b) September water dosed with iron or the novel coagulant.](image-url)
4(B).3.3 Zeta potential vs. removal

Direct comparison of the residual concentration of turbidity and DOC to the zeta potential reveals that residual concentrations are minimised at low zeta potentials. For instance, residual turbidity remained below 0.5 NTU between zeta potentials of -18 to +5 mV (Figure 4(B).4a). Comparison of the two coagulants revealed no statistical difference between the two systems over the above zeta potential range. Similar results were observed in terms of residual DOC concentration except that the optimised range was much narrower than for turbidity and was centred around a zeta potential of 0 mV (Figure 4(B).4b). The use of the highly charged novel coagulant also appeared to extend the range over which residuals remained low for both turbidity and DOC. In the case of turbidity this was observed as an extension to more positive value whereas the range extended in both positive and negative values for organics removal.

![Graphs showing zeta potential vs. removal]

*Figure 4(B).4: Zeta potential vs. removal performance in terms of (a) turbidity and (b) DOC residuals.*
4(B).4 Conclusions

From results presented, it is apparent that the raw water characteristics for the period September to December 2003 alter considerably even though the DOC level remained stable. This variability has been demonstrated for both fractional make up and charge density. The impact of the variation in charge density has been to alter the charge response of the system at set dose rates such that the zeta potential can vary considerably even though nothing in the system appears to have been altered. The effect zeta potential variation may have on treatment has been indicated by the relationship between zeta potential and residual turbidity and DOC. Whilst the optimum range for turbidity removal is fairly broad the equivalent range for DOC is narrow. The implication is that changes in make up in the water may reduce organics removal whilst the plant appears to be operating at steady state.

Results presented here have shown the potential benefit of using alternative chemicals. The experiments with the highly charged novel coagulant appear to generate a better level of removal at a comparative zeta potential, a less sensitive system to changes in the raw water and a broader range of operationally suitable zeta potentials. However, when considering the use of this novel coagulant, the economic costs should also be considered as at present it is still an expensive alternative.

Finally, results from this investigation show that better understanding of the charge density variations in the water is important. Consequently, zeta potential monitoring may become important during periods of operational difficulties to develop more robust solutions.

5.0 References


CHAPTER 5
PILOT SCALE COAGULATION

5(A) The application of zeta potential measurements for coagulation control: Pilot plant experiences from UK and US waters with elevated organics.

Published in: Water Science and Technology: Water Supply (IN PRESS).

5(B) Operational zeta potential windows for optimal DOC removal.


5(C) Coagulation of NOM: Linking character to treatment.

Submitted to: Water Science and Technology.
The application of zeta potential measurements for coagulation control: Pilot plant experiences from UK and US waters with elevated organics.

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Abstract

At present little is known about the relationship between raw water characteristics, such as natural organic matter (NOM) content, and the universal applicability of coagulation optimisation through surface charge measurement. This research aims to investigate this issue by comparing case study sites in the US (Poudre River, Fort Collins, Colorado) and the UK (Albert Reservoir, Halifax) across periods of elevated organic levels. During the period of April to June 2004, raw Poudre River water dissolved organic carbon (DOC) levels increased rapidly from 3.5 to 7.4 mg.l\textsuperscript{-1} as a direct result of the spring snowmelt run-off. Whereas at Albert reservoir, which is a moorland peat catchment, DOC concentrations varied between 7.8 and 10.1 mg.l\textsuperscript{-1} during the period of January to March 2004. NOM is a highly heterogeneous mixture of organic compounds that vary with regards to acidity, molecular weight, hydrophobicity and charge density. XAD resin adsorption techniques were employed to fractionate the water into their hydrophobic and hydrophilic components. Results revealed that NOM composition and characteristics can vary both temporally and spatially, with increased DOC concentrations associated with both an increase in hydrophobic content and charge density. Optimising coagulation based on a zeta
potential range (-10 to +5 mV) produced stable average DOC residuals for both locations. The exact value is also dependent on the hydrophilic composition of the water and the coagulant used, with alum removing approximately 0.5 mg.l\(^{-1}\) less DOC compared to ferric.

**Keywords**

Coagulation, Natural organic matter (NOM), Zeta potential.
5(A).1 Introduction

Natural waters throughout the world contain natural organic matter (NOM) as a result of the interactions between the hydrological cycle and both the biosphere and geosphere. This is dependent on the surrounding environmental biogeochemical cycles, resulting in a highly heterogeneous mixture of organic compounds that vary with regard to acidity, molecular weight and charge density (Goslan et al., 2002; Edzwald, 1993; Collins et al., 1986). A number of UK and US water utilities, particularly those in the moorland peat catchment areas of northern England, and mountain catchment areas in the US, are experiencing difficulties during specific times of the year associated with periods of elevated organics following heavy rainfall or snow melt. The removal of NOM has become increasingly important in light of the potential for carcinogenic disinfection by-products (DBP) to form from residual organics during the disinfection process. However, it is the operational robustness, especially in terms of dissolved organic carbon (DOC) removal and subsequent DBP formation, which is being reduced during these periods of elevated organic concentrations.

NOM is traditionally removed through conventional coagulation with trivalent metal ions (Fearing et al., 2004). Coagulants such as ferric chloride or alum interact with the NOM by forming complexes with the positively charged hydrolysis products. Further removal occurs as additional NOM adsorbs onto metal hydroxide precipitate and the NOM-coagulant complexes (Duan and Gregory, 2003). At present little is known about the relationship between raw water characteristics, such as NOM content and character on optimising the coagulation process. Previous research at bench-scale using Albert reservoir water has highlighted that the coagulation process could be optimised through surface charge measurement (Sharp et al., 2004).

The aim of this study was to investigate the link further on a pilot scale by comparing two case study sites, in the US and the UK, across periods of varying raw water characteristics and coagulated with both ferric and alum based coagulants. Hence investigating the relationship with regards to NOM composition, character, source and coagulant type.
5(A).2 Materials and Methods

The first case study was the Poudre river, at the Fort Collins water treatment facility (FCWTF), Colorado, USA. During the period of April to June 2004, the raw Poudre river DOC levels increased rapidly from 3.5 to 7.4 mg.l$^{-1}$ as a result of the spring snowmelt run-off. The second case study was the Albert reservoir, situated at the Albert water treatment works (WTW), Halifax, UK, during the period of January to March 2004 when the DOC concentrations varied between 7.8 and 10.1 mg.l$^{-1}$. This is a moorland peat catchment area producing a more coloured water for the majority of the year, and is also subject to increased DOC levels following periods of heavy rain. Variations in water quality at both locations are shown below (Table 5(A).1).

Table 5(A).1: Raw water quality variations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Albert Reservoir (Jan-Mar)</th>
<th>Poudre River (Apr-June)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>mg.l$^{-1}$</td>
<td>7.8-10.1</td>
<td>3.5-7.4</td>
</tr>
<tr>
<td>UV-Abs</td>
<td>l.m$^{-1}$</td>
<td>39.7-43.6</td>
<td>11.0-22.5</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>5.9-6.1</td>
<td>7.0-7.6</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>3.7-7.0</td>
<td>0.5-19.6</td>
</tr>
</tbody>
</table>

5(A).2.1 Pilot plant facilities

The FCWTF Pilot included two parallel trains designed to reflect the operational characteristics of full-scale treatment, including rapid mix, 3 stage plug flow flocculation and lamella plate settling (Figure 5(A).1). Raw Poudre River water was pumped into each train at a flow of 1.82 M$^3$.h$^{-1}$. Lime (Mississippi Lime Company, MO, USA) and carbon dioxide (Fisher Scientific, USA, 10-752-1G regulator and Omega, USA, model FMA1916 gas mass flow controller) were added to the raw Poudre River water before it was split between the two trains, in order to both achieve an alkalinity of 25-35mg.l$^{-1}$ as CaCO$_3$ and manipulate the coagulation pH. The pilot plant was run using both aluminum sulphate and ferric sulphate at doses ranging from 14 to 44 mg.l$^{-1}$ (1.3-4 mg.l$^{-1}$ as Al) and from 10.4 to 17.4 mg.l$^{-1}$ (3-5 mg.l$^{-1}$ as Fe) respectively (General Chemical, USA).

Two pilot plants were operated using raw water from Albert reservoir. The first (Cranfield), was operated in January 2004 at a flow of 450 L.h$^{-1}$, and included a rapid mix stage followed by two stage flocculation. pH was controlled through the addition of 0.1M NaOH into the rapid mix tank. The second pilot plant (DA20), was operated
in March 2004 at a flow of 15 M$^3$.h$^{-1}$ and included inline static mixing of the coagulant and 25% Kalic suspension (Buxton Lime, UK), the latter was added to control the coagulation pH. This was followed by three stage plug flow flocculation and dissolved air flotation. Both pilot plants were run using ferric sulphate (EA West, UK) with doses varying between 5 and 15mg.l$^{-1}$ as Fe (0.09 mMol-0.18 mMol as Fe). For all pilot investigations, coagulant dose and pH were varied in order to manipulate the zeta potential. A more detailed description of all three pilot plants has been published previously (Parsons et al., 2005).

Figure 5(A).1: (a) Fort Collins, (b) Cranfield and (c) DA20 pilot plants

5(A).2.2 Analysis

Once pilot plant conditions had stabilised, samples were taken in triplicate and analysed for UV absorbance at a wavelength of 254nm (Jenway 6505 UV/Vis spectrophotometer, Jenway, UK), pH, DOC, in some cases TOC, (Shimadzu TOC-5000A analyser in the UK and Sievers Model 800TOC analyzer at FCWTF ), and high performance size exclusion chromatography (HPSEC) (Shimadzu VP series, Shimadzu, UK). The HPSEC analysis used a TSK gel, GW3000SW column, 7.5mm internal diameter and 30cm in length. The guard column was also TSK, 7.5mm internal diameter and 7.5cm in length (Tsoh Biosep GmbH, Stuttgart, Germany). All samples were filtered to remove suspended solids before UV$_{254}$, DOC and HPSEC analysis (Glass microfibre in the UK and Durapore membrane filter at FCWTF, Fisher Scientific). The surface charge was measured with a Zetasizer (Malvern Instruments, UK) at 25°C. The Zetasizer yields estimates and standard deviations of the zeta potential directly, and all measurements were conducted in triplicate on unfiltered samples. The general accuracy of the Zetasizer was determined using standard solutions (Malvern Instruments, UK.)
5(A).2.3 Fractionation

Raw water samples were collected from Albert reservoir in January 2004, and from the Poudre river both before and during the spring snowmelt run-off (April and May 2004). The samples were fractionated by XAD resin adsorption techniques into their hydrophobic (HPOA) and hydrophilic (HPIA) components using a method adapted from Malcolm and MacCarthy (1992). An Amberlite XAD-7HP and Amberlite XAD-4 resin pair was used (Rohm and Haas, PA, USA). This method has been previously used on raw water collected from Albert reservoir (Goslan et al., 2002). The hydrophobic fractions were then separated further by reducing the pH to 1 and precipitating the humic acid fraction (HAF), with the fulvic acid fraction (FAF) remaining in the supernatant. The non-adsorbed fraction was categorised as hydrophilic non adsorbed (HPINA).

5(A).2.4 Charge density

The charge density of the raw water samples was determined using the Malvern Zetasizer and PolyDADMAC (Sigma-Aldrich, UK). A beaker containing 1 litre of raw water and a magnetic stirrer bar were placed on a magnetic stirrer. Varying amounts of 0.1% PolyDADMAC were added to the beaker, with the pH adjusted to 7 with NaOH, and the zeta potential measured until the point of zero charge or iso-electric point (IEP) had been established.

5(A).3 Results and Discussion

5(A).3.1 Characterisation

Bulk water analyses demonstrated the effect of increased surface run-off on the total organic levels at each location. For instance, a rapid rise in Poudre river DOC concentrations, from 4.4 mg.l\(^{-1}\) to 7.4 mg.l\(^{-1}\), was recorded during the period of May 4\(^{th}\) to May 13\(^{th}\) as a direct result of the spring snowmelt run-off. Albert reservoir is located in a moorland peat catchment and therefore subject to more frequent rainfall events, the impact of which is that organic levels remain high over the majority of the year, with a variation in DOC concentrations between 7.8 mg.l\(^{-1}\) and 10.1 mg.l\(^{-1}\) recorded for the period of January to March.

HPSEC traces of the raw Poudre river water samples clearly demonstrate an increase in UV\(_{254}\) absorbing compounds associated with the increased DOC concentrations
(Figure 5(A).2a). For instance, the area under the graph increased by an additional 122% coinciding with a 40% increase in DOC from 4.4 mg.l$^{-1}$ to 7.4 mg.l$^{-1}$. Results also revealed a shift in the main peak from 8.5 to 8.3 minutes, indicating an increase in the molecular weight of the organic material (Pikkarainen et al., 2004). At Albert reservoir, the HPSEC traces exhibited less variation, with the area under the graph increasing by just 1% with an associated increase in DOC of 30% from 7.8 mg.l$^{-1}$ to 10.1 mg.l$^{-1}$ (Figure 5(A).2b).

![HPSEC Profiles](image)

**Figure 5(A).2**: HPSEC profiles for (a) Raw Poudre river water during the initial stages of the 2004 spring snowmelt run-off with corresponding DOC concentrations and (b) Poudre river and Albert reservoir water.
Fractionation data revealed an increase in the hydrophobic content (HAF and FAF combined) of the Poudre river from 65% to 75% during the spring snowmelt run-off, and was similar to the 74% hydrophobic content present at Albert reservoir in January (Figure 5(A).3). The charge density of the Poudre river raw water increased from 0.009 meq.l\(^{-1}\) to 0.029 meq.l\(^{-1}\) compared to 0.023 meq.l\(^{-1}\) at Albert reservoir in January. This corresponds to an increase from 2.0 meq.g\(^{-1}\)DOC to 3.9 meq.g\(^{-1}\)DOC for the Poudre river. Green (1997), also recorded an increase of 2.0 to 2.5 meq.g\(^{-1}\)DOC during the 1997 Poudre river snowmelt run-off period. The increased charge density is attributed to the fact that hydrophobic fractions contribute the largest proportion of colloidal charge, at least one order of magnitude greater than the hydrophilic components. Hence their increased presence will exert a greater coagulant demand required to minimise the surface charge and promote particle agglomeration (Sharp et al., 2004; Edzwald, 1993; Collins et al., 1986). However, comparing the relative charge densities for both locations revealed a lower value for Albert reservoir, at 2.7 meq.g\(^{-1}\)DOC. Further consideration of fractionation data revealed that despite their similarities, the individual NOM fraction make-up between the two samples also varied. For instance the HAF, FAF, HPIA and HPINA contributions were 23%, 52%, 9% and 16% for Poudre river run-off water, compared to 15%, 59%, 12% and 14% for Albert reservoir in January. Previous research has also looked at the charge density of individual fractions and found no correlation between DOC concentration, percentage contribution and charge density could be determined (Sharp et al., 2004). Hence indicating that the nature of the molecules within each fraction varies considerably throughout the year, and therefore making it very difficult to dose coagulant stoichiometrically based on bulk parameters such as UV\(_{254}\) absorbance. Consequently, some consideration of charge is also required in order to optimise the coagulation process.
5(A).3.2 Coagulation and zeta potential

The zeta potential profiles demonstrate the impact of surface charge on coagulation performance despite the varying NOM composition, character, pilot plant scale and raw water source (Figure 5(A).4). Operating within a zeta potential window of -10 to +5 mV produced stable DOC residuals of $1.5 \pm 0.2$ mV and $1.2 \pm 0.2$ mV for Poudre river and Albert reservoir respectively. The definition of a range, as opposed to a single value, suggests that in general, colloidal destabilisation occurs before complete charge neutralisation of surface charge which is why good optimal residuals are still possible although the zeta potential may not necessarily be zero (Ratnaweera et al., 1999). The extent of the range is likely to be determined by additional non Derjaguin Verwey Landau Overbeek (DVLO) forces present in the system, such as hydrophobic or steric effects, and is therefore likely to be dependent on the character of the organics present. However, although the operational window at Albert reservoir was slightly wider, with stable DOC residuals still possible at a zeta potential of -13 mV, these results demonstrate a degree of overlap and the definition of an operational window that would suit both systems.

The principle difference in zeta potential profiles between the two water sources was the variation in optimal DOC residual, with an additional 0.3 mg removal possible with Albert reservoir water compared to the Poudre river, when coagulating both with ferric sulphate. However, the variation in NOM fraction make-up can also influence
the achievable residual DOC concentration when operating within the optimum zeta potential range, with previous research having reported poor removal during conventional coagulation of NOM fractions with more hydrophilic tendencies (Edwards, 1997; White et al., 1997). In this case, comparison of the HPINA fraction contribution from both sources revealed similar values, 1.0-1.2 mg.L\(^{-1}\) and 1.2 mg.L\(^{-1}\) for the Poudre river and Albert reservoir respectively. Nevertheless, previous research has identified a link between the HPINA fraction and the DOC residual when samples relate to the same source (Parsons et al., 2005). Consequently, fractionation in this instance is a useful tool, indicating if the DOC residual following treatment is likely to meet current regulations or whether an additional treatment stage should be considered.

![Zeta potential vs. DOC residual for both raw water sources when coagulated with ferric sulphate.](image)

*Figure 5(A).4: Zeta potential vs. DOC residual for both raw water sources when coagulated with ferric sulphate.*

The concept of optimisation through zeta potential measurements was investigated further when alum and ferric sulphate based coagulants were both trialled using the Poudre river water. Similar zeta potential profiles with respect to residual DOC and turbidity concentrations were achieved, although, a lower DOC residual was possible with ferric sulphate, removing 0.5 mg more DOC at the optimum zeta potential, compared to alum (Figure 5(A).5). Similar findings have been reported by Bell-Ajay et al. (2000), who looked at 16 different sites with initial TOC concentrations ranging from 1.5 to 16.3 mg.L\(^{-1}\), and found it was possible to remove on average 0.86 mg.L\(^{-1}\) more DOC with ferric chloride than alum. It has been suggested that the improved
performance is due to the fact that alum based coagulants are more selective and ferric can remove more DOC at higher doses, especially when treating elevated levels of organics (Budd et al., 2004; Kastl et al., 2004).

![Zeta potential vs. DOC residual for raw Poudre river water when coagulated with either alum or ferric.](image)

- **Ferric (Poudre May-04)** ○ **Alum (Poudre Apr-04)** ○ **Alum (Poudre May-04)**

*Figure 5(A).5: Zeta potential vs. DOC residual for raw Poudre river water when coagulated with either alum or ferric.*

5(A).4 Conclusions

The results presented here demonstrate both the similarities and differences in NOM composition and character of source waters. However, despite this variability it was shown that the coagulation process could be optimised by surface charge measurements. The existence of operational windows was identified, such that, when operating within the zeta potential range of -10 to +5 mV produced optimal DOC residuals for both water sources. However, the exact DOC residual is dependent on both the organic composition of the water, the HPINA fraction in particular, and the coagulant used, with ferric resulting in an increased DOC removal of approximately 0.5 mg.L\(^{-1}\) compared to alum. Analysis of NOM composition will provide a straightforward guide to the mechanistic understanding of treating NOM rich waters and, in combination with zeta potential monitoring, should help with the development of more robust solutions during periods of elevated organic levels.
5(A).5 References


5(B) Operational zeta potential windows for optimal DOC removal.

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Abstract

Pilot-scale coagulation studies were conducted using waters from an upland peat catchment and snowmelt run-off waters from a high mountain watershed to investigate the relationship between changing characteristics and concentrations of natural organic matter (NOM) and the use of zeta potential to optimise the removal of dissolved organic carbon (DOC). XAD resin adsorption techniques were employed to fractionate the water samples into their hydrophobic and hydrophilic components. The charge density of both the raw water and NOM fractions was determined with the addition of the cationic polyelectrolyte, polydiallyldimethylammoniumchloride (PolyDADMAC). With both water sources, despite the changing NOM composition and character, optimum DOC removal was achieved when the zeta potential was minimised for both aluminium and iron based coagulants. Results from this investigation indicate the existence of an operational window of zeta potential (-10 to
+5 mV) within which hydrophobic NOM removal efficiencies are high and effluent DOC concentrations are minimized.

Keywords

Charge density, Coagulation, Natural organic matter, Water treatment, Zeta potential.
5(B).1 Introduction

A number of UK and US water treatment facilities experience operational difficulties when raw water dissolved organic carbon (DOC) levels increase during run-off periods or after heavy rainfall. Changes in land management, such as the disturbance of peat or vegetation damage, can lead to increased decomposition and the production of loosely bound natural organic matter (NOM) (Worrall and Burt; 2005; Niskavaara et al., 1997). The accumulated organics are then flushed into the aquatic environment during the first rainfall following a dry period (Hurst et al., 2004; Goslan et al., 2002). Mountain regions are also affected by a first flush phenomenon, when snowmelt waters percolate through undisturbed forest floors containing organic material, resulting in high DOC concentrations.

NOM is a highly heterogeneous mixture of organic compounds that vary with regards to acidity, molecular weight (MW), hydrophobicity and charge density (Goslan et al., 2002; Hwang et al., 2001; Vuorio et al., 1998; Edzwald, 1993). However, it is not NOM itself but the residual organics remaining after treatment which pose the greatest problem. The residual organics are converted into disinfection by-products (DBP), such as trihalomethanes (THM) and haloacetic acids (HAA), when chlorine is used in water treatment. These have been shown to cause cancer in laboratory animals (Rodriguez et al., 2000; Singer et al., 1999), therefore prompting legislation in the US to reduce the limit for THMs from 100 µg.l⁻¹, as is currently in force in the UK, to 80 µg.l⁻¹ (Crozes et al., 1995). However, reactivity with chlorine is known to vary depending on the NOM composition, with the hydrophilic NOM typically less reactive (Collins et al., 1986; Croué et al., 1996). Malcolm (1985), showed that, as the DOC of a water increases, the additional organic matter is likely to be hydrophobic in character and therefore optimising NOM removal in order to reduce residual organics is of increased importance during these periods.

The application of charge measurement for the diagnosis and control of water and wastewater treatment processes is not new, and the basic understanding of how charge controls performance has not changed considerably over recent years. As the zeta potential diminishes, the particles can approach one another more closely, increasing the likelihood of agglomeration. Consequently, colloid destabilisation occurs before
complete neutralisation of surface charge, hence the zeta potential may not necessarily be zero (Ratnaweera et al., 1999). Optimisation of the coagulation process occurs under acidic conditions between the iso-electric point (IEP) of the coagulant and the NOM. This is typically around pH 4.5-5 for iron and pH 5-6 for aluminum based coagulants (Amirtharajah and O’Melia, 1990). In reality, optimised charge conditions occur over a range of values, rather than specifically at the IEP of the system, such that operational zeta potential windows exist within which residuals are minimised. Several studies have reported conditions favourable for particle removal with zeta potential values ranging between +10 and –10 mV (McCurdy et al., 2004; Tseng et al., 2000, Carlson et al., 1996).

The NOM content of the water controls the critical coagulant concentration due to its high charge content. However, this may change significantly with raw water characteristics known to vary both temporally and spatially, often experiencing rapid increases during periods of elevated organics (Carlson et al., 1994; Owen et al., 1993). Water treatment is often controlled on bulk water parameters such as UV$_{254}$ absorbance or residual turbidity levels. However, previous research has shown that such an approach may fail to detect changes in the NOM composition and character of the water, the change in charge and associated coagulant demand. (Sharp et al., 2004).

At present, little is known about the relationship between water characteristics and the applicability of optimisation through charge measurement during periods of elevated organics. Therefore, the overall objectives of this paper were to investigate this issue further in relation to conventional treatment, coagulation and flocculation using metal salts. Two different water sources were investigated, in the UK and US, both subject to rapidly changing levels of organics.

5(B).2 Materials and Methods

5(B).2.1 Study site locations
The first case study was located at the Fort Collins water treatment facility (FCWTF), Colorado, USA. During the period from April to June 2004, the TOC levels in the Poudre river, a raw water source for the FCWTF, increased rapidly from a baseline of approximately 2 mg.L$^{-1}$ to 7.7 mg.L$^{-1}$ as a direct result of the spring snowmelt run-off (Figure 5(B).1). The second case study site was located at Albert water treatment
works (WTW), Halifax, UK, in January, March, August, and September 2004, when the DOC concentrations increased from 8.3-10.1 mg.l\(^{-1}\) to 11.4-13.8 mg.l\(^{-1}\). This is an upland peat catchment area producing coloured water throughout the year, although still subject to rapid changes and increases in organic levels following periods of heavy rain.

5(B).2.2 Pilot plants

The FCWTF pilot plant includes two parallel trains designed to reflect the operational characteristics of full-scale treatment, including rapid mix (1000 RPM), 3 stage plug flow flocculation (11, 8 and 3.5 RPM) and lamella plate settling (0.83 m\(^3\).m\(^{-2}\).h\(^{-1}\) or 0.34 gpm.ft\(^{-2}\)). This pilot plant has also been used in previously reported experimental work at FCWTF (Gregory and Carlson, 2003; Billica and Gertig, 2000). For the current research, raw Poudre river water was pumped into each pilot train at a flow of 1.8 m\(^3\).h\(^{-1}\) (8 gpm). Lime (Mississippi Lime Company, MO, USA) and carbon dioxide (Fisher Scientific, USA, 10-752-1G regulator and Omega, USA, model FMA1916 gas mass flow controller) were added to the raw water before it was split between the two trains, in order to both achieve an alkalinity of 25-35 mg.l\(^{-1}\) as CaCO\(_3\) and to manipulate the coagulation pH. Trials were conducted using both aluminium sulphate (General Chemical, USA) and ferric sulphate (Eaglebrook Inc, USA) at doses of 1.3-4 mg.l\(^{-1}\) as Al and 3-5 mg.l\(^{-1}\) as Fe respectively.

Two pilot plants were operated using raw water from the Albert reservoir. The first, the DA20, was located at the Albert reservoir and a second was based at Cranfield and raw water was transported by tanker for the trials. The DA20 was operated during two periods, March and August/September 2004, and included inline static mixing (Series 100, Statiflow, UK), of both the aluminium or ferric based coagulants and the 12% Calic suspension (Buxton Lime, UK). This was followed by three stage plug flow flocculation (5 RPM for 20 mins) and dissolved air flotation (6.3 m.h\(^{-1}\), 8% recycle and 5 bar saturator pressure). The Cranfield pilot plant was operated in January 2004, and included a rapid mix (200 RPM) and 2 stage flocculation (30 RPM for 10 mins per stage). pH was controlled through the addition of 0.1M NaOH (Fisher Scientific, UK) into the rapid mix tank. Both pilot plants were run using a ferric sulphate coagulant (Ferripol XL, EA West, UK), with varying doses between 5 and 15 mg.l\(^{-1}\) as Fe (0.09-0.18 mMol as Fe). The DA20 was also operated using aluminium sulphate
(Alum, EA West, UK) during the August/September 2004 period, at a dose of 10 mg.l\(^{-1}\) as Al (0.37 mMol as Al).

For all pilot trials, coagulant dose and pH were varied in order to manipulate the zeta potential. Once conditions had stabilised, samples were taken in triplicate and analysed for UV absorbance at a wavelength of 254nm (Jenway 6505 UV/Vis spectrophotometer, Jenway, UK), pH, DOC, in some cases TOC, (Shimadzu TOC-5000A analyser in the UK and Sievers Model 800TOC analyzer at FCWTF ), and high performance size exclusion chromatography (HPSEC) (Shimadzu VP series, Shimadzu, UK). The HPSEC analysis used a TSK gel, GW3000SW column, 7.5mm internal diameter and 30cm in length. The guard column was also TSK, 7.5mm internal diameter and 7.5cm in length (Tsoh Biosep GmbH, Stuttgart, Germany). All samples were filtered to remove suspended solids before UV\(_{254}\), DOC and HPSEC analysis (Glass microfibre in the UK and Durapore membrane filter at FCWTF, Fisher Scientific). The surface charge was measured with a zetasizer (Malvern Instruments, UK) at 20°C. The zetasizer yields estimates and standard deviations of the zeta potential directly, and all measurements were conducted in triplicate on unfiltered samples. The general accuracy of the zetasizer was determined using standard solutions (Malvern Instruments, UK.)

5(B).2.3 Raw water monitoring

Raw water characteristics were monitored daily at FCWTF, including HPSEC, DOC and TOC analysis, throughout the rapidly changing run-off period. Two raw Poudre river water samples, one collected before the snowmelt run-off and the second collected at the height of run-off, were fractionated by XAD resin adsorption techniques into their hydrophobic (HPOA) and hydrophilic (HPIA) components using a method adapted from Malcolm and MacCarthy (1992). An Amberlite XAD-7HP and Amberlite XAD-4 resin pair was used (Rohm and Haas, PA, USA). This method has been previously used on raw water collected from Albert reservoir (Fearing et al., 2004; Goslan et al., 2002). The hydrophobic fractions were then separated further by reducing the pH to 1 and precipitating the humic acid fraction (HAF), with the fulvic acid fraction (FAF), remaining in the supernatant. The non-adsorbed fraction was categorised as hydrophilic non adsorbed (HPINA).
The charge density of both the run-off and pre run-off raw water samples was determined using the zetasizer and the cationic polymer polydialyldimethylammoniumchloride (PolyDADMAC), with a MW of 100,000-200,000 and a calculated charge density of 6.2 meq.g\(^{-1}\) (Sigma-Aldrich, UK). A beaker containing one litre of Poudre river water, was placed on a magnetic stirrer. Varying amounts of 0.1% PolyDADMAC solution were added to the beaker, with the pH adjusted to 7 with 0.1 M NaOH, and the zeta potential measured until the point of zero charge, or IEP, had been established. This was then repeated twice and the volume of PolyDADMAC solution used to calculate the charge density of the raw water both per litre and per mg of DOC. The process was then repeated for each of the NOM fractions, at a concentration of 25 mg.l\(^{-1}\) in 100 ml of deionised water. The HPINA fraction was only available in an unconcentrated form, between 1-2mg.l\(^{-1}\) DOC, and a 0.001% PolyDADMAC solution was therefore used for charge density determination.

All raw water analysis, including fractionation and charge density determination, was repeated with Albert reservoir water samples from January and August 2004 when the DOC increased from 8.3 to 13.3 mg.l\(^{-1}\). The charge density of the filtered raw water samples was also determined, using a 1 \(\mu\)m glass microfibre filter (Fisher Scientific, UK) and filtering to 1\(\mu\)m was shown to have no effect on the charge density of the sample.

**5(B).3 Results and Discussion**

**5(B).3.1 Raw water composition**

Raw water characteristics were monitored at both sites throughout the investigation period. At FCWTF, over the period of April to June 2004, the main increase in organic levels occurred over a relatively short period of time. DOC concentrations increased from 4.4 mg.l\(^{-1}\) to 7.4 mg.l\(^{-1}\) DOC between the 4\(^{th}\) and the 13\(^{th}\) May 2004 (Figure 5(B).1). The DOC at FCWTF contributed over 90% of the TOC, corresponding to in increase in TOC from 4.5 mg.l\(^{-1}\) to 7.7 mg.l\(^{-1}\) for the same period. Comparison of 2003 and 2004 data reveal some annual variation with the TOC concentration in 2003 reaching a peak of 11.5mg.l\(^{-1}\). At Albert reservoir DOC concentrations also show both seasonal and annual variation. In 2003 a low of 4.3
mg.l\textsuperscript{-1} DOC was recorded in September 2003, rising to 8.6 mg.l\textsuperscript{-1} following heavy rains at the beginning of October. However, in 2004 concentrations remained above 8 mg.l\textsuperscript{-1} for the majority of the year and rose to between 13.3-13.8 mg.l\textsuperscript{-1} following heavy rains in August 2004 (Table 5(B).1).

![Figure 5(B).1: Raw water TOC and DOC levels for FCWTF and Albert during 2003 and 2004.](image)

Table 5(B).1: Raw water and NOM fraction characteristics

<table>
<thead>
<tr>
<th>Sample date</th>
<th>Location</th>
<th>HAF mg.l\textsuperscript{-1} (meq.g\textsuperscript{-1})</th>
<th>FAF mg.l\textsuperscript{-1} (meq.g\textsuperscript{-1})</th>
<th>HPIA mg.l\textsuperscript{-1} (meq.g\textsuperscript{-1})</th>
<th>HPINA mg.l\textsuperscript{-1} (meq.g\textsuperscript{-1})</th>
<th>Raw water mg.l\textsuperscript{-1} (meq.g\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apr-02</td>
<td>Albert</td>
<td>1.5 (6.8)</td>
<td>3.9 (4.2)</td>
<td>0.8 (0.06)</td>
<td>1.3</td>
<td>7.5</td>
</tr>
<tr>
<td>Jan-04</td>
<td>Albert</td>
<td>1.2 (4.3)</td>
<td>4.9 (4.5)</td>
<td>1.0 (1.5)</td>
<td>1.2</td>
<td>8.3 (2.7)</td>
</tr>
<tr>
<td>Aug-04</td>
<td>Albert</td>
<td>4.9 (3.7)</td>
<td>2.9 (3.5)</td>
<td>2.9 (1.2)</td>
<td>2.5</td>
<td>13.3 (3.7)</td>
</tr>
<tr>
<td>Apr-04</td>
<td>FCWTF</td>
<td>0</td>
<td>2.8</td>
<td>0.6</td>
<td>1.0</td>
<td>4.4 (2.0)</td>
</tr>
<tr>
<td>May-04</td>
<td>FCWTF</td>
<td>1.7 (3.7)</td>
<td>3.8 (3.7)</td>
<td>0.7</td>
<td>1.2</td>
<td>7.4 (3.9)</td>
</tr>
</tbody>
</table>

HPSEC analysis, of the raw waters under investigation, identified an increase in the higher MW components for FCWTF during the spring snowmelt run-off, when the
DOC increased from 4.4 to 7.4 mg.l⁻¹ (Figure 5(B).2). This was demonstrated by a shift in position of the main peak from an elution time of 8.5 to 8.1 minutes, corresponding to an increase in MW distribution from <3 kDa to 3-4 kDa, respectively (Pikkarainen et al., 2004). In comparison, the samples from Albert reservoir also represent a shift in MW distribution when the DOC concentration increases from 8.3 to 13.3 mg.l⁻¹. However, in this case, it represents an increase in the lower MW material. The position of the main peak did not change significantly, increasing from 8.0 to 8.2 minutes elution time (4-5 kDa), although the magnitude of the peak did increase slightly. However, this coincided with an increase in peaks at the later elution times of 8.5, 9.0, 9.8 and 10.2 minutes (3-0.5 kDa). The Albert HPSEC profiles also identified a peak at approximately 5.8 minutes (>5 kDa), which was not present with either of the FCWTF samples.

