

COMPARISON OF COAGULATION PERFORMANCE AND FLOC
PROPERTIES USING A NOVEL ZIRCONIUM COAGULANT AGAINST
TRADITIONAL FERRIC AND ALUM COAGULANTS

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Abstract

Coagulation in drinking water treatment has relied upon iron (Fe) and aluminium (Al) salts throughout the last century to provide the bulk removal of contaminants from source waters containing natural organic matter (NOM). However, there is now a need for improved treatment of these waters as their quality deteriorates and water quality standards become more difficult to achieve. Alternative coagulant chemicals offer a simple and inexpensive way of doing this. In this work a novel zirconium (Zr) coagulant was compared against traditional Fe and Al coagulants. The Zr coagulant was able to provide between 46 and 150% lower dissolved organic carbon (DOC) residual in comparison to the best traditional coagulant (Fe). In addition floc properties were significantly improved with larger and stronger flocs forming when the Zr coagulant was used with the median floc sizes being 930 μm for Zr; 710 μm for Fe and 450 μm for Al. In pilot scale experiments, a similar improved NOM and particle removal was observed. The results show that when optimised for combined DOC removal and low residual turbidity, the Zr coagulant out-performed the other coagulants tested at both bench and pilot scale.

KEYWORDS: Natural organic matter; NOM; coagulation; water treatment; flocs; floc strength; coagulants; zirconium

38. 1. INTRODUCTION

39 Coagulation by hydrolysing metal salts, typically of iron (Fe) or aluminium (Al), is the main
40 reaction stage that drives the removal of natural organic matter (NOM) and other
41 contaminants in potable water treatment. Recent work reconsidering the description of
42 coagulation pathways has suggested that NOM is removed through a combination of direct
43 precipitation of metal-NOM solids and adsorption onto metal hydroxide precipitates (Shin et
44 al., 2008). In both cases the demand for coagulant is stoichiometric and that whenever NOM
45 is present in a source water these two mechanisms dominate. The role of the coagulant
46 depends on many factors including: speciation of the hydrolysis products, quantity and
47 reactivity of complexing ligands, and the rate of mass transfer between these components
48 (Shin et al., 2008). Consequently, the choice of coagulant has a major influence on
49 performance with reported comparisons indicating that, in the case of NOM removal, Fe
50 based coagulants remove approximately 0.5 mg.L^{-1} more dissolved organic carbon (DOC)
51 than Al versions under optimised conditions (Eikebrokk, 1999; Matilainen et al., 2005; Jarvis
52 et al., 2008). The reason for this difference is linked to the distribution of charged hydrolysis
53 species (Johnson and Amirtharajah, 1983; Hundt and O'Melia, 1988; Edzwald and Tobiasson,
54 1999) but difficulties persist in identifying all of these forms and the complexