Processes for enhanced NOM removal: beyond Fe and Al coagulation

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ABSTRACT

Source waters containing high concentrations of natural organic matter (NOM) have conventionally been treated using metal salts (normally Fe\(^{3+}\) and Al\(^{3+}\) based products). The main reason for NOM removal in potable water production is to prevent disinfection by-products (DBPs) from forming during disinfection processes. Using a common water source containing up to 15 mg L\(^{-1}\) dissolved organic carbon (DOC), NOM removal was assessed using 1) advanced oxidation processes (AOPs) (ultra-violet light/hydrogen peroxide (UV/H\(_2\)O\(_2\)) and Fenton’s reagent (FR)); 2) a novel coagulant ZrCoag\(^{w}\) (Zr\(^{4+}\)); and, 3) ion-exchange (magnetic ion-exchange resin, MIEX\(^{w}\)) combined with coagulation at reduced coagulant doses. These results were compared with optimised conventional coagulation using ferric sulphate (Fe). High levels of NOM removal were achievable, with between 7–11% increased DOC removal for the advanced treatments over coagulation with Fe\(^{3+}\). The formation of DBPs (trihalomethanes) for the treatment systems were compared. There were also significant differences in the properties of the floc formed for the different treatment systems. Flocs formed after coagulation following pre-treatment with magnetic resin and coagulation using Zr\(^{4+}\) resulted in significantly larger flocs compared with Fe\(^{3+}\) coagulation by 37 and 27% respectively. Flocs formed using FR were smaller than Fe\(^{3+}\) coagulant flocs by 28%. The paper discusses the practical implications of using the different advanced treatment processes to achieve incremental increases in overall NOM removal when compared with conventional coagulation.

Key words | adsorption, advanced oxidation processes, coagulation, ion-exchange, natural organic matter

INTRODUCTION

Natural organic matter (NOM) is the term used to describe the complex matrix of organic material present in varying concentrations in all water sources. This includes hydrophobic humic and fulvic acids, hydrophilic acids, proteins, lipids, hydrocarbons and carbohydrates (Edzwald 1993; Scott et al. 1998). This material is derived from living and dead plants, animals and microorganisms, waste products from organism metabolism and from the natural degradation of these different compounds (Chow et al. 1999).

The removal of NOM during potable water treatment is key for a number of well established (and well studied) reasons. These include:

1. The prevention of the formation of harmful and regulated disinfection by-products (DBPs) from the reaction between residual NOM and chlorine based disinfectants.
2. To remove taste, odour and colour from drinking water.
(3) The removal of a food source for microbial re-growth in drinking water distribution systems.

(4) To stop a transfer route for metals into drinking water.

The standard process for bulk removal of NOM in water treatment has been coagulation using salts of iron (Fe$^{3+}$) and aluminium (Al$^{3+}$) followed by a solid-liquid separation process such as sedimentation or dissolved air flotation (Sharp et al. 2006a). By optimisation of coagulation, high levels of NOM removal can normally be achieved (a process sometimes referred to as enhanced coagulation) using these commonly used coagulants. Through a combination of pH and coagulant adjustment in relation to the changing character of the organic compounds in the water, it has been demonstrated that maximum NOM removal can be achieved in a zeta potential window between −10 to +3 mV (Sharp et al. 2006b).

The character and concentration of NOM in raw water sources has been demonstrated to change throughout the year, normally reflecting a change in seasonal climatic conditions. For example, the first heavy rains after a dry summer or spring snow melts can both lead to an increase in NOM load in a water source. In addition to seasonal increases of NOM in surface waters, there has also been a trend for increasing year on year concentrations of NOM in waters across Europe and North America (Skjelkvale 2003; Eikkebrokk et al. 2004; Worrall 2004). Significant increases have been observed in 6 out of 10 regions assessed by the International Co-operative Program (ICP) on assessment of acidification of rivers and lakes over the last 10 years. This includes sampling regions in the UK, Norway, Quebec, Vermont, the Upper Midwest (US) and Adirondacks (US). The most likely explanations for these observations are due to climate change, land use change and other anthropogenic influences. A recent paper on future trends in Australian water quality predicts a change in NOM character to more algal/macrophyte derived NOM, with surges of soil and plant derived NOM during extreme weather events (Soh et al. 2008).