![Figure 5(B).2: HPSEC chromatograms for FCWTF and Albert WTW raw waters during high and low TOC and DOC periods.](image)

Raw water fractionations revealed that at FCWTF the increase in organics corresponds to an increase in the hydrophobic content of the water (Figure 5(B).3). Interestingly, there was no HAF present when the DOC was 4.4 mg.l⁻¹, although when the DOC increased to 7.4 mg.l⁻¹, the increase occurred principally through the existence of a new HAF fraction which contributed 1.7 mg.l⁻¹ of the increased DOC (Table 5(B).1). The total hydrophobic fraction (HAF and FAF) at FCWTF increased from 2.8 mg.l⁻¹ to 5.5 mg.l⁻¹ whereas the hydrophilic fractions (HPIA and HPINA)
only increased from 1.6 to 1.9 mg l\(^{-1}\). In contrast, results from Albert revealed a 33% increase in hydrophobic material from 5.9 mg.l\(^{-1}\) to 7.8mg.l\(^{-1}\), but more importantly a 145% increase in hydrophilic material from 2.2 to 5.4 mg.l\(^{-1}\), as the total DOC increased from 8.3 to 13.3 mg.l\(^{-1}\).

The observed changes can be related to the changes in the condition in the catchment throughout the year. For instance, variations in total organic levels, with regards to snowmelt run-off, depends on the moisture content of the snowpack just prior to the spring melting period. In 2003, the snow water equivalent in the FCWTF catchment was over 300% of average, resulting in a TOC peak of 11.5 mg.l\(^{-1}\) during the height of run-off. In 2004, the snow water equivalent was only 53% of average, resulting in a TOC peak of 7.7 mg.l\(^{-1}\). Dissolved organic matter in peat drainage systems varies in a more complex manner, exhibiting both seasonal and year by year variations, and affected by both the duration and intensity of rainfall. Consequently, Albert WTW samples exhibited a greater annual variation compared to FCWTF, with a low of 4.5 mg.l\(^{-1}\) in September 2003 at the end of a dry summer period, compared to a high of 13.8 in August 2004 at the end of a relatively wet summer. Elucidating this relationship, Scott et al., (1998) observed a 55% reduction in the production of dissolved organic matter (DOM), from 15 to 7 g.m\(^{-2}\).a\(^{-1}\) when the annual rainfall decreased from 1299 mm to 904 mm. Comparison with published data reveals similar levels and variation in DOC across different seasons for river and lake systems from both Europe (Ratnaweera et al., 1999) and the United States of America (Aiken et al., 2004). The Santa Ana river for example, exhibited DOC variations between 2.2 mg.l\(^{-1}\) and a high of 9 mg.l\(^{-1}\) during the period from June 2000 to May 2002 (Aiken et al., 2004).
With regards to NOM fraction make-up during the period of elevated organics, FCWTF raw water contained a higher proportion of hydrophobic NOM (74%) compared to Albert WTW samples (59%). Carlson et al. (1994) also observed an increase in the higher MW hydrophobic content (HAF and FAF) of the water due to snowmelt run-off at FCWTF, from 33% to 50% during snowmelt run-off. However, the hydrophobic content may have been lower as the total TOC concentration was reported to be significantly lower in 1994, at approximately 4.8 mg.L\(^{-1}\) compared to 7.7 mg.L\(^{-1}\) during the 2004 run-off period. Therefore the results for FCWTF are in agreement with Malcolm (1985) who stated that elevated organic levels are likely to coincide with a higher hydrophobic proportion of NOM. At Albert however, this was not the case as the increased organic concentrations were due to an increase in both the hydrophobic and hydrophilic content of the water. Similarly, Scott et al. (1998), looked at the seasonal variations in NOM obtained from a UK upland peat catchment system. They observed variations in the hydrophilic content of the water of between 20 and 80%, with the higher proportions occurring during the summer months. This can be compared to a variation of 27% to 41%, of the total DOC, between January and August in the current study. The increases in hydrophilic content following the initial periods of heavy rain during the late summer and autumn were attributed to its relative ease of dissolution, whereas the hydrophobic material is leached more slowly.
5(B).3.2 Charge density measurements

Charge density measurements of the raw water samples in the current study were shown to increase as the organic concentrations increased. For example, in relation to water fractionated from samples collected from FCWTF, the charge demand of the raw water increased from 0.009 meq.l\(^{-1}\) when the DOC concentration was 4.4 mg.l\(^{-1}\), to a charge density of 0.029 meq.l\(^{-1}\) when the DOC concentration was 7.4 mg.l\(^{-1}\) (Table 5(B).1). A similar increase was observed with the samples from Albert when the charge demand increased from 0.023 meq.l\(^{-1}\) in January, when the DOC concentration of the sample was 8.3 mg.l\(^{-1}\), to 0.049 meq.l\(^{-1}\) when the DOC concentration of the sample had increased to 13.3 mg.l\(^{-1}\). Comparing both water sources reveal similar charge densities for both water sources, at initial values of 2.0 and 2.7 meq.g\(^{-1}\)DOC for FCWTF and Albert respectively, increasing to 3.7-3.9 meq.g\(^{-1}\)DOC during the period of elevated organics. Green (1997) also calculated the colloid charge capacity (CCC) of blended Horsetooth reservoir and Poudre river water at FCWTF, using a fluorescence polarization colloid titration method. The CCC was found to increase from 2 to 2.5 meq.g\(^{-1}\)DOC, during the 1997 spring snowmelt run-off period. This run-off value is lower than calculated during this study for the 2004 run-off, which was solely for Poudre river water. According to Carlson et al. (1994), the blended water studied by Green (1997) has been shown to contain a lower hydrophobic content which would explain the reduced charge. Furthermore, Collins et al. (1986), also achieved similar values when using a potentiometric titration method to determine the carboxylic acidity of the hydrophobic organic matter for a number of raw waters and fulvic acid components. For instance, charges of 0.035 meq.l\(^{-1}\) and 0.030 meq.l\(^{-1}\) were determined for the Grasse River and Floridan aquifer samples respectively.

Charge density measurements of the raw water fractions in the current study revealed the majority of the total colloidal charge to exist in the hydrophobic fractions. Although the charge density for the FAF fractions of both FCWTF and Albert WTW were similar at 3.7 meq.g\(^{-1}\)DOC and 3.5-4.5 meq.g\(^{-1}\) DOC respectively (Table 5(B).1). These values are in agreement with other reported studies where humic and fulvic waters have shown charge densities ranging between 2 and 15 meq.g\(^{-1}\)DOC (Kam and Gregory, 2001; Scott et al., 2001; Edzwald, 1993; Collins et al., 1986). The charge density of the hydrophilic fractions however, was significantly lower. For instance the
charge density of the HPIA fraction varied between 0.06 and 1.5 meq.g\textsuperscript{-1}DOC. There is also a significant difference between the charge density result for the April 2002 HPIA, at 0.06 meq.g\textsuperscript{-1}DOC, and both the January and August 2004 HPIA samples at 1.5 and 1.2 meq.g\textsuperscript{-1}DOC respectively, obtained from the Albert fractionation. HPSEC chromatograms of the HPIA fractions (Figure 5(B).4) show a significant shift in the MW distribution for the April 2002 sample. The HPSEC chromatograms for Albert HPIA samples show the main peak at an elution time of 6.9 minutes for both the January and August 2004, corresponding to a MW of >5 kDa. However, with regards to the April 2002 HPIA fraction, HPSEC peaks have been identified at 8.9, 9.4, 10.2 and 12.1 minutes (3-<0.5 kDa). In all cases, the charge density for the HPIA fraction was below the level of detection. Edzwald (1993) reported similar findings for both hydrophilic bases and neutrals and found that the acid fraction was at least an order of magnitude smaller that the hydrophobic fractions. Relating these findings and their influence on coagulation requirements, the differences in carboxylic acidity or charge density will therefore influence the coagulant demand and the water treatment process and a higher charge is associated with the larger MW fractions (Collins et al., 1986; Ratnaweera et al., 1999). These variations however, cannot be detected by simple DOC measurement.

![Figure 5(B).4: HPSEC chromatograms for HPIA fractions.](image-url)
5(B).3.3 Operational envelope

An operational envelope can be described where turbidity and DOC removal is high and effluent concentrations are low and stable in relation to the zeta potential of the NOM-coagulant complexes. The operational envelope for DOC removal is often over a narrower zeta potential than for turbidity as shown by normalised plots taken from the DA20 during trials in March 2004 (Figure 5(B).5). To illustrate with regard to the negative zeta potential boundary, turbidity residuals remained stable as the zeta potential increased from 0 mV to -15.5 mV, whereas both the DOC and UV$_{254}$ residuals increased gradually over the same zeta potential range. This is in agreement with Dennett et al. (1995), who state that optimising for DOC removal also produces good turbidity removal (Dennett et al., 1995). Therefore, with regards to this research, results will be discussed in terms of the conditions required for optimum DOC removal. Direct comparison of the residual DOC concentration with the zeta potential reveals that residual concentrations are minimised at zeta potentials near zero. At FCWTF, coagulating with ferric and operating at a coagulation zeta potential of between -10 and +5 mV, the residual DOC remained stable at 1.5 ± 0.2 mg.l$^{-1}$. Operating outside this envelope resulted in residuals which were no longer stable and increased rapidly. When operating within the same operational envelope, similar results were also observed at Albert WTW. For instance, when operating the DA20 in August and September 2004, if the zeta potential remained between the values of -10 and +5 mV, the residual DOC was stable at 2.1 ± 0.3 mg.l$^{-1}$. These results are in agreement with previously suggested zeta potential ranges for optimum organic and turbidity removal, ranging from +10 to -10 mV. However, the lack of clear correlation between zeta potential and optimum coagulation for different systems suggests that mechanisms other than charge neutralisation, which are not identified by zeta potential monitoring, may also be in operation (Ratnaweera et al., 1999).
Trials were undertaken simultaneously on the two identical trains of the FCWTF pilot plant, during the run-off period when the TOC was approximately 6 mg.l⁻¹, in order to compare the performance of aluminium sulphate (alum) and ferric coagulants. Similar experiments were also carried out at Albert WTW with the DA20 during August and September 2004. Results from both coagulants display similar profiles for DOC residuals with respect to zeta potential. Within the optimum operational envelope, as identified previously at between -10 and +5 mV, DOC residuals remained stable at 2.1 ± 0.5 mg.l⁻¹ and 2.9 ± 0.5 mg.l⁻¹ for the FCWTF and DA20 pilot plants, respectively, with alum. However, a lower DOC residual was possible with the ferric coagulant, removing 0.5- 0.8 mg.l⁻¹ more DOC than alum (Figure 5(B).6). Overlaying data from clarified spot samples obtained from a number of upland, reservoir and river based water works across the UK, also follows a similar trend, depending on whether iron or aluminium is used in the coagulation process. Note, however, that coagulation at these sites was not optimised using zeta potential at the time of sampling.
Similar findings were reported by Bell-Ajay et al. (2000), who looked at 16 different sites with initial TOC concentrations ranging from 1.5 to 16.3 mg.L$^{-1}$, and found it was possible to remove on average 0.86 mg.L$^{-1}$ more DOC with ferric chloride than alum. In fact, a number of authors have achieved higher DOC removal with ferric salts compared to aluminium salts (Hwang et al., 2001; Edzwald and Tobiason, 1999). Ratnaweera et al. (1999) looked at the coagulation of eight Norwegian high TOC waters and found that optimised alum coagulation produced fewer, more positively charged flocs than ferric based coagulants thus leading to a reduced number of collisions. Vigle-Ritter (1999), state that floc structure may be affected by coagulation pH, with alum operating at a higher pH compared to ferric, as increasing the coagulation pH produces a more loosely connected NOM aggregate. However, although there is little evidence in the literature to explain the difference in floc properties of alum and ferric based systems, it has been suggested that the improved performance is due to the fact that alum based coagulants are more selective and ferric can remove more DOC at higher doses, especially when treating elevated levels of organics (Budd et al., 2004; Kastl et al., 2004).
5(B).3.5 Zeta potential

Zeta potential profiles for both coagulants indicate that achieving a certain zeta potential should produce a given DOC residual, regardless of the combination of coagulant dose or pH. This was demonstrated at FCWTF, when ferric and alum doses were increased and the coagulation pH was varied, in order to maintain a constant zeta potential of +4 for alum and +3 for ferric (Figure 5(B).7). The DOC residual remained constant at approximately $2.1 \pm 0.1 \text{mg.l}^{-1}$ for a pH range 4.9-6.5 and an alum dose of 32-44 mg.L$^{-1}$ (0.29-0.4 mg.l$^{-1}$ as Al). Increasing the ferric dose from 5 to 15mg.l$^{-1}$ (as Fe) also had no effect on the DOC residual which remained at $1.4 \pm 0.1 \text{mg.l}^{-1}$.

Similar results were also achieved when a negative zeta potential was maintained. For instance, when the zeta potential was maintained at -4 mV, the DOC residual remained constant at approximately $2.5 \pm 0.2 \text{mg.l}^{-1}$ for a pH range 6.3-7.0 and an alum dose of 20-40 mg.l$^{-1}$ (1.8-3.6 mg.l$^{-1}$ as Al). Once optimal removal has been achieved, increasing the coagulant dose further, whilst maintaining the same zeta potential, did not produce increased removal. Krasner et al. (1994) carried out jar tests on California State Project Water at incremented alum doses from 22 to 111 mg.l$^{-1}$. They also found that after a certain dose of 47 mg.l$^{-1}$ (as alum), there was a plateauing of DOC removal. With regards to pH, Hundt and O’Melia (1988) achieved a constant 80% DOC fulvic acid removal for the pH range 6-8 when the alum doses were increased accordingly. These findings promote the theory that attaining the optimum zeta potential is more important for achieving optimal DOC removal than separately considering specific values of coagulation pH and coagulant dose.
Figure 5(B).7: Coagulation pH versus DOC residual and coagulant dose for FCWTF samples operating within optimum zeta potential range +4 (alum) and +3 (ferric).

5(B).3.6 DOC Residual

Comparison of results from the different water samples, all coagulated with ferric, present similar profiles with respect to zeta potential (Figure 5(B).8). However, when operating within the operational envelope of -10 to +5 mV, the residual DOC remaining at optimum has been shown to differ. The difference was greatest with the trials using water from Albert WTW. In January 2004 a residual of 1.1 ± 0.1 mg.L\(^{-1}\) was achieved, compared to 2.1 ± 0.3 mg.L\(^{-1}\) in August and September 2004. The observed increase in residual DOC coincided with an increase from 1.2 to 2.5 mg.L\(^{-1}\) over the same period in terms of the polar hydrophilics (HPINA). In contrast, the residual concentration at FCWTF exhibited less variation over the period studied, at 2.0 mg.L\(^{-1}\) in April and 2.2 mg.L\(^{-1}\) at the height of run-off although the raw water changed from 4.4 mg.L\(^{-1}\) to 7.4 mg.L\(^{-1}\). However, in this case, fractionation data revealed that HPINA content only increased from 1.0 to 1.2 mg.L\(^{-1}\). Similar results have been previously reported by Krasner et al. (1994), when they blended two waters, both with low MW DOC concentrations of 1.3- 1.4 mg.L\(^{-1}\), and found the residual after alum coagulation was 1.0-1.3 mg.L\(^{-1}\) DOC, regardless of the blend. Further, a number of authors have identified that the higher MW, more hydrophobic NOM fraction is generally more sorbable and easily removed during coagulation, and there is also a
non sorbable fraction, with more hydrophilic tendencies, that is not (Randtke, 1988; Owen et al., 1993; Krasner et al., 1994; Edwards, 1997; White et al., 1997) Combining the work indicates that the polar hydrophilic level in the raw water provides a useful guide as to the likely residual DOC concentration achievable through coagulation with metal salts. Further, as the hydrophobic components contain the majority of the charged species the concentration of this fraction gives an indication of the likely coagulant demand. Consequently, fractionation of raw waters appears a useful tool to understand the demands and limitations of coagulation of NOM.

![Figure 5(B).8: DOC residual versus zeta potential for all water samples coagulated with ferric.](image)

**Figure 5(B).8:** DOC residual versus zeta potential for all water samples coagulated with ferric.

### 5(B).4 Conclusions

Results from this investigation indicate the existence of an operational window of zeta potential (-10 to +5 mV) within which DOC removal efficiencies are high and effluent DOC concentrations are minimized. This operational window appears unaffected by changing organic concentrations and characteristics. However, the increased hydrophobic content of the water, and the associated increase in raw water charge density, results in an increased coagulant demand required to minimize the surface charge of the organics. The variation in NOM fraction make-up and the coagulant
used also influence the achievable residual DOC concentration at optimum zeta potential, especially when there is a portion of the hydrophilic NOM which cannot be removed through conventional coagulation processes, with either aluminium or iron based coagulants.

5(B).5 References


5(C) Coagulation of NOM: Linking character to treatment.

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Abstract

The paper presents an overview and discussion on the link between NOM character and its treatability by coagulation. Trials were conducted on a series of bench scale and pilot plant trials on three source waters: Two from UK moorland catchments and one from a US snowmelt source. Overall the work demonstrates the importance of the polarity balance and the charge density of the NOM contained within the source water. The hydrophobic content controls the coagulant demand such that variation in the demand between sources or sampling periods can be accounted for by changes in the hydrophobic content and its charge density. The raw water hydrophilic content, and specifically the non acid fraction, provides a useful indicator of the achievable residual. Analysis of coagulation performance revealed a clear relationship between zeta potential and residual DOC. For each source an operational zeta potential range exists within which the residual concentration is optimal. Comparison of the ranges achieved during each trial demonstrated that a communal range between -10 and +3 mV exists for all waters thus providing a useful guide range for operational control.

Keywords

Coagulation, Natural organic matter, Zeta potential.
5(C).1 Introduction

Natural waters throughout the world contain natural organic matter (NOM) which is composed of a diversity of compounds with respect to acidity, molecular weight and charge density (Edzwald, 1993). NOM is known to vary in terms of its organic concentration and character due to both temporal and spatial variations between sources (Scott et al., 2001). Process options for the treatment of NOM are well established and for the most part produce stable high quality product waters. However, a number of plants are experiencing difficulties during specific times of the year associated with periods of elevated organics due to heavy rainfall or snowmelt. During these periods of elevated organics the current treatment streams are failing to maintain quality and throughput especially in terms of dissolved organic carbon (DOC), trihalomethane formation potential (THMFP) and colour.

NOM is traditionally removed by coagulation with trivalent metal ions. The coagulation mechanisms that are thought to prevail with regards to NOM removal, are charge neutralisation for colloidal material and charge complexation for soluble compounds. Accordingly, optimisation of the coagulation process occurs under acidic conditions between the isoelectric point (IEP) of the coagulant and the NOM; pH 4.5-5.5 for iron based system and pH 5-6 for aluminium based coagulants. Understanding of the specific mechanisms and control points is much less well understood due to a paucity of knowledge on which individual species are present, the variation in all the possible species as a function of time and location, their specific interaction with the coagulant and how the combination of all the possible components interact. Nevertheless at a practical level a lot of information can be gained by utilising relatively straightforward diagnostic techniques to understand the link between character and treatability.

The current paper describes and discusses this link through three case study sites situated either in the USA (snowmelt water) or the UK (2 moorland waters). All three sources can be described as high colour, low turbidity, low alkalinity source waters.
5(C).2 Materials and Methods

Water was collected from three sites: Fort Collins water treatment facility (FCWTF), Colorado, USA which experiences changes in organic concentration due to spring snowmelts between April and June, Albert water treatment works (WTW), Halifax, and Bamford WTW, Derbyshire, both in the UK which experience elevated organics following periods of heavy rainfall after the summer. Jar tests were conducted with Albert WTW and Bamford WTW water and pilot plant trials were conducted for FCWTF and Albert WTW water.

5(C).2.1 Pilot plant facilities

The FCWTF Pilot included two parallel trains designed to reflect the operational characteristics of full-scale treatment, including rapid mix, 3 stage flocculation and lamella plate settling (Figure 5(C).1). Raw water was pumped into each train at a flow of 1.82 M$^3$.h$^{-1}$. Lime (Mississippi Lime Company, MO, USA) and carbon dioxide (Fisher Scientific, USA, 10-752-1G regulator and Omega, USA, model FMA1916 gas mass flow controller) were added to the raw water before it was split between the two trains, in order to both achieve an alkalinity of 25-35mg.l$^{-1}$ as CaCO$_3$ and manipulate the coagulation pH. The pilot plant was run using ferric sulphate at doses ranging from 10.4 to 17.4 mg.l$^{-1}$ (3-5 mg.l$^{-1}$ as Fe) (General Chemical, USA).

Two pilot plants were operated using raw water from Albert reservoir: one was a 450 L.h$^{-1}$ plant including a rapid mix stage followed by two stage flocculation. The other pilot plant, which was operated in March and August 2004 at a flow of 15 m$^3$.h$^{-1}$ included inline static mixing of the coagulant and 25% Calic suspension of pH control (Buxton Lime, UK). This was followed by a three stage flocculation and dissolved air flotation. Both pilot plants were run using ferric sulphate (EA West, UK) with doses varying between 5 and 15mg.l$^{-1}$ as Fe (0.09 mMol-0.18 mMol as Fe). A more detailed description of all three pilot plants has been published previously (Parsons et al., 2005). Bench scale trials were undertaken in accordance with procedures outlined in detail elsewhere (Sharp et al., 2004) and involved coagulation with ferric sulphate with an initial rapid mix period of 1.5 minutes at 200 RPM and a slow stir for 15 minutes at 30 RPM after which the jars were left to settle for an additional 20 minutes before taking the samples, which were extracted from the centre of the jar.
5(C).2.2 Analysis
All samples were filtered to remove suspended solids before DOC and high performance size exclusion chromatography (HPSEC) analysis (Glass microfibre in the UK and Durapore membrane filter at FCWTF, Fisher Scientific). DOC, (Shimadzu TOC-5000A analyser in the UK and Sievers Model 800TOC analyzer at FCWTF) and high performance size exclusion chromatography (HPSEC) (Shimadzu VP series, Shimadzu, UK) were conducted on both raw and fractionated samples. The HPSEC analysis used a TSK gel, GW3000SW column, 7.5mm internal diameter and 30cm in length. The guard column was also TSK, 7.5mm internal diameter and 7.5cm in length (Tsoh Biosep GmbH, Stuttgart, Germany). The surface charge was measured with a zetasizer (Malvern Instruments, UK) at 25°C.

5(C).2.3 Fractionation
Raw water samples were fractionated by XAD resin adsorption techniques into their hydrophobic (HPOA) and hydrophilic (HPIA) components using a method adapted from Malcolm and MacCarthy (1992). An Amberlite XAD-7HP and Amberlite XAD-4 resin pair were used (Rohm and Haas, PA, USA). The hydrophobic fractions were then separated further by reducing the pH to 1 and precipitating the humic acid fraction (HAF), with fulvic acid fraction (FAF) remaining in the supernatant. The non-adsorbed fraction was categorised as hydrophilic non acid (HPINA).

5(C).2.4 Charge density
The charge density of the raw water samples was determined using the Malvern zetasizer and PolyDADMAC (Sigma-Aldrich, UK). A beaker containing 1L of raw water and a magnetic stirrer bar were placed on a magnetic stirrer. Varying amounts of 0.1% PolyDADMAC were added to the beaker, with the pH adjusted to 7 with NaOH, and the zeta potential measured until the point of zero charge or IEP had been established. This was then repeated twice and the volume of PolyDADMAC solution used to calculate the charge density of the raw water both per litre and per mg of DOC. The process was then repeated for each of the NOM fractions, at a concentration of 25 mg.l⁻¹ in 100 ml of deionised water.
5(C).3 Results and Discussion

5(C).3.1 Characterisation

The DOC of the three water sources varied from a minimum of 4.4 mg.L\(^{-1}\) in April 2004 (FCWTF) to a maximum of 13.3 mg.L\(^{-1}\) in August 2004 (Albert WTW). The most significant increase in DOC occurred after either the first period of heavy rain in autumn in the UK or snowmelt in spring in the USA. Fractionation of the raw waters revealed that the majority of the organic material was hydrophobic in character with on average 66-75% of the organic material being accounted for by the HAF and FAF fractions (Figures 5(C).1, 5(C).2). Similar findings have been reported for NOM source waters fractionated in Europe (Ratnaweera et al., 1999) and the USA (Aiken et al., 2004). In general, the increased DOC was accounted for by changes in the hydrophobic content in the water in line with previous findings (Malcolm, 1985). However, after the first heavy storm events during the autumn in the UK, the increase occurred by an equal amount in both hydrophobic and hydrophilic fractions. To illustrate, after the first heavy rainfall in the autumn of 2003 the increased DOC was generated by a 1.1-1.3 mg.L\(^{-1}\) increase in hydrophobic material and a 1-1.1 mg.L\(^{-1}\) increase in hydrophilic material. The consequence of which was to alter the polarity balance of the water from a relative hydrophilic content of 25 to 40%. Such observations are consistent with the work of Scott et al. (2001) which has shown that the initial increase in hydrophilic material after the first storm is attributed to its relative ease of dissolution relative to hydrophobic material, resulting in a faster release rate.

![Graph 1](image1.png)  
![Graph 2](image2.png)

*Figure 5(C).1: Raw water NOM fraction make up at Albert WTW*  
*Figure 5(C).2: Raw water NOM fraction make up at Bamford WTW and Fort Collins*

The findings are supported by analysis of HPSEC chromatograms of raw water samples before and after increased organic events. At the UK sites, the autumnal rain
event caused an increased absorbance but no shift in the primary peak (c5.7 minutes) combined with a decreased absorbance and shift in elution time from c7.7 to c8.5 minutes in the secondary peak. The shift in elution time represents an approximate decrease in molecular weight (MW) from 4-5 to 3-4 kDa (Figure 5(C).3). In contrast, the equivalent chromatograms for the snowmelt events in the USA revealed a general increase across larger MW species (<9 minutes) and no significant change at longer elution times (small MWs) (Figure 5(C).4).

![Graph](image1)

**Figure 5(C).3: HSPEC of the raw water samples from Albert WTW and Bamford WTW across a storm event**

**Figure 5(C).4: HSPEC of raw water samples from Fort Collins WTP across a snowmelt event across a storm event**

Charge characterisation of the raw waters revealed the total charge load to vary between 0.009 and 0.029 meq.l⁻¹ at Fort Collins WTP, and between 0.023 and 0.047 meq.l⁻¹ at Albert WTW (Table 5(C).1). The observed changes occurred because of a combined change in the DOC and the charge density of the water indicating stoichiometric dosing/monitoring of the DOC does not provide a control strategy in line with the nature with which the water changes. Analysis of the individual fractions demonstrates that the majority of the colloidal charge resides in the hydrophobic fractions. To illustrate, the average charge densities of the HAF, FAF and HPIA fractions were 5.1±1.3, 3.6±0.6 and 1.0±0.6 meq.g⁻¹DOC respectively which are similar to previous reported levels (Tipping, 1993). Further, the charge density of the HPINA fraction was below the level of detection in all cases which concurs with the findings of Edzwald (1993). Conversion of the charge densities to load reveals that the hydrophilic material makes up a maximum of 11 % of the total charge demand. The implications of the findings are that the charge character of raw waters and hence their coagulant demand is controlled by the changes in the hydrophobic fraction within the water with regard to both its concentration and its character.
Table 5(C).1: Charge density (meq.g\(^{-1}\)DOC) of the raw water samples and NOM fractions

<table>
<thead>
<tr>
<th>Date</th>
<th>Location</th>
<th>DOC (mg.l(^{-1}))</th>
<th>HAF</th>
<th>FAF</th>
<th>HPIA</th>
<th>HPINA</th>
<th>Raw water</th>
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<td></td>
<td></td>
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<td>3.6</td>
<td>1.0</td>
<td>n.d.</td>
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<td>10.2</td>
<td>5.1</td>
<td>3.1</td>
<td>1.0</td>
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<td>-</td>
</tr>
<tr>
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<td>7.5</td>
<td>6.8</td>
<td>4.2</td>
<td>0.06</td>
<td>n.d.</td>
<td>-</td>
</tr>
<tr>
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<td>5.4</td>
<td>4.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>June 03</td>
<td>Albert</td>
<td>8.9</td>
<td>3.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>June 03</td>
<td>Bamford</td>
<td>7.2</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Sep 03</td>
<td>Albert</td>
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<td>6.2</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>3.0</td>
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<td>-</td>
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<td>-</td>
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<td>4.3</td>
<td>4.5</td>
<td>1.5</td>
<td>n.d.</td>
<td>2.7 (0.023 meq.l(^{-1}))</td>
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<tr>
<td>Apr 04</td>
<td>FCWTF</td>
<td>4.4</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.7 (0.009 meq.l(^{-1}))</td>
</tr>
<tr>
<td>May 04</td>
<td>FCWFT</td>
<td>7.4</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.8 (0.029 meq.l(^{-1}))</td>
</tr>
<tr>
<td>Aug 04</td>
<td>Albert</td>
<td>13.3</td>
<td>3.7</td>
<td>3.5</td>
<td>1.2</td>
<td>n.d.</td>
<td>3.7 (0.049 meq.l(^{-1}))</td>
</tr>
<tr>
<td>Oct 04</td>
<td>Albert</td>
<td>13.3</td>
<td>3.7</td>
<td>4</td>
<td>1.2</td>
<td>n.d.</td>
<td>3.5 (0.047 meq.l(^{-1}))</td>
</tr>
</tbody>
</table>

n.d. below the level of detection.
- insufficient sample to determine charge density.

5(C).3.2 Zeta vs. removal

Analysis of the performance of the coagulation process revealed a clear relationship between zeta potential and residual DOC concentration. In each case a range of zeta potentials exist, termed operational windows, within which the residual DOC is optimised and stable for both jar tests (Figure 5(C).5) and pilot scale trials (Figure 5(C).6). The exact range of zeta potentials and residual obtainable is not constant across all the waters sampled. However, a number of common features exist. The operational windows are not symmetrical around the zero zeta potential point. Instead, the zeta potential range for optimum residual extended to only small positive values but much greater negative values. For example, in the case of Albert water sampled in September 2003 a DOC residual of 0.8± 0.1 mg.l\(^{-1}\) was obtained within the zeta potential range of +2.9 to -4.3 mV. The non symmetrical shape of the curves indicates the importance of patchwork agglomeration where only partial neutralisation of the charge is required (Ratnaweera et al., 1999) and the large negative values that still provide optimal treatment suggest the potential importance of polymer bridging from the large MW material. No direct correlation could be found between the exact limits of the operational window and the characteristics of the source water with the exception that the more hydrophilic waters tended to extend to greater positive value before performance deterioration was observed and this remains an area of investigation. Across all the sites and sources tested a value of -10 mV was observed.
to be within all the operational windows and potentially represents a safe target threshold value for coagulation monitoring and control.

![Figure 5(C).5: DOC residual vs zeta potential (Jar tests)](image1)

![Figure 5(C).6: DOC residual vs zeta potential (Pilot plants)](image2)

![Figure 5(C).7: HPSEC at different zeta potentials (Albert)](image3)

![Figure 5(C).8: HPSEC at different zeta potentials (Fort Collins)](image4)

Inspection of the HPSEC traces of the residual organics post coagulation reveals that as the zeta potential decreases in magnitude a progressively greater proportion of the larger MW weight material is removed. Comparison of the trials with Albert WTW (Figure 5(C).7) and Fort Collins WTW (Figure 5(C).8) water reveal that the residual material within the operational window is based around the same elution times of 8 to 11 minutes which approximately represents material with a molecular weight of 3 – 0.5 kDa (Goslan et al., 2004). Further, once the zeta potential had been reduced to a sufficiently low magnitude negative value, -9.9 mV for Albert WTW and -7.7 mV for Fort Collins WTW, the HPSEC traces approximately overlapped indicating very little additional treatment. The importance of this is that once the zeta potential is within the operational window, increased coagulant dose and changes in pH do not improve the performance. For instance, in the case of water sampled from Albert WTW in September 2003, coagulated with 5 or 10 mg.L\(^{-1}\) ferric sulphate as Fe at a pH of 5.2 and 5.8 respectively to maintain the same zeta potential, the resultant HPSEC
chromatograms were virtually identical (Figure 5(C).10). Further investigation into the differences in the achievable residual DOC from each trial demonstrated a clear relationship between the raw water HPINA concentration and the total residual DOC (Figure 5(C).9). The gradient of the regression line ($R^2 = 0.91$) represents a correlated ratio of 90% indicating the majority of the residual is contained within the HPINA fraction. Such findings support previous studies which have shown that the HPINA fraction is very poorly removed by coagulation (Fearing et al., 2004; Bolto et al., 2001) and relates to the fact that the material contained within this fraction is predominately uncharged (Sharp et al., 2005), low MW (Goslan et al., 2004) and comprised of carbohydrates and other very stable compounds in water (Leenheer et al., 2000). Whilst the residual organics are likely to contain other material the results suggest the initial HPINA can serve as a useful guide to the likely achievable residual DOC by coagulation.

Figure 5(C).9: Residual DOC vs initial HPINA concentration

Figure 5(C).10. HPSEC at the same zeta, different doses and pH.

