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 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); water treatment; zeta potential

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 isoelectric point (i.e.p.) 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 conditions 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 novel high charge coagulant was also investigated.
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., 2002). Seasonal variations in water quality at Albert WTW are shown below (Table 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 254 nm was measured using a Jenway 6505 UV/Vis spectrophotometer. All samples were passed through a Fischer Scientific MF200 1 μm 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.

Reagents

The coagulants under investigation were: Ferric sulphate (Ferripol xl, EA West) and a highly charged novel coagulant (patent pending). The cationic polymer polydiallyl dimethylammoniumchloride (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. Details of the preparation of the novel coagulant are provided in Parsons and Jefferson (2004).

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., 2002; 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 acid (HPINA).

The charge density of the NOM fractions was determined using the Malvern zetasizer and PolyDADMAC. A beaker containing 100 ml of deionised water, 2.5 mg 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 isoelectric point (i.e.p.) had been established.

With regards to the coagulation–flocculation experiments only one jar was used at any

<p>| Table 1 | Raw water quality at Albert WTW |</p>
<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>
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.

Results and discussion

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 ± 0.3 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 mg L⁻¹ (Figure 1a). Fractionation of the raw water revealed that the make up of the water varied throughout the year even during a period 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 1b). From meteorological observations, the periods of high hydrophobic content follow periods of increased rainfall. Rainfall in the north increased from 17.6 mm in August to 43.6 mm for September, followed by an additional increase from 55.6 mm in November to 79.1 mm 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., 2002), and showed the charge density of the hydrophobic fractions to be nearly two orders of magnitude greater than the hydrophilic fractions (Figure 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 charged 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 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.

Coagulation conditions for i.e.p.

The zeta potential profiles demonstrate the impact of NOM concentration and character on the surface charge (Figure 3a). The i.e.p. 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 i.e.p. 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 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 novel coagulant highly charged (Figure 3b). This has a charge density of 0.04 eq g⁻¹ and exists principally in its 2⁺ form across a broad range of pHs. Coagulants are typically based on iron (III) and aluminium (III) and the charge density of the coagulant is a significant factor in determining
the efficiency of coagulation and particle removal; the higher the charge density, the better the coagulation and the more organics and particles that can be removed. The charged ions though exist only under acidic conditions and it is often lower charged intermediate or complete hydrolysis species that exist in water under the pH range 4–10. The novel coagulant is an inorganic salt that exists as a stable cation over the range of pH tested making it more available for a charge neutralisation mechanism rather than sweep flocculation. Comparison of the September 03 water revealed that using the novel 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.

**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 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 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

![Figure 2](https://iwaponline.com/ws/article-pdf/4/4/95/417511/95.pdf)

(a) The impact of (a) NOM fraction and (b) season on charge density
more positive value whereas the range extended in both positive and negative values for organics removal.

**Conclusions**

From the results presented, it is apparent that the raw water characteristics for the period September to December 2003 altered 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

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**Figure 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.
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 a 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 new 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.

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References