Coagulation is a well understood and practiced process but in the presence of high concentrations of NOM, fragile flocs are formed and there is increased risk of formation of DBPs. Operational experience has suggested that pronounced floc breakage during solid–liquid separation phases can also impact on downstream processes such as filtration, resulting in the carryover of greater loads of fine particles onto the filters giving earlier turbidity breakthrough and reduced filter run times. The normal response to elevated DOC events is to increase the amount of coagulant added. The result of which is an increase in chemical usage and sludge production with a commensurate increase in waste disposal costs. Increased NOM removal at these higher coagulant doses is not always guaranteed.

As a combined consequence of more strict regulatory requirements for DBPs in drinking water and a deterioration in water sources, many NOM laden waters have become more difficult to treat using traditional coagulation means in order to comply with current legislation (Eikkebrokk et al. 2004). Furthermore, recent issues have arisen for water utilities around the increased costs of coagulants (linked to increased transport costs) and security of supply. For these reasons alternative and additional treatment stages have been researched and implemented at full-scale (Singer & Bilyk 2002; Parsons et al. 2007).

A range of processes have been studied at Cranfield University that show promise for high levels of NOM removal. The objective of this work was to compare the treatment of NOM laden waters using a range of advanced treatment processes designed to give improved levels of NOM removal compared to optimised coagulation processes. This included a comparison of: 1) advanced oxidation processes (AOPs) (ultra-violet light/hydrogen peroxide (UV/H$_2$O$_2$) and Fenton’s reagent (FR)); 2) a novel coagulant (ZRCoag$^*$ containing a Zr$^{4+}$ salt)); 3) ion-exchange (magnetic ion-exchange resin, MIEX®) combined with coagulation at reduced coagulant doses.

**MATERIALS AND METHODS**

Moorland source water from the Yorkshire Water was used in these trials from Albert WTWs (Halifax, UK) and Ewden WTWs (Sheffield). These waters are typically highly coloured and contain a high dissolved organic carbon (DOC) content, normally between 8–20 mg/L DOC, low turbidity (<2 NTU) and low alkalinity (<20 mg/L as CaCO$_3$). These source waters have been the subject of numerous studies covering...
their character, fractionation and reactivity (Goslan et al. 2002; Fearing et al. 2004; Jarvis et al. 2005).

The raw water was treated with optimum treatment using:

1) **Coagulation using ferric sulphate** (Ferripol XL, EA West, UK). Fe$^{3+}$ coagulation is the conventional treatment option for this type of water in the UK. Coagulant doses were selected based on jar testing. As waters were collected at different times of the year for comparison of the processes with Fe$^{3+}$, the coagulant dose varied between 8–10 mg/L as Fe$^{3+}$ using a coagulation pH of 4.5. Zeta potential measurements were taken to ensure that the coagulation was within the pre-defined charge window.

2) **UV/H$_2$O$_2$**. Experiments were conducted using a collimated beam device as the UV source (Wedeco, AG, Germany) equipped with 4 low pressure UV lamps, providing a power density of 19.2 W/m$^2$. Raw water (250 mL) was placed in an open Petri dish (19 cm diameter) and stirred with a magnetic bar. Optimum conditions for UV/H$_2$O$_2$ testing was UV exposure for 30 minutes (3.5 J/cm$^2$) at pH 4 with 6.8 mg/L H$_2$O$_2$.

3) **Fenton’s reagent** (FR). Ferrous sulphate heptahydrate (EA West, UK) and H$_2$O$_2$ were used for FR experiments. Optimum concentrations of FR were 5.6 mg/L as Fe$^{2+}$ and 85 mg/L H$_2$O$_2$ at pH 4.

4) **Coagulation using ZRCoag (containing a Zr$^{4+}$ salt)** (Water Innovate, UK). Zr$^{4+}$ was dosed as described for Fe$^{3+}$ coagulation. The optimum coagulation conditions were found to be 8 mg/L as Zr$^{4+}$ at pH 5. Zeta potential measurements were taken to ensure that the coagulation was within the pre-defined charge window.

5) **Ion-exchange (magnetic ion-exchange resin) followed by coagulation.** Optimum MIEX resin dosing conditions were 10 mL/L resin for 10 minutes followed by Fe$^{3+}$ coagulation at 4 mg/L as Fe (a 60% coagulant reduction compared to optimised Fe coagulation alone).