5(C).3.3 Overall interpretation

The work conducted on the three water sources at different times before, during and after periods of elevated organics suggest that the polarity balance of the source water is the key to understanding the dose requirements and achievable performance of the coagulation process. The hydrophobic content of the raw water controls the coagulant demand which can be predicted through monitoring of the charge density and concentration of the appropriate fractions. Whereas, the initial hydrophilic content of the water, and specifically the non acid fraction, is an indication of the achievable DOC residual by coagulation. The consequence of this is that it should be possible to conduct a simple and rapid fractionation test to determine the requirements for and limitations of coagulation without the need for jar testing.
Interpretation of the data demonstrates that a single raw water over a period of time and two waters of the same bulk DOC can have very different coagulant demands and achievable residuals. Further, stoichiometric dosing in proportion to flow does not provide a robust means of coagulation control. Improved dose control can be achieved by linking dose to an indicator of the hydrophobic content such as UV$_{254}$ monitoring. Although such an approach will fail to account for changes in the character of the hydrophobic material it provides a simple solution as long as the dose algorithms as sufficiently robust.

Comparison of snowmelt and moorland waters during periods of elevated organic concentrations reveals that in the case of snowmelt waters the increased DOC occurs principally in the hydrophobic, large MW bands. This indicates that the elevated organic levels should not significantly alter the achievable organics residual but should increase the coagulant demand considerably. In contrast, in the case of the moorland waters the increase in DOC occurs across all MW bands and in both hydrophobic and hydrophilic components. Consequently, the impact is that the coagulant demand does not increase as significantly but the achievable organic residual is higher such that alternative treatment processes may become necessary.

The combination of bench scale and pilot plant trials clearly indicated that the use of charge measurement is a useful operational indicator in relation to the coagulation of organic dominated waters. The operational range, as derived through zeta potential measurements, was seen to alter from one source to another without a clear correlation as to why. This is likely to reflect the diversity of organic compounds that can be present and the differences they exert on the force balance involved in generating agglomerates. However, in all cases the range fell within the limits of -10 mV to +3 mV irrespective of which source water or treatment system was used and so provides a useful guide range for operational monitoring. Importantly, within the operational ranges the combination of dose and pH used to reach any given zeta potential appears to be unimportant. Consequently, charge measurement provides a straightforward means of control of the coagulation chemistry which requires semi regular rather than continuous monitoring due to the specific temporal pattern of the changes in the source water.
5(C).4 Conclusions

The present study has generated a number of observations in relation to the coagulation of NOM source waters. They relate to the importance of understanding the character of the NOM in terms of the polarity balance and charge density which can be used as a decision support tool in operating coagulation processes for NOM removal (Figure 5(C).11):

1. The hydrophobic fraction of the NOM controls the coagulant demand.
2. The observed variations in coagulant demand between sources and sampling periods are due to changes in the organic concentration and the charge density of the hydrophobic fractions.
3. The raw water HPINA concentration provides a useful indicator of the achievable residual DOC.
4. Operational zeta potential ranges exist, within which the residual concentration is optimised.
5. A threshold range between -10 and +3 mV represents a safe guide to appropriate zeta potential for optimised treatment.
6. Within the threshold values the exact dose and pH used to achieve the given zeta potential is unimportant.

Figure 5(C).11: Decision flow sheet for coagulation of NOM
5(C).5 References


CHAPTER 6
LINKING SOURCE WATER CHARACTERISTICS TO TREATMENT USING ZETA POTENTIAL MEASUREMENTS.

Submitted to: Water Research
6 Linking source water characteristics to treatment using zeta potential measurements: A mechanistic approach to coagulation.

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Abstract

Traditional approaches to coagulation control focus directly on the impact of dose and pH. However, this does not always allow the system to respond adequately to changes in organic levels and the variations in associated coagulant demand. A number of different organic dominated systems were investigated in order to link zeta potential to treatment performance. For all systems, results demonstrated the existence of a U shaped profile which in general produced low and stable DOC residuals when the zeta potential was within the range of -10 mV to +3 mV, despite the pH dose combination, with the achievable DOC residual under optimum conditions linked to the initial hydrophilic concentration. A similar relationship was seen between zeta potential and turbidity residuals, although the positive threshold value was extended beyond +3 mV as the specific UV absorbance (SUVA) value decreased.

Keywords

Clarification, Coagulation, Natural organic matter, Water Treatment, Zeta potential.
6.1 Introduction

Coagulation using metal salts to remove fine particles, colloids and dissolved contaminants such as natural organic matter (NOM), is a well established process in water treatment. When a metal salt is added to water it hydrolyses, producing a series of cationic dissociation products which act to reduce the net negative surface charge of the system, enabling particles to overcome the forces maintaining the stable suspension, thus promoting aggregation. Practical measurement is achieved through electrokinetic measurement as either zeta potential or streaming current. Advances in robustness and ease and reliability of measurements for the former are enabling it to be used more routinely on real sites in order to understand and optimise the process.

When organics such as NOM dominate the water source, the coagulation process is subject to a combination of mechanisms: charge neutralisation for colloidal material and charge complexation/precipitation for soluble compounds, with additional removal occurring due to adsorption on to precipitated flocs and metal hydroxides (Randtke, 1988), and as such is sensitive to the balance of electrical forces. However, the nature of the contaminant load varies with location. For instance, rivers can contain a high proportion of suspended clay colloids, upland peaty areas generate elevated levels of NOM, whereas algae is ubiquitous in all source waters. Consequently, the sensitivity of the system to variations in surface charge is also influenced by the source water characteristics. For example, optimum removal for *cryptosporidium* when coagulated with alum was found to occur when the zeta potential was 0 mV (Dai and Hozalski, 2002). Other systems however, were less sensitive with optimum kaolin removal, once again coagulating with alum, achieved at a zeta potential greater than -10 mV (Han *et al.*, 2001) and -13 mV for *Chlorella vulgaris* (Edzwald and Wingler, 1990).

The aim of the current paper is to investigate how the character of different organic dominated source waters influences the relationship between zeta potential and coagulation performance.
6.2 Materials and Methods

A number of different systems were investigated relating treatment performance to zeta potential. The processes were all operated during periods of rapidly changing raw water characteristics, with varying operation in terms of treatment process, scale, coagulant and contaminant (Table 6.1). Full-scale data were obtained as spot samples, whereas details for the bench and pilot trials have been previously published elsewhere as shown.

Samples were analysed for pH, Dissolved organic carbon (DOC) (Shimadzu TOC-5000A analyser in the UK and Sievers Model 800TOC analyzer in the USA), UV absorbance at a wavelength of 254nm (Jenway 6505 UV/Vis spectrophotometer, Jenway, UK) and turbidity (HACH2100 in the UK and HACH 2100AN turbidimeter in the USA). High performance size exclusion chromatography (HPSEC) analysis was undertaken using a high performance liquid chromatography device (Shimadzu VP series, Shimadzu, Milton Keynes, UK). All samples were filtered to remove suspended solids before DOC and UV$_{254}$ analysis (Glass microfibre in the UK and Durapore membrane filter in the USA, Fisher Scientific). The surface charge was measured with a zetasizer (Malvern Instruments, UK) at 25°C.
### Table 6.1: Clarification processes and source water characteristics

<table>
<thead>
<tr>
<th>Process</th>
<th>Scale</th>
<th>Water Source</th>
<th>Coagulant</th>
<th>pH</th>
<th>DOC (mg.l(^{-1}))</th>
<th>SUVA (m(^{-1}).l.mg(^{-1}).DOC)</th>
<th>Turbidity (NTU)</th>
<th>Experimental Set-up</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Lamella Plate</td>
<td>Full</td>
<td>Mountain</td>
<td>Alum</td>
<td>6.1-7.1</td>
<td>1.6-10.6**</td>
<td>-</td>
<td>0.4-22.0</td>
<td>-</td>
</tr>
<tr>
<td>(2) Various</td>
<td>Full</td>
<td>Moorland Peat</td>
<td>Various</td>
<td>5.7-6.3</td>
<td>1.7-3.1</td>
<td>-</td>
<td>0.2-2.2</td>
<td>-</td>
</tr>
<tr>
<td>(3) Lamella Plate</td>
<td>Pilot</td>
<td>Mountain</td>
<td>Alum</td>
<td>6.3-7.9</td>
<td>4.3-6.8</td>
<td>2.8-3.4</td>
<td>1.4-8.3</td>
<td>Parsons et al., 2005</td>
</tr>
<tr>
<td>(4) DAF*</td>
<td>Pilot</td>
<td>Moorland Peat</td>
<td>Ferric Sulphate</td>
<td>4.7-7.5</td>
<td>7.5-9.3</td>
<td>4.2-5.4</td>
<td>4.5-5.5</td>
<td>Parsons et al., 2005</td>
</tr>
<tr>
<td>(5) Sedimentation</td>
<td>Bench</td>
<td>Moorland Peat</td>
<td>Ferric Sulphate</td>
<td>3-7</td>
<td>9.7</td>
<td>4.6</td>
<td>9.3</td>
<td>Parsons et al., 2005</td>
</tr>
<tr>
<td>(6) Sedimentation</td>
<td>Bench</td>
<td>Moorland Peat</td>
<td>Ferric Chloride</td>
<td>4.9-7.8</td>
<td>8.0</td>
<td>1.4</td>
<td>14.3</td>
<td>Edwards, 2002</td>
</tr>
<tr>
<td>(7) Sedimentation</td>
<td>Bench</td>
<td>River (+5 mg.l(^{-1}) HA)</td>
<td>Ferric Chloride</td>
<td>4.9-7.8</td>
<td>13.0</td>
<td>4.4</td>
<td>14.3</td>
<td>Edwards, 2002</td>
</tr>
<tr>
<td>(8) Sedimentation</td>
<td>Bench</td>
<td>Algae</td>
<td>Alum</td>
<td>5-7</td>
<td>0.7-1***</td>
<td>0.6</td>
<td>3.2</td>
<td>Henderson et al., 2005</td>
</tr>
</tbody>
</table>

*Dissolved air flotation (DAF) **Total Organic Carbon (TOC) ***Chorella vulgaris 5 x 10^5 cells.ml\(^{-1}\)
6.3 Results and Discussion

6.3.1 Characterisation

The raw water systems investigated were subject to varying organic levels (Table 1). For instance, total organic carbon (TOC) values for the mountain catchments were reported to vary between 1.6 mg.l\(^{-1}\) and 10.6 mg.l\(^{-1}\), with the organic content generated when snowmelt waters percolate through undisturbed forest floors. Organic levels in moorland regions are also subject to similar variation, with the DOC concentrations reported to vary between 1.7 mg.l\(^{-1}\) and 10.7 mg.l\(^{-1}\), arising when accumulated organics were flushed into the aquatic environment during rainstorm events (Hurst et al., 2004). However, although river waters also contained a relatively high organic content of 8 mg.l\(^{-1}\), in general the NOM character is less hydrophobic compared to reservoir sources (Martin-Moussset et al., 1997). This is demonstrated by a Specific UV Absorbance (SUVA) value of less than 2 m\(^{-1}\).l.mg\(^{-1}\)DOC, which indicates low hydrophobicity, low molecular weight (MW) non-humic material (Edzwald and Tobiason, 1999). A low SUVA value of 0.6 m\(^{-1}\).l.mg\(^{-1}\)DOC was also recorded for the algal water source, indicating similar organic characteristics to the river water.

6.3.2 Particulate removal

Analysis of clarification performance revealed a clear relationship between zeta potential and turbidity residual. For instance, results demonstrate the existence of a U shaped profile which in general produced low and stable residuals when the zeta potential was within the range of -10 mV to +3 mV. This observation was valid despite the variations in experimental set-up; from bench to full-scale, flotation and gravity separation processes and varying source water characteristics (Figure 6.1a).

For each individual system, once operating the coagulation process within this operational window, with respect to zeta potential, the resultant turbidity was unaffected by an increase in coagulant dose provided the surface charge was maintained through pH adjustment. For instance, a residual post clarification turbidity of 0.98 NTU was achieved when coagulating the mountain water source with 3.5 mg.l\(^{-1}\) as Al at pH 7.1. A similar residual, of 1.09 NTU, was also achieved when the dose was reduced to 2.2 mg.l\(^{-1}\) as Al and the pH decreased to 6.3. A similar performance can be explained as the resultant zeta potentials of both coagulation
combinations were similar at -6.0 mV and -3.3 mV respectively, and more importantly both values were within the range of -10 mV to +3 mV, where the residual was stable at 1.27 ± 0.4 NTU.

Further investigation, however, highlights some variations in the profile with respect to zeta potential, particularly in relation to the location of the boundaries on either side of the operational window. The threshold or boundary values were determined by calculating the rate of change of the residual, and revealed that, in all cases, at negative zeta potentials beyond -10 mV to -15 mV the effluent turbidity rose sharply as the suspended particles became more stable. The deterioration in residual quality was more significant for raw waters with a higher initial turbidity, indicating a heightened sensitivity to the operational window. For instance, the residual turbidity of the treated river water, with an initial turbidity of 14.3 NTU, increased from 1.0 NTU at -10.2 mV to 10.4 at -12 mV. This corresponds to a decline of 4.7 NTU per mV. A similar deterioration was observed for the river water spiked with 5 mg.l\(^{-1}\) humic acid (HA) with the same initial turbidity, despite the increased organic content. Conversely, the increase in residual turbidity of the moorland source, with a lower initial turbidity of 9.3 NTU, was less pronounced at approximately 0.6 NTU per mV.

The raw water characteristics were shown to influence the positive boundary of the operational window, as results revealed that an increased organic content reduced the magnitude of the positive zeta potential at the boundary. For example, the addition of 5 mg.l\(^{-1}\) HA to the river water source decreased the magnitude of the zeta potential at the boundary from 17 to 7 mV. The window for the moorland water samples, which is highly coloured in comparison, was observed at 3 mV, and was obtained from the sedimentation jar tests when the initial DOC concentration was 6.5-9.9 mg.l\(^{-1}\). Whereas for the algae, with a significantly lower DOC concentration of 0.7-1 mg.l\(^{-1}\), the boundary was extended, with good turbidity residuals still achievable at a zeta potential of 15 mV. Further examination of the data also indicates that the character of the organic matter may also influence the positive boundary. For instance, the gradient of the regression line \(R^2 = 0.89\) demonstrates a good correlation exists between the specific UV absorbance (SUVA) and the positive threshold zeta potential values (Figure 6.1b). SUVA can be used to describe the composition of the water in terms of polarity, with a value greater than 4 m\(^{-1}\).l.mg\(^{-1}\)DOC indicating high MW
hydrophobic material (Edzwald and Tobiason, 1999). Consequently, this suggests that the hydrophobicity of the organic material may also reduce the positive extent of the operational window. For instance, the positive operational boundary for the river water, with a SUVA value of $1.4 \text{ m}^{-1} \text{l.mg}^{-1} \text{DOC}$, occurred at a zeta potential of $+17 \text{ mV}$. However, when this was spiked with $5 \text{ mg.l}^{-1} \text{ HA}$, increasing the SUVA to $4.4 \text{ m}^{-1} \text{l.mg}^{-1} \text{DOC}$, this reduced the positive zeta potential boundary to $+7 \text{ mV}$.

![Figure 6.1: Turbidity residual and (a) the relationship between clarified turbidity and zeta potential (b) the relationship between the positive zeta potential boundary and SUVA (Full-scale: 1, 2, Pilot-scale: 3, 4 Bench-scale: 5, 6, 7 and 8).](image)

6.3.3 Dissolved contaminant removal

Analysis of DOC residuals, with respect to zeta potential, also revealed a U shaped profile with optimum DOC removals for all systems achieved between a zeta potential
of -10 mV to +3 mV. However, as with the turbidity residual, this profile also lacks symmetry, revealing a steep decline in performance as the magnitude of the positive zeta potential increased beyond +3 mV, and a more gradual decline for negative zeta potential values beyond -10 mV. Nevertheless, despite the coagulant dose and pH combination, similar removals were achieved when operating within the zeta potential window. This is supported by HPSEC chromatograms showing almost identical residual profiles for zeta potentials. For example, the mountain source water was coagulated with 4 mg.l\(^{-1}\) and 4.5 4 mg.l\(^{-1}\) Fe at pH 5.9 and 5.7 respectively, although a similar performance was observed as the resultant zeta potentials of both coagulation combinations were within the range of -10 mV to +3 mV, at -9.1 mV and -2.4 mV respectively (Figure 6.2a). However, increasing the negative zeta potential beyond -10 mV also increased residual profile, as demonstrated with the moorland water source (Figure 6.2b).

Traditional approaches to coagulation diagnostics focus directly on the impact of dose and pH, as they represent the main operational variables (Duan and Gregory, 2003). However, such an approach withdraws from a mechanistic understanding, leading to a heightened sensitivity to changes in either variable. This is manifested in a belief by many operators that NOM must be coagulated at a low pH to achieve maximum removal, whereas in fact any combination of dose and pH is possible provided that it generates a net zeta potential within the operational window. This is not contradictory to established practice as the minimum dose requirement will occur under acidic conditions due to the nature of metal-humic complexes (Amirtharajah and O’Melia, 1990). However, with regards to the stability of the complexes formed, the same results have been observed whether the change in zeta potential was due to a pH change or the concentration of adsorbed organic matter (Kretzschmar et al., 1998).