All samples were filtered prior to DOC and UV$_{254}$ analysis to remove suspended solids. A Shimadazu TOC-5000A analyzer was used for determining the DOC content (mg/L), UV$_{254}$-Abs (1/m) was measured using a Jenway 6505 UV/Vis spectrophotometer. The zeta potential was measured on unfiltered samples for the raw water and for the treated waters. Both measurements were carried out with a Zetasizer (Malvern Instruments, UK) that directly yields estimates and standard deviations of the zeta potential. Samples were fractionated by XAD resin adsorption techniques into their hydrophobic (fulvic and humic acid fractions (FAF and HAF)) and hydrophilic fractions (hydrophilic acid and non acid fractions (HPIA and HPINA)) using a method described elsewhere and previously used on samples from the same water source (Goslan et al. 2002; Sharp et al. 2004). THM formation potential (THM-FP) was carried out using an adapted method from Standard Methods for the Examination of Water and Wastewater (APHA et al. 1992). The method involved buffering samples at pH 7, chlorinating with excess chlorine for 7 days. Samples were quenched with NaSO$_4$. Total THMs were measured using an Autosystem XL Gas Chromatogram coupled with a Turbomass Gold Mass Spectrophotometer ((Perkin Elmer, USA).

High performance size exclusion chromatography (HPSEC) analysis was carried out using a high performance liquid chromatogram (HPLC) (Shimadazu VP Series, Shimadzu, UK) with UV detection set to 254 nm. The mobile phase was 0.01 M sodium acetate at a flow rate of 1 mL/min. The column was a BIOSEP-SEC-S3000 7.8 mm (ID) × 30 cm and the guard column was fitted with a GFC-3000 disc 4.0 mm (ID) × 3.0 mm (Phenomenex UK). For each sample a chromatogram of UV absorbance (measured in relative absorbance units (AU)) against time (minutes) was produced. Large molecules were eluted from the column first and smaller molecules later. The injection volume was 500 µL (0.5 mL).

Floc size experiments were conducted using an identical setup to Jarvis et al. (2005). Water samples were placed on 1L jar tester to carry out the treatments studied under the following conditions: a rapid mix at 200 rpm for 1.5 minutes, followed by a slow stir phase at 50 rpm for 15 minutes. Suspensions were monitored by drawing it through the optical unit of a laser diffraction instrument (Malvern Mastersizer) and back into the jar by a peristaltic pump using transparent 5 mm internal diameter peristaltic pump tubing. The holding ports for the inflow/outflow.
tubing were positioned opposite to one another at the same depth every time (in the upper part of the solution) and secured on to the sides of the jar. Flocs were pumped through the system at a flow rate of 25 mL/min since preliminary studies demonstrated that lower flow rates allowed flocs to settle down inside the tube while higher flow rates brought about floc breakage. Chemicals were added during the rapid mix, in which the pH was also adjusted to the optimum for each treatment. Then flocs were sized on-line, taking measurements every 1 minute during the jar tests and logged onto a PC.

RESULTS & DISCUSSION

NOM removal

A range of treatment processes were benchmarked against Fe³⁺ coagulation for NOM removal. As a bulk parameter for removal, DOC is a good measure to show how much NOM can be removed from a source water. The DOC removal in relation to Fe³⁺ coagulation was shown to be dependent on treatment process (the DOC removal varied due to differences in the character of the NOM in the source water from different sampling times) (Figure 1). Of the processes investigated, UV/H₂O₂ was unable to give a better DOC removal than Fe³⁺ coagulation (3% lower removal than Fe³⁺ coagulation). Subsequent coagulation of the UV/H₂O₂ treated water with an Fe dose of 8 mg/L did not significantly improve DOC removal (76% to 80% DOC removal) and was equivalent to that possible with coagulation alone at 8 mg/L Fe.

The other three processes investigated (FR, Zr⁴⁺ and MIEX + coagulation) had between 7–9% additional DOC removal with respect to Fe³⁺ coagulation, indicating significant potential for improved NOM removal with these alternative and additional processes. The Zr⁴⁺ and MIEX + coagulation treatment processes that gave significantly better DOC removal than Fe³⁺ coagulation also gave significantly improved levels of trihalomethanes (THMs) (Figure 2). Although not measured in this work, FR has also been shown to give low levels of THMs in relation to Fe³⁺ coagulation (Murray & Parsons 2004). The FR process is a combined oxidative/coagulation treatment and other research has shown that the oxidative power of the process can degrade brominated THMs from water (Tang & Tassos 1997). Both Zr⁴⁺ and MIEX + coagulation processes significantly lowered the THM-FP. For MIEX pre-treatment + coagulation, numerous other studies have also shown THM and haloacetic acid (HAA) reductions of 30–70% when compared to Fe³⁺ and

Figure 1 | DOC removal for different treatment processes and the level of removal above that of optimised Fe³⁺ coagulation (solid bars—left axis; spots—right axis).
Al$^{3+}$ coagulation (Singer & Bilyk 2002; Fearing et al. 2004; Son et al. 2005; Mergen et al. 2008). The reduced THM-FP for Zr$^{4+}$ has not previously been shown and further research into DBP formation is required, particularly at continuous scale for Zr$^{4+}$ and FR which have not been researched or developed to the extent of the magnetic resin process.