However, the comparison of DOC residual profiles, with respect to zeta potential, across different water sources is less uniform (Figure 6.3a). Within this operational window, for instance, optimum residuals for the moorland water source (4) was 1.2 ± 0.2 mg.l\(^{-1}\) and 1.6 ± 0.2 mg.l\(^{-1}\) for the mountain water source (3). This is attributed to the complexity of coagulation, which depends on not only the surface charge of the formed particles but also the organic make-up for the water. The organic make-up of the water can be determined using ion exchange resins, fractionating the sample into
hydrophobic acid (HPO), hydrophilic acids (HPIA) and non acids (HPINA) (Malcolm and MacCarthy, 1992). Comparison across the schemes revealed a clear relationship between raw water hydrophilic content and total residual concentration achieved under optimum conditions (Figure 6.3b). This agrees with previous work on specific systems that have shown it is the hydrophobic fraction which is the most amenable to removal by coagulation, attributed in part to its high charge content (Edzwald, 1993).

Figure 6.2: HPSEC chromatograms of (a) Mountain source water coagulated with ferric sulphate at 4.5 mg.l$^{-1}$ and pH 5.9 (-9.1 mV) and 4 mg.l$^{-1}$ and pH 5.7 (-2.4 mV) and (b) Moorland source water coagulated with ferric sulphate at 12 mg.l$^{-1}$ and pHs 5.5-7.5 (-15 mV to 0 mV).
Figure 6.3: DOC residual in terms of (a) zeta potential and (b) the relationship between initial HPINA and total hydrophilic (HPINA + HPIA) concentration (Adapted from Sharp et al., 2005). (Full-scale:1,2 Pilot-scale: 3,4 Bench-scale: 5).
6.4 Conclusions

The overall picture has lead to the development of a number of operational guidelines when coagulating systems containing NOM:

- Coagulation should be operated at a zeta potential greater than -10 mV
- Rapid deterioration in DOC removal is expected at a zeta potential greater than +3 mV
- Initial hydrophilic content is a good indicator of the achievable DOC residual under optimum conditions
- Positive threshold for turbidity removal is extended beyond +3 mV as the SUVA value of the raw water decreases.

Consequently, for water utilities operating the coagulation processes at a zeta potential of -10 to -15 mV, hence very close to the observed boundary, this could increase their susceptibility to changes in raw water characteristics, making them liable for process upset. However, in the majority of situations, simple monitoring and minor adjustment can provide a cost effective option for maintaining a robust operation.
Chapter 6: Source Water Characteristics

6.5 References


CHAPTER 7
THE IMPACT OF ZETA POTENTIAL ON FLOC
PROPERTIES

Submitted to: Environmental Science and Technology.
7 The impact of zeta potential on the physical properties of NOM flocs.

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Abstract

The physical properties of natural organic matter (NOM) flocs, such as size, growth rate and strength, were investigated using a laser diffraction particle sizing device. Conditions were set such that varying carbon: coagulant ratio and zeta potential could both be investigated. Results demonstrate a link between zeta potential and coagulation and flocculation performance, with the production of strong flocs and low residual concentrations when the zeta potential was minimised. The overall strength of the connection points within the floc are believed to be determined by a combination of steric interactions, polymer bridging, Van der Waals forces and electrostatic forces. Hence, both dose ratio and zeta potential are important in understanding floc properties. Floc growth was influenced by dose ratio, whereas the response to elevated shear seemed to strongly relate to zeta potential. The steady state floc size appeared to be a combination of both factors. This allowed the continued development of a qualitative model in order to engineer optimal floc properties when coagulating NOM.

Key Words

Coagulation, Floc size, Floc strength, Natural organic matter, Zeta potential.
7.1 Introduction

The addition of metal salts to remove natural organic matter (NOM), is a well established process in water treatment. Chemical addition acts to reduce the negative surface charge, destabilizing the suspension, and promoting agglomeration and the formation of highly porous, irregularly shaped and loosely bound aggregates called flocs (Kim et al., 2001). As the coagulation of NOM is a charge related process (Sharp et al., 2005), an appropriate measurement is that of zeta potential which measures the charge character of colloids and particles. In complex heterogeneous systems such as NOM, zeta potential measurements relate to the range of hydrophobic and hydrophilic colloids but cannot directly measure soluble compounds. Such components will only be detected once they have reacted with the coagulant precipitate, although measurements still provide a reproducible relationship which can be used to understand and optimize the coagulation process. For instance, previous research has identified a link between zeta potential and coagulation performance whereby residuals are both low and stable when the zeta potential is maintained between -10 mV and +3 mV (Sharp et al., 2005). However, although the removal of NOM by coagulation has been researched extensively, less attention has been placed on the properties of the flocs produced.

In terms of the operation of physical treatment processes, floc properties are considered fundamental. For instance, resistance to shear is important as newly exposed surfaces of aggregates may alter the surface charge of the floc aggregate, leading to partial restabilisaton (McCurdy et al., 2004). In addition, floc breakage and the formation of smaller particles could also result in lower removal efficiencies (Boller and Blaser, 1998). Operational experience has suggested that pronounced floc breakage during solid liquid separation phases can also impact on downstream processes such as filtration, resulting in carryover onto the filters, greater particle loads, turbidity breakthrough and reduced filter run times.

The strength of flocs depends on the magnitude and number of inter-particle bonds (Parker et al., 1972; Bache et al., 1997). Traditionally, flocs formed from the coagulation of NOM are considered weak and fragile, attributed to a lack of bridging bonds (Bache et al., 1997; Jarvis et al., 2005a). For hydrolyzing coagulants, such as
Chapter 7: Floc Properties

alum or ferric, a major route for NOM floc formation is a combination of charge neutralization and entrapment/adsorption of NOM onto the metal precipitate (Bache et al., 1999; Gregor et al., 1997; Rantke, 1988). Hence, the strength of the floc is thought to be derived from a combination of organic interactions, such as steric and bridging mechanisms, and electrostatic forces. The latter is commonly investigated by measuring the charge behaviour of the system through either streaming current or zeta potential. Floc diagnostics, such as floc strength, can provide valuable information in terms of the likely separation efficiency of aggregates formed. The strength of an aggregate can be described in a number of ways. This is generally considered in terms of the energy required to break flocs under tension, compression or shear (Zhang et al., 1999), and has been investigated in terms of the following empirical relationship (Francois, 1987; Bache et al., 1999):

\[
\log d = \log C - \gamma \log G
\]

\(d\) is the floc diameter, \(C\) is the floc strength constant, \(G\) is the average velocity gradient and \(\gamma\) is the stable floc size exponent. A modified version has also been used, with RPM in place of the velocity gradient \(G\) (Jarvis et al., 2005a; Henderson et al., 2005):

\[
\log d = \log (C') - (\gamma') \log \text{RPM}
\]

The modified relationship having arisen following some debate as to whether the velocity gradient was able to accurately describe the complexities of turbulent flow in stirred vessels (Boller and Blaser, 1998; Jarvis et al., 2003).

The relative breakage of different flocculated systems have also been compared previously through the calculation of a strength factor (Fitzpatrick et al., 2003):

\[
\text{Strength factor} = \frac{d(2)}{d(1)} \times 100
\]

The strength factor value indicates the ability of flocs to withstand shear, such that a higher value suggests a stronger floc.

Previous research has suggested that it is an increase in carbon content, during periods of elevated organics that has an adverse effect on floc properties and subsequent removal (Jarvis et al., 2005b). However, the observed changes occurred with variations in both organic content and zeta potential, such that further resolution is required to decouple the two factors. Consequently, the overall objective of this paper
was to investigate the impact of zeta potential on floc properties with different organic contents, in order to identify the relative impact of surface charge and carbon content in relation to the physical properties of NOM flocs.

7.2 Materials and Methods

7.2.1 Sampling
The raw water investigated in the current study was sampled from a moorland water works in the north of England and is typically characterized as a low turbidity (3.7-7.0 NTU), low alkalinity (20 mg.l\(^{-1}\) CaCO\(_3\)), high colour (44-160 hazens), high DOC (4.3-14.5 mg.l\(^{-1}\)) water. The treatment process train consists of coagulation with ferric sulphate, dissolved air flotation and deep bed filtration prior to chlorination and is mainly designed to control DOC and metal ions in the water. Samples were taken from the inlet channel from the reservoir in October 2004 and February 2005, when the DOC was 13.3 and 10.8 mg.l\(^{-1}\) respectively.

7.2.2 Characterisation
Raw water samples were fractionated by XAD resin adsorption techniques into their hydrophobic (HPOA) and hydrophilic (HPIA) components using a method adapted from Malcolm and MacCarthy (1992). The charge density of the raw water samples was determined using a method adapted from Kam and Gregory (2001), and used previously for a number of raw water sources (Sharp et al., 2005).

7.2.3 Coagulation tests
Raw water samples were stored at 5°C prior to coagulation jar testing, which was subsequently undertaken at room temperature (20°C) and involved a 1.5 minute rapid mix at 200 RPM, a 15 minute 30 RPM flocculation stage and 20 minute settlement period.

7.2.4 Apparatus
Coagulated samples were analysed for UV absorbance at a wavelength of 254nm (Jenway 6505 UV/Vis spectrophotometer, Jenway, UK), pH and dissolved organic carbon (DOC) (Shimadzu TOC-5000A analyser). All samples were filtered to remove suspended solids before UV\(_{254}\) and DOC analysis (Glass microfibre, Fisher Scientific).
The coagulation and flocculation experiments were undertaken using a Phipps and Bird PB-900 six paddle jar tester. The surface charge was measured with a zetasizer (Malvern Instruments, UK) at 25°C. The zetasizer yields estimates and standard deviations of the zeta potential directly, and all measurements were conducted in triplicate on unfiltered samples. The general accuracy of the zetasizer was determined using standard solutions (Malvern Instruments, UK.)

7.2.5 Floc size and breakage

Floc size and breakage experiments were performed using an identical experimental set-up to Jarvis et al. (2005a) and also similar to previous work by other authors (Biggs and Lant, 2000; Spicer et al., 1998). Coagulation tests were undertaken on a jar tester as before. However, following the 15 minute flocculation phase, the effect of increased shear was investigated by increasing the RPM for an additional 15 minutes. Each experiment was repeated twice for an RPM of 30, 40, 50, 75, 100 and 200. The dynamic floc size was measured during the growth and breakage of the flocs using a laser diffraction instrument (Malvern mastersizer 2000, Malvern UK). The suspension was monitored by drawing water through the optical unit of the mastersizer and back to the jar by a peristaltic pump on the return tube using a 5mm internal diameter peristaltic pump tubing at a flow rate of 1.5 L.h⁻¹. Size measurements were taken every minute for the duration of the jar test and the data logged on a PC.

7.3 Results

7.3.1 Characterisation and removal

Characterisation of the raw water revealed the DOC concentrations of the Albert raw water samples were 13.3 mg.l⁻¹ and 10.8 mg.l⁻¹ for October 2004 and February 2005 respectively. The majority of the organic content (53-62%) was hydrophobic, as reservoir waters tend to be proportionally more abundant in the hydrophobic fraction (Martin-Mousset et al., 1997). The 23% decrease in DOC, from October 2004 to February 2005, also corresponded with a 24% decrease in charge density and a 21% decrease in UV₂₅₄ absorbance over the same period (Table 7.1).
Table 7.1: Raw water characteristics.

<table>
<thead>
<tr>
<th>Source</th>
<th>Date</th>
<th>pH</th>
<th>DOC (mg.L⁻¹)</th>
<th>Hydrophobic content (%)</th>
<th>UV_{254} abs.</th>
<th>Charge density (meq.L⁻¹)</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albert</td>
<td>Oct-04</td>
<td>5.9</td>
<td>13.3</td>
<td>53</td>
<td>55.2</td>
<td>0.047</td>
<td>3.32</td>
</tr>
<tr>
<td>Albert</td>
<td>Feb-05</td>
<td>6.1</td>
<td>10.8</td>
<td>61</td>
<td>45.3</td>
<td>0.038</td>
<td>2.90</td>
</tr>
</tbody>
</table>

Analysis of coagulation performance revealed a U shaped relationship between zeta potential and residual concentrations for the two Albert water sources, such that both DOC and turbidity residuals were low when the zeta potential is minimised, despite the initial differences in raw water characteristics (Figure 7.1). Consequently, residual concentrations are strongly related to the zeta potential during coagulation. For instance, the October 2004 sample was coagulated with 10mg.L⁻¹ Fe to a 1.33:1 DOC:Fe ratio and a zeta potential of -12.1 mV resulting in a turbidity residual of 0.93 NTU. Whereas the February 2005 sample produced a similar turbidity residual of 0.89 NTU when a similar zeta potential was achieved, -13.2 mV, despite the decreased DOC:Fe ratio of 1:1. However, although the exact range of zeta potentials and residual obtainable is not always identical (Sharp et al., 2005), a number of common features exist. The operational windows were not symmetrical around the zero zeta potential point, such that the zeta potential range for optimum residual extended to only small positive values but much greater negative values. For example, a residual turbidity of 0.6 ± 0.2 NTU was obtained within the zeta potential range of +3.9 to -13.2 mV. The operational zeta potential range for optimum DOC residuals was also slightly narrower than for turbidity, with the achievable value also linked to the hydrophilic content of the raw water. This result agrees with work undertaken across a range of raw waters (Sharp et al., 2005). For instance, a DOC residual of 3.3 ± 0.3 mg.L⁻¹ was obtained within the zeta potential range of +3.3 to -12.4 mV for the October 2004 raw water. The stable DOC residual for the February 2005 raw water was lower at 2.5 ± 0.3 mg.L⁻¹, as the original hydrophilic content was 30% lower compared to October 2004.
7.3.2 Floc size

Analysis of the growth profile revealed an increase in floc size, as indicated by the median equivalent diameter ($d_{50}$), as the zeta potential changed from positive to negative values (Figure 7.2). For instance, when coagulating the October 2004 raw water with a set dose of 10mg.l$^{-1}$ ferric sulphate (as Fe) and varying the pH between 3 and 7, a resultant zeta potential of +5.1 mV produced a maximum floc size of 535 ± 37µm. Corresponding median floc sizes produced at zeta potentials of -18.1 mV, -3.3 mV and +3.5 mV were 795 ± 36µm, 603 ± 24µm and 594 ± 28µm respectively.
Furthermore, results revealed that the steady state floc size, whilst maintaining a constant zeta potential, was also influenced by the DOC:Fe ratio. For instance, coagulating with 15 mg.l\(^{-1}\) Fe to a DOC:Fe ratio of 0.7:1, at a zeta potential of -10.5 mV, produced a d\(_{50}\) floc size of 602 ± 66 µm. This was reduced to 465 ± 41 µm when the coagulant dose was reduced to 5 mg.l\(^{-1}\) Fe (DOC:Fe ratio of 2:1), even though the zeta potential remained relatively constant at -9.5 mV. Previous work undertaken on Albert water also identified a decrease in floc size from 1000 µm to 400 µm as the DOC:Fe ratio increased from 0:1 to 3.8:1 (Jarvis et al., 2005b).

![Figure 7.2: d\(_{50}\) floc size during the flocculation stage for Oct-04 sample coagulated with 10 mg.l\(^{-1}\) Fe at pH 4-6.](image)

7.3.3 Floc growth rate

Monitoring of the floc growth rate, for a constant DOC:Fe ratio of 1.3:1, revealed that whilst the ultimate size changes as a function of zeta potential, the growth rate remained relatively constant at 89-96 µm.min\(^{-1}\) at all zeta potential values. However, the floc formed at a zeta potential of +5 mV took 10 minutes to reach d\(_{50}\), compared to 5 minutes at -18.1 mV, owing to differences in the final size (Table 7.2). In contrast, the DOC:Fe ratio impacted on the initial growth rate, with values of 56-62 µm.min\(^{-1}\), 80-96 µm.min\(^{-1}\) and 146-202 µm.min\(^{-1}\) for DOC:Fe ratios of 2.2:1, 1.3:1 and 0.7:1 respectively, such that increasing the Fe content increased the growth rate.
7.3.4 Floc breakage

Once the flocs had reached a steady state size during the slow stir phase, they were then exposed to increased shear. Analysis of the profile revealed a classical response composed of two components: an initial large drop in floc size, followed by a more gradual decline (Figure 7.3).

The response of the flocs formed at different zeta potentials, to increases in shear were quite different (Figure 7.4). When the floc size after 15 minutes of elevated shear was plotted against RPM a straight line relationship was identified on a log-log scale. Interpretation of such plots is through the value of the gradient or stable floc size exponent (\(\gamma'\)), revealing that as the magnitude of the zeta potential increased, so did the value of the slope, representing a lower resistance to shear. For instance, at a zeta potential of -18 mV the value for the slope was (-0.58), this was reduced to (-0.46) for a zeta potential of -3.3 mV. A more pronounced reduction was observed when the positive zeta potential was reduced from +5.1 mV to +3.5 mV, from (-0.64) to (-0.52), suggesting both the magnitude and sign of the zeta potential is important in relation to the flocs response to elevated shear. Previous studies (Jarvis et al., 2005a) have shown the strength plots to converge at higher RPMs, suggesting a limiting strength to the network. However, in the current study, no convergence was observed indicating the possible importance of zeta potential in understanding the strength of floc networks. An additional point to observe is the steady state floc size after exposure to 200 RPM, which also revealed differences with varying zeta potential as opposed to a convergence towards a single floc size. Consequently, even when exposed to high levels of shear some floc systems retain some level of resistance.
In general, bigger flocs are thought to break more easily. However, regardless of initial maximum floc size, results here revealed that the flocs produced at a zeta potential of -3.3 mV were most resistant to both low (50 RPM) and high (200 RPM) shear, and the smallest flocs formed at a zeta potential of +5.1 mV were also the
weakest. This was demonstrated through the calculation of strength factors, with values of 39 and 29 for -3.3 mV and +5.1 mV respectively, which are similar to the 40 calculated for NOM flocs by Jarvis et al. (2005a). Previous reports of the floc strength values for alum-kaolin flocs were lower at 14-21 (Fitzpatrick et al., 2003).

The floc strength constant can also be used as an indicator of the dominant floc breakage mechanism, where $\gamma$ values of 0.5 are indicative of floc fragmentation while $\gamma$ values of 1 suggest erosion mechanisms dominate. The floc strength constant $\gamma'$ was converted to $\gamma$ resulting in a range of 0.3 to 0.42 for all the systems investigated, which is similar to those obtained by Bache and Rasool (2001) for alumino-humic flocs, where $\gamma$ ranged from 0.44 to 0.64, and slightly higher than the 0.35 obtained by Biggs and Lant (2000) for activated sludge flocs. Analysis of the particle size distribution along the growth and breakage phases revealed two main characteristics. The shape of the distribution remained similar when the flocs were only exposed to relatively small increases in shear such that only a small shift in the median floc size was observed, combined with a slight reduction in peak height. This suggests a broadening of the distribution, although this was not significant in comparison to the other effects. The distribution did change shape at higher shears, with a larger fraction observed at smaller sizes. This is visualized by an increase in the slope of the distribution between floc sizes of 10-50 µm (Figure 7.5). This trend appeared consistent in all cases but was more prominent when a positive zeta potential was measured. The implication is that combinations of erosion and fragmentation are occurring, although fragmentation becomes more noticeable at high shears.
Figure 7.5: Oct-04 particle size distributions after 15 minutes flocculation time (30 RPMa), followed by (a) an additional 15 minutes (30 RPMb), (b) 15 minutes low shear (50 RPM) or (c) 15 minutes high shear (200 RPM), all coagulated with 10 mg.l\(^{-1}\) Fe at pH 4-6.

Contrary to varying zeta potential values, the response of the different Fe:DOC ratios to increases in shear were similar, providing the zeta potential was constant (Figure 7.6). For instance, coagulating to a DOC:Fe ratio of 1.3:1 with a zeta potential of -18.1 mV produced a slope value of (-0.58). However, altering the ratio to 0.1:7 still produced a similar slope value of (-0.57) as the zeta potential remained constant at -18.1 mV. In fact, maintaining a zeta potential within the range defined previously for optimum coagulation performance (+3.9 mV to -13.2 mV), produced flocs with similar responses to increased shear, despite differences in raw water characteristics and coagulation conditions (Figure 7.6c). Monitoring the floc size distribution revealed that alterations in the distribution appear related to the DOC:Fe ratio. For instance, at higher ratios, the pattern described previously appears to exist. Whereas, at lower DOC:Fe ratios with a higher coagulant dose, the distribution appears to alter...
the shape more significantly. This indicates a more substantial breakage is occurring, confirmed by the gradient of the floc breakage curve (Figure 7.7).

Figure 7.6: Floc breakage rates for varying DOC:Fe ratios at a constant zeta potential. *Additional data adapted from Jarvis et al., 2005b.

Figure 7.7: Feb-05 particle size distributions after 15 minutes floculation time (30 RPMa), followed by (a) an additional 15 minutes (30 RPMb), (b) 15 minutes low shear (50 RPM) or (c) 15 minutes high shear (200 RPM), coagulated with 5 (2.2:1) or 15 (0.7:1) mg.l\(^{-1}\) Fe.
7.3.5 Floc strength and removal

Combining both residual performance and the response to shear revealed a clear link when plotted against zeta potential, such that flocs with a greater resistance to shear produced the lowest residuals. (Figure 7.8). For example, a residual turbidity of 0.6 ± 0.2 NTU was obtained within the zeta potential range of +3.9 to -13.2 mV, corresponding to 0.5 ± 0.03 for the value of the slope (γ') which increased to 0.6 ± 0.07 when the zeta potential was outside the range. The profile also lacks symmetry, with a gradual decline in both removal performance and response to shear as negative zeta potential exceeds -10 mV. Whereas for the positive zeta potential values, a rapid deterioration in performance and floc properties was observed once the +3 mV threshold value was surpassed.

![Figure 7.8: Zeta potential vs. γ' (slope) and removal (NTU residual). Albert-04 data adapted from Jarvis et al. (2005b).](image)

7.4 Discussion

Results from this investigation agree with previous work, demonstrating a link between surface charge and optimum coagulation and flocculation performance, with low and stable residuals achieved when the zeta potential is minimised (Ratnaweera et al., 1999; Gregory and Carlson, 2003; Sharp et al., 2005). The results demonstrate further a definite change in floc properties with changes to either dose ratio or zeta
potential of the resultant floc. Each parameter appears to have a differing importance in relation to each characteristic. For instance, the rate of growth appears to be dominated by the dose ratio, which is to be expected as it relates to the amount of coagulant available. The steady state size achieved during the growth phases appears to be related to a combination of both factors. Whereas the response to elevated shear seems to be strongly related to the zeta potential. As such, the importance of both factors in determining steady state floc size reflects the balance of growth and breakage which occurs during flocculation.

Previous work (Jarvis et al., 2005b) proposed a qualitative model to explain the importance of dose ratio on floc properties. The model was based on the interaction or organic layers on the surface of particles within the floc matrix, with NOM as the limiting factor. This has been demonstrated as the amount of NOM removed appears to be insensitive to coagulant dose, such that a greater amount of DOC was removed in high DOC:Fe flocs than at a lower ratio. The organics are believed to influence the floc properties through a combination of steric repulsion and changes in the hydrodynamic layer thickness. The separation distances between particles and microflocs within the agglomerate increase as the DOC content increases, reducing the strength of the bond and hence producing a weaker floc. Support for such a theory is provided from work investigating haematite particles, where the presence of organic layers on the particle reduce the attractive forces by 50%, due to larger separation distances (Amal et al., 1992). Similar results have also been reported for solid latex and iron oxide particles in the presence of humic and fulvic acid (Amal et al., 1992; Walker and Bob, 2001). However, more specific interpretation is restricted due to the complexity of the system under investigation, although the principle appears to fit the observed behaviour.

The overall strength of the connection points within the floc is likely to be determined by the combination of steric interactions, polymer bridging, van der Waals forces and electrostatic forces, and hence it is evident that both dose ratio and zeta potential are important in understanding floc properties. This present work extends the previous model by including the role of electrostatics, through zeta potential measurements. The role of zeta potential is in determining the extent to which electrostatics control the properties of the flocs. For instance, low magnitude zeta potential values reduce
the electrostatic force, thus generating stronger flocs. However, this is complicated by the fact that the floc is made up of regions of positive and negative charges in places, where the coagulant or NOM have concentrated. Consequently, where opposing charges connect, an increase in strength is likely to occur. This follows the principle of electrostatic patch agglomeration (Gregory, 1973), which was originally developed to describe the behaviour of polymers. This results in the formation of local excesses of both positive and negative charges within the floc matrix, such that complete charge neutralisation is not always required (Roussy et al., 2005).

The critical observation of this is the asymmetrical nature of the plot showing zeta potential against floc gradient coefficient, where the flocs retain a better resistance to shear over a wide range of negative zeta potential values compared to when the zeta potential is positive. This is ultimately seen by the threshold values of -10 mV and +3 mV. Consequently, electrostatic patch agglomeration appears more effective when the resultant floc has a negative charge overall (Roussy et al., 2005). Presumably, this reflects the need for NOM components to bond to spots of the positive charge derived from localized concentrations of coagulant. Once the floc becomes positively charged, the opportunity for patch agglomeration is restricted, so that the reduction in electrostatic repulsion is then critical for agglomeration. The +3 mV limit thus appears as a guide for the point at which other interaction forces outweigh any repulsive forces due to electrostatics. This is seen by the sharp increase in the coefficient for zeta potential values beyond the +3 mV threshold.

The operational significance of the proposed model suggests that both dose ratio and zeta potential are important factors affecting the resulting floc structure. This work is based on an existing model to explain the properties of NOM flocs, based on steric interactions, polymer bridging and van der Waals forces. This work extends this concept further with the inclusion of electrostatic forces, based on zeta potential measurements. Zeta potential is important in terms of the impact on steady state floc size and the response to increased levels of shear. The dose ratio has been shown to impact on both steady state floc size and growth rate. Floc properties impact significantly on the overall process efficiency. For instance, reduced floc sizes have been shown to result in lower removal efficiencies (Gray et al., 1997; Aguilar et al., 2003), whereas a poor response to shear has been shown to shift the zeta potential
outside the operational window (McCurdy et al., 2004), also resulting in poor removal
due to partial re-stabilisation. Nevertheless, both floc properties and optimal removal
can be engineered through the selection of an appropriate coagulant dose and pH, in
order to achieve a certain dose ratio whilst operating at a zeta potential within the
range -10 mV to +3 mV. However, owing to the highly heterogeneous nature of NOM
which is known to vary both spatially and temporally (Owen et al., 1993; Scott et al.,
2001), more research is now needed to further validate this model and test its
application to a wide range of NOM dominated systems.
### Table 7.2: Summary data for average floc properties

<table>
<thead>
<tr>
<th>ζ</th>
<th>DOC :Fe</th>
<th>$d_{50}$ (µm) (30RPM)</th>
<th>$d_{50}$ (µm) (50RPM)</th>
<th>$d_{50}$ (µm) (200 RPM)</th>
<th>$γ$</th>
<th>$γ'$</th>
<th>Initial growth rate (µm, min$^{-1}$)</th>
<th>Time to stable floc size (mins)</th>
<th>Strength Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>15 mins</td>
<td>30 mins</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+5.1</td>
<td>1.3:1</td>
<td>535</td>
<td>425</td>
<td>289</td>
<td>125</td>
<td>0.42</td>
<td>0.64</td>
<td>83</td>
<td>10</td>
</tr>
<tr>
<td>+3.5</td>
<td>1.3:1</td>
<td>596</td>
<td>448</td>
<td>283</td>
<td>158</td>
<td>0.35</td>
<td>0.52</td>
<td>86</td>
<td>7</td>
</tr>
<tr>
<td>-3.3</td>
<td>1.3:1</td>
<td>589</td>
<td>486</td>
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<td>190</td>
<td>0.30</td>
<td>0.46</td>
<td>96</td>
<td>6</td>
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<td>1.3:1</td>
<td>795</td>
<td>724</td>
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<td>248</td>
<td>0.39</td>
<td>0.58</td>
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<td>0.48</td>
<td>62</td>
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<td>146</td>
<td>5</td>
</tr>
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<td>602</td>
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<td>212</td>
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8 Discussion of practical significance

8.1 Operational Diagram

Traditional approaches to coagulation diagnostics focus on the impact of coagulant dose and pH, as they represent the main operational variables (Duan and Gregory, 2003). However, such an approach does not allow the process to adequately respond to rapid changes in organic levels, providing a route for non-compliance. Conversely, the findings from this investigation draw attention to zeta potential as both a straightforward means of coagulation monitoring and/or diagnostic tool, which would enable the system characteristics to be directly linked to performance. This has lead to the development of an operational diagram for NOM coagulation, with the principal aim being to both predict and engineer optimal coagulation conditions, and demonstrate the integral role of zeta potential in the treatment of NOM by metal coagulants (Figure 8.1).

![Figure 8.1 Operational diagram for NOM coagulation.](image)

Each component of the operational diagram will be discussed in order to present an overview of the results in terms of the practical significance for the water utilities. Hence, by understanding and maintaining operational parameters within the limits set by the diagram, water utilities subject to rapidly changing organic levels should be able to operate under a more robust treatment strategy.
8.2 Operational zeta potential

Proposed mechanisms for the removal of NOM with metal salts include a combination of charge neutralisation by complexation with metal species and adsorption onto hydroxide/ precipitate surfaces (Dennett et al., 1995; Gregor et al., 1997; Bell-Ajy et al., 2000). Given that the process is strongly related to charge, the balance of electrical forces is important (Misra and Barnett, 1991). In addition, the existence of a zeta potential range, as opposed to a single value, suggests that in general colloidal de-stabilisation occurs before complete neutralisation of surface charge (Gray et al., 1997; Ratnaweera et al., 1999; Gregory and Carlson, 2003). This generates a U shaped profile, which in general produces low and stable residuals when the zeta potential was minimised to within -10 mV and +3 mV. This profile has been investigated in terms of varying source water (Paper 5 & 8), source water characteristics (Paper 9), NOM fraction composition (Paper 4), coagulant type (Paper 6 & 7), floc properties (Paper 11) for both coagulation and clarification processes (Paper 10) at varying scales from laboratory experiments to full scale works. The exact location of the operational boundaries were seen to vary slightly, and this is likely to reflect the diversity of organic compounds present and their influence on the balance of forces involved in generating agglomerates. Furthermore, turbidity removal is less sensitive to zeta potential when compared to DOC (Paper 10), such that optimising for DOC removal will also produce minimum residual turbidity (Edzwald, 1993; Dennett et al., 1995), added confirmation that it is the presence of organic material which is the main factor in determining optimum coagulation conditions, (Edzwald, 1993; Tseng et al., 2000). Nevertheless, in all cases the range fell within the limits of -10 mV to +3 mV irrespective of which source water or treatment system was used and so provides a useful guide for operational monitoring. Conversely, many processes currently operating in the water treatment industry operate within -8 mV to -15 mV (Bourgeois et al., 2005), very close to the observed boundary, as indicated by the problem areas highlighted in the operational diagram. This heightens process sensitivity to changes in both raw water characteristics and the associated charge balance, therefore increasing the likelihood of a process upset. Furthermore, although the exact response depends on the system characteristics, performance has been shown to deteriorate rapidly once the threshold value has been exceeded (Paper 10). For instance, the residual turbidity of the treated river water, with an initial
turbidity of 14.3 NTU, was shown to increase from 1.0 NTU at -10.2 mV to 10.4 at -12 mV. Nevertheless, in the majority of situations, this can be avoided through simple and semi regular zeta potential monitoring, followed by minor adjustment, resulting in a cost effective option for maintaining a robust operation.

The removal of DOC is an important concern for water utilities due to the formation of potentially carcinogenic disinfection by products (DBP) from residual organics during the disinfection process. DOC removal is independent of the solid liquid separation process (Malley, 1990; Edzwald and Malley, 1991), therefore, the achievable DOC residual is dependant on interaction with the coagulant which forms the metal-humic complexes. Results reveal a poor level of interaction of the hydrophilic NOM fractions, HPINA in particular, with both iron and aluminium coagulants (Paper 2 & 3). This was attributed to a negligible charge density, of at least an order of magnitude lower than the hydrophobic fractions (Edzwald, 1993). This fraction also contains lower molecular weight (MW) material (Fearing, 2004) as well as carbohydrates and other very stable compounds in water (Leenheer et al., 2000), which could also contribute to a poor removal. Comparison across different source waters has revealed a good correlation between residual DOC and the initial level of hydrophilic material (Papers 9 & 11). It is also possible to remove a portion of the hydrophilic material, as the DOC removal is greater than the total hydrophobic content of the water (White et al., 1997). The implication for water utilities is that simple monitoring of the polar NOM fraction can provide a good indication of the achievable DOC residual under optimum conditions without the need for additional jar testing. This is less significant for snowmelt waters, when the increase in DOC was attributed to a rise in the hydrophobic content whilst the hydrophilic concentration remained relatively stable (Paper 8). Conversely, for the moorland source waters the increase was observed for both hydrophobic and hydrophilic NOM fractions (Paper 5). Ultimately, this provides a tool to assess potential asset needs. For instance, when the initial hydrophilic content of the raw water is too high then additional treatment strategies, such as magnetic ion exchange resins (MIEX®)(Fearing et al., 2004), should be considered in order to remove more of this fraction.
Further investigation has revealed that NOM fraction make-up not only influences the achievable residual, but also the DOC residual profile with respect to zeta potential (Paper 4), attributed in part to the mechanisms involved in the formation of the metal-humic complexes. The humic acid fraction (HAF) can be removed over a wide range of operational zeta potentials, through a combination of charge neutralisation (for colloids), complexation/precipitation and ligand exchange adsorption (Huang and Shiu, 1996). Whereas the profile for the fulvic acid fraction (FAF) is similar to the raw water, and is thought to be principally removed through an adsorption pathway (McKnight et al., 1992) and as such adsorption may be hindered as the electrostatic repulsion is increased. This presents further support for a charge based operating strategy, as UV$_{254}$ monitoring is unlikely to distinguish between the two hydrophobic NOM fractions sufficiently.