Previous work on NOM characterisation has shown that the limit of what coagulation can achieve is closely correlated to the HPINA content of the source water because this organic material is difficult to coagulate (Sharp et al. 2004). Therefore a process that can achieve a lower residual than the HPINA content of the source water is advantageous and should be the goal of an advanced process for NOM removal. Residual DOC after coagulation with Fe$^{3+}$ was always higher than the HPINA concentration in the source water (Figure 3). The AOPs studied in this work have shown that they are unable to offer much removal of this recalcitrant organic fraction for moorland water. Zr$^{4+}$ was able to reduce the treated water DOC below the HPINA concentration in the source water. The MIEX + coagulation system was able to give lower DOC residuals than coagulation alone, but did not give a lower DOC residual than the HPINA in the raw water. However, it should be noted that the HPINA in this source water was initially very low.

The HPSEC chromatograms for MIEX + coagulation and Zr$^{4+}$ show lower absorbance profiles and different shaped chromatograms with respect to Fe$^{3+}$ and Al$^{3+}$ coagulation. This indicates a different and better range of NOM removal for different MW organic molecules that absorb UV$_{254}$ for the advanced processes (Figure 4). This links with the improved overall NOM removal seen from Figures 1–3.

**Floc formation**

Another important operational consideration for NOM removal is the downstream impact of the process. Given
that the three processes that have shown improved DOC removal compared to Fe$^{3+}$ coagulation involve the formation of a floc aggregate, an understanding of these flocs is important. Floc size data showed that FR flocs were nearly 30% smaller than Fe$^{3+}$ flocs whilst Zr$^{4+}$ and MIEX$^+$ coagulation flocs were 27 and 37% larger than Fe$^{3+}$ flocs respectively (Figure 5). Previous work suggests that these larger flocs are better removed in solid-liquid separation processes as the size is linked to an increase in floc strength (Jarvis et al. 2008). This was further evidence that the advanced processes offer additional treatment benefits over Fe$^{3+}$ coagulation.

**CONCLUSIONS & IMPLICATIONS FOR WATER TREATMENT**

A range of different treatment processes have been assessed for improved levels of NOM removal when compared to conventional coagulation using Fe$^{3+}$. Zr$^{4+}$ coagulation, FR, MIEX + coagulation demonstrated higher levels of DOC removal when compared to Fe$^{3+}$ coagulation alone. UV/H$_2$O$_2$ was not considered as being powerful enough for sufficient oxidation of NOM. For each of the processes a number of important potential operational benefits and drawbacks have been summarised.
ACKNOWLEDGEMENTS

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REFERENCES

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<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
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<td>UV/H₂O₂</td>
<td>Potential low chemical treatment</td>
<td>Poorer performance than Fe³⁺ coagulation</td>
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<td>Proven technology for organic micropollutants</td>
<td>Requires coagulation to remove downstream turbidity (data suggests a high coagulant dose needed)</td>
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<td>Hydrogen peroxide residual must be removed from finished water</td>
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<td>Cost of UV irradiation</td>
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<td>Fenton’s reagent</td>
<td>High levels of NOM removal</td>
<td>Hydrogen peroxide residual must be removed from finished water</td>
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<td>Poorer floc formation</td>
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<td></td>
<td>Potential for combined oxidation of any formed DBPs</td>
<td>Unproven process stability</td>
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<td>Switch on/off as required</td>
<td>Poor removal of recalcitrant NOM</td>
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<tr>
<td>Zr⁴⁺ coagulation</td>
<td>High levels of NOM removal</td>
<td>Unproven process stability in continuous operation</td>
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<td>Large strong flocs formed – robust downstream processes</td>
<td>Currently un-regulated compound as a coagulant</td>
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<td>Could be installed in existing WTWs infrastructure</td>
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<td>Excellent removal of recalcitrant NOM</td>
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<td>Switch on/off as required</td>
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<td>MIEX + Coagulation</td>
<td>High levels of NOM adsorption possible</td>
<td>Additional treatment stage required (OPEX &amp; CAPEX costs)</td>
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<td>Proven technology</td>
<td>Increased turbidity load downstream of ion-exchange</td>
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<td>Very low levels of DBP formation demonstrated</td>
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<td>Large, strong flocs formed</td>
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