The lack of symmetry in the profile, such that large negative zeta potential values still provide optimal treatment, indicates the existence of other mechanisms such as polymer bridging, hydrogen bonding and electrostatic patch (Amal et al., 1992; Ashmore and Hearn, 2000; Bob and Walker, 2000; Das and Somasundaran, 2003; Roussy et al., 2005). An example of where this has been described previously is with the electrostatic patch theory (Gregory, 1973) which is believed to operate for polymers of a very high charge density interacting with oppositely charged particles of low charge density. Applying a similar principle to the current system provides one explanation for the extended range for the negative zeta potential values, although the electrostatic patch mechanism does appear to be more effective when the overall zeta potential is negative and only partial neutralisation of the negative charge is required (Gray et al. 1997; Roussy et al., 2005). Once the zeta potential exceeded the positive threshold of +3 mV, this resulted in a sharp deterioration in performance. Nevertheless, with regards to turbidity removal, results reveal that the positive threshold of the operational window could be extended further (Edwards, 2002), depending on the nature of organics. For instance, the higher charge content associated with an increased SUVA value leads to a heightened sensitivity to increased positive zeta potential values due to a greater degree of electrostatic repulsion between aggregates (Paper 11). However, when coagulating a water with a low SUVA value (>2 m$^{-1}$.l.mg$^{-1}$DOC), optimum turbidity removal can still be
achieved at higher positive zeta potential values, therefore extending the operational range as shown in the diagram (Figure 8.1).

8.3 Chemical dosing regime

Results support the hypothesis that achieving the required zeta potential is more important than achieving a certain coagulant dose or pH, provided that it generates a net zeta potential within the operational window. In general, an increasing DOC content does create a greater coagulant demand (Owen et al., 1993; Crozes et al., 1995; Bell-Ajy et al., 2000; Volk et al., 2000). However, the coagulant dose required to maintain the zeta potential within this range, or at the IEP, is dependent on both the character and polarity of the organic matter (Papers 2, 3 & 4). The composition and character of organic material varies, especially in terms of MW, solubility, hydrophobicity, charge density and functional group composition (Edzwald, 1993; Korshin et al., 1997; Schlautman and Morgan, 1994; Vuorio et al., 1998). Consequently, differences in carboxylic acidity or charge density between the fractions are likely to influence the coagulant demand, as a higher charge is associated with the larger MW hydrophobic fractions (Collins et al. 1986; Edzwald, 1993). In addition, hydrophobic NOM fractions not only contribute to the majority of the charge load, but also impact most significantly on the resultant zeta potential of the metal-humate precipitate. Reports in the literature suggest this is due to competitive interaction between coagulants and NOM, which are favoured towards the larger MW, more hydrophobic, more highly charged components (Gu et al., 1995; Huang and Shiu, 1996) due to the combination of charge neutralisation, complexation/precipitation and ligand exchange mechanisms which are thought to dominate NOM removal (McKnight et al., 1992; Filius et al., 2003). The implication for the water utilities in this instance is that stoichiometric dosing in proportion to flow, or bulk water parameters such as total DOC, does not always provide a robust means of coagulation control, such that any two waters with the same bulk DOC concentration can have very different coagulant demands. Improved dose control can be achieved by linking dose to an indicator of the hydrophobic content such as UV<sub>254</sub> monitoring, although such an approach will fail to account for changes in the NOM character. Streaming potential or streaming current measurement, an on-line technique originally patented by Gerdes (1966), is one option for automatic
Chapter 8

Discussion

coaulation control. However, an offset is known to exist between elecrophoretic mobility and streaming current measurements, depending on the particular streaming current detector (SCD) probe and the SCD gain setting used (Briley and Knappe, 2002). Consequently, preliminary jar tests are still required to determine the equivalence endpoint for any particular water source. Furthermore, not only are SCD sensors prone to fouling (Barron et al., 1992), but electrical charges have been shown to vary depending on the time of day, outside temperature and the weather (de Haas, 1996). In contrast, zeta potential measurement is an off line technique, and an extremely useful operational indicator, universally applicable irrespective of source water, process scale and coagulant. Furthermore, the fact that the exact pH coagulant dose combination within the threshold values is unimportant generates a greater degree of flexibility, so that conditions can be adapted to manage the process as the source water characteristics vary. In this way, semi regular monitoring can provide the necessary control, especially as changes in water character do not occur instantaneously.

In terms of the impact of different coagulants, the exact understanding of the way both aluminium and iron coagulants operate in relation to NOM removal is far from complete. Ferric based coagulants present approximately two times more active positive charges per dry weight of coagulant when compared to alum, and consume approximately twice as much alkalinity, therefore resulting in a lower pH (Crozes et al., 1995). However, examination of the differences in NOM-coagulant interactions appears to be minimal in terms of the IEP when based on a charge ratio (Paper 3). In fact, the main observed difference was that a greater degree of DOC removal was possible with iron compared to aluminium (Budd et al., 2004; Bell-Ajy et al., 2000; Edzwald and Tobiason, 1999). Nevertheless, if the differences do not originate from electrical interactions such as charge, then they may be controlled by the affinity of each coagulant to adsorb to the contaminant surface, or to form complexes with a particular functional group. In this respect, the increased removal with ferric ions could be attributed in part to a higher affinity for carboxylic groups present in the NOM (Leja, 1982).
8.4 Clarification performance

Clarification performance is dependent not only on the zeta potential but also the clarification process involved and the characteristics of the floc aggregates. Flocs are held together by both chemical and physical bonds which depend on the nature of the interactions between particles (Yukselen and Gregory, 2004). This work has revealed that both DOC:Fe ratio and zeta potential are important in determining the resulting floc structure (Paper 11). A previous explanation was based on an existing model which attributed the NOM floc properties to steric interactions, polymer bridging and van der Waals forces (Jarvis et al., 2005). However, the inclusion of zeta potential in this work adds another dimension to the model, therefore allowing water utilities to effectively engineer floc properties, such as size, growth and resistance to shear, in relation to a particular process. For instance, results from this investigation have revealed that floc aggregates formed within the operational window, \(-10 \text{ mV to } +3 \text{ mV}\), are stronger and therefore more likely to withstand exposure to increased shear regions. This is important in effective coagulation (Gregory, 1989), particularly as newly exposed surfaces of aggregates may alter the surface charge of the floc aggregate, leading to partial re-stabilisation (McCurdy et al., 2004). Furthermore, floc breakage and the creation of smaller particles could also result in lower removal efficiencies (Boller and Blaser, 1998). However, increasing the zeta potential beyond the threshold value will produce larger, more loosely connected NOM aggregate, attributed to the increased electrostatic repulsion within the matrix (Bache et al., 1999). A theory supported by Vigle-Ritter (1999), who observed an adverse effect on floc structure with a higher coagulation pH and associated charge increase.

A number of authors have concluded that increased floc size is a good indicator of floc strength for a given shear condition (Bache and Papavasilopoulos, 2003; Yukselen and Gregory, 2004; Jarvis et al., 2005). This work has indicated that increased floc sizes could result in increased removal, provided the zeta potential is maintained within the operation envelope. This has also been observed when coagulating latex with alum (Chakraborti et al., 2003). Larger floc sizes can be engineered by increasing the coagulant dose. One of the mechanisms in the coagulation of NOM involves the binding of metal species to anionic sites, neutralising the negative charge and leading to the precipitation of a metal humate.
complex (Duan and Gregory, 2003). Hence, increasing the coagulant dose, and number of binding sites, is likely to increase both precipitation and floc size (Ching et al., 1994). However, in terms of the benefits of increased floc size for the water industry, this must be assessed in relation to the particular process involved and the costs associated with increased coagulant usage. Finally, the initial growth rate is another variable which is also dependent on the DOC:Fe ratio, with higher rates observed for lower ratios, irrespective of the operational zeta potential. This is an important consideration when optimising the capacity time of an existing process.

8.5 Overall recommendations

Two major recommendations have arisen from this work, the first being the need for a greater understanding of the system characteristics and the impact of NOM on coagulation, whereas the second is to maintain the coagulation process within a predefined operational window.

With regards to the first recommendation, rapid fractionation tests can provide information on the polarity of the water in terms of the hydrophilic/hydrophobic balance, and coupled with charge density measurements this can provide a useful tool when optimising coagulation. For instance, the hydrophobic content indicates the amount of organic material which can be removed by conventional coagulation, and can be used to predict the required coagulant dose when used in combination with charge density measurements. The non adsorbed or HPINA fraction however, is a good indicator for the residual DOC concentration remaining after treatment. This is important, as residual organics can lead to the formation of potentially carcinogenic disinfection by products (DBP), such as Halo acetic acids (HAA) and Trihalomethanes (THM), during the disinfection process (Singer, 1999).

In order to maintain a robust process, zeta potential can be used as both a straightforward means of coagulation control as well as a diagnostic tool, by maintaining a value within the range of -10 mV to +3 mV. In reality, a mid range set point is recommended, therefore allowing operators time to respond and adapt to fluctuations in the organic charge load. This can be achieved cost effectively though simple monitoring on a semi regular basis. Zeta potential can be manipulated through
either coagulant dose or pH adjustment. In fact, the exact combination is unimportant, provided the zeta potential remains within the threshold values. However, the DOC:Fe dose ratio is important when considering the properties of the floc aggregates formed, with an optimal ratio of 1:1 having been identified previously (Jarvis et al., 2005). For instance, a reduction in the DOC:Fe ratio will increase both the steady state floc size and the initial growth rate. This is an important consideration for processes in which floc size and characteristics are important, such as sedimentation.

In general, results suggest that a robust operational performance can be maintained through the implementation of a series of flowsheet diagrams. For instance:

1. If the WTW is failing to meet the required residual organic concentration (Figure 8.2a):
   (a) Check the post coagulation zeta potential, which should not exceed -10 mV and can be manipulated by altering either pH of coagulant dose
   (b) If the zeta potential is within the operational range, fractionate the raw water to determine the non adsorbed fraction concentration (HPINA). If the level exceeds the required residual concentration then additional treatment options should be investigated.

2. If the floc properties are failing to meet the operational requirements (Figure 8.2b):
   (c) Check the post coagulation zeta potential, which should also not exceed -10 mV in order to produce flocs with the most resistance to shear.
   (d) Check the DOC:Fe ratio and adjust to 1:1.
   (e) If floc properties are still not suitable for clarification, then process options should be reviewed.
Does the works meet required residual organic conc?

- **Yes**: Take no Action
- **No**: Measure post coag zeta potential
  - **Exceeds -10mV**: Adjust dose and/or pH
  - **Does not exceed -10mV**: Measure HPINA conc
    - **Does not exceed required residual**: Optimise coagulation process/Change coagulant
    - **Exceeds required residual**: Additional treatment required

Are flocs ok for clarification process?

- **Yes**: Take no Action
- **No**: Measure post coag zeta potential
  - **Exceeds -10mV**: Adjust pH
  - **Does not exceed -10mV**: Check DOC:M² ratio
    - **Not 1:1**: Adjust Ratio
    - **1:1**: Additional treatment required

Figure 8.2: Flow sheet diagrams for (a) optimal NOM removal and (b) optimal floc properties.
8.6 References


CHAPTER 9
CONCLUSIONS AND FURTHER WORK
9 Conclusions and Further work

9.1 Conclusions

This project has extended previous characterisation studies and demonstrates that the DOC, polarity and charge density of the waters vary considerably as both a function of location (source) and time of year or season. Furthermore, coagulation investigations at varying scales, from bench to full, clearly indicate the importance of zeta potential in terms of a universal indicator of the appropriateness of the treatment strategy, irrespective of the chemical used or the system investigated. The following overall conclusions have been drawn:

- The variation in raw water characteristics for all sources was observed in terms of both DOC concentration and UV$_{254}$ absorbance. However, characteristics also varied in terms of hydrophilic/hydrophobic content and charge density. Consequently, stoichiometric dosing of coagulants based on bulk water parameters, such as DOC and UV$_{254}$, is not a viable option for maintaining a robust coagulation performance during these periods.

- Raw water monitoring and characterisation revealed that during the period of elevated organics, the changes in NOM composition and character of snowmelt and moorland waters were considerably different. The increase in DOC for the snowmelt water source was attributed to an increase in the high MW hydrophobic material, whereas for the moorland waters the increase was observed for both the hydrophobic and hydrophilic NOM fractions, across a broad spectrum of molecular weights.

- The hydrophobic NOM content contributes the majority of the charge load and subsequent coagulant demand, although this fraction is also most readily removed during conventional coagulation with metal salts. Fractionation and charge density measurements are an effective way to determine both the charge density and hydrophobic content of the water.

- The FAF fraction most readily resembles the raw water with regards to both coagulation conditions and floc properties. This presents further support for a charge based operating strategy, as UV$_{254}$ monitoring is unlikely to distinguish between the two hydrophobic NOM fractions sufficiently.
• The hydrophilic NOM fraction is less amenable to removal when coagulating with metal salts. Consequently, measurement of the polar NOM fraction (HPINA in particular) provides a good indication of the achievable DOC residual concentration when coagulating under optimum conditions.

• Coagulation with ferric salts removed approximately 0.5 mg.L\(^{-1}\) more DOC than when coagulating with alum. However, results revealed no significant difference in the influence on the IEP based on charge ratio.

• Comparison across different source waters, seasons, scales and chemical solutions revealed that good coagulation performance was achieved for all systems, in terms of DOC removal, when the zeta potential was maintained within the range \(-10<\zeta<+3\) mV.

• The combination of pH and coagulant dose is unimportant provided the resulting zeta potential is within the pre-determined operational window.

• A similar operational zeta potential range exists for clarification processes, although the zeta potential value at the positive threshold is influenced by the nature of the organics. The positive zeta potential range, within which good turbidity residuals are achieved, is increased as the SUVA value of the raw water decreases.

• Raw water sources with a higher turbidity were found to be more sensitive to the negative zeta potential threshold value, resulting in a more rapid deterioration in performance.

• Both dose ratio and zeta potential are important factors in determining the resulting floc structure. Operating within the zeta potential range of \(-10<\zeta<+3\) mV will increase the flocs resistance to shear, whereas increasing the coagulant dose and lowering the DOC:Fe ratio, whilst maintaining the zeta potential within the operational range, will increase the steady state floc size.
9.2 Further work

This work has highlighted the benefit of characterisation techniques to evaluate the composition and character of organic matter present in each system. This has demonstrated that by understanding how the systems change, and the subsequent impact on both the coagulation process and the level of removal achieved, a WTW may be able to adapt their treatment processes in order to optimise both coagulation and downstream solid-liquid separation processes. However, more research is required in this area and should concentrate on:

(1) The influence of raw water source. This work presented data from a number of sources, all containing a high hydrophobic NOM fraction. More research is required based on sources of a more hydrophilic nature, such as lowland or river waters, in order to test the strength of the relationships identified.

(2) The use of zeta potential as a strategic planning tool in order to link catchment management and source water selection to optimal treatment performance. For instance, the development of a simple fractionation method for determining the hydrophilic content of the water, combined with enhanced raw water monitoring in terms of HPSEC and charge density, would allow source waters to be ranked in terms of both treatability and coagulant demand.

(3) The use of highly charged novel coagulants. This study presented encouraging performance data using zirconium, a highly charged novel coagulant, based on bench scale experiments with one NOM rich water source. Consequently, more research is needed, especially in terms of the effect of varying NOM composition and increasing operational scale, in order to propose zirconium as a viable option for the future.

(4) A further understanding of the differences observed between Iron and Aluminium based coagulants. This work has shown that these two coagulants give rise to different DOC residuals under optimum coagulation conditions. However, examination of the differences in NOM-coagulant interactions appears to be minimal in terms of the IEP when based on a charge ratio. Hence, the mechanistic description for these differences has not been adequately explained and therefore more research should focus on a fundamental analysis.
of the molecular attraction between the metal hydroxide and the NOM using tools such as atomic force microscopy.

(5) A reduction in flocculation time. This work has shown that under all the conditions investigated, the $d_{50}$ floc size was reached within 10 minutes, with no net increase observed for any subsequent increase in slow stir flocculation time. Hence, the impact of a reduced flocculation time on treatment performance could be investigated as this could potentially reduce the residence time at a full-scale WTW.

(6) The impact of zeta potential on downstream processes. This work has highlighted the relationship between zeta potential and the initial treatment stages of coagulation and clarification. However, more research is needed to investigate the impact of zeta potential on controlling downstream processes such as filtration, and in particular the influence residual organics may have on the system.
High Performance Size Exclusion Chromatography (HPSEC) size calibration (Goslan, 2003; Pikkarainen et al., 2004).

Figure A.1: HPSEC chromatogram of Albert raw water with peaks assigned.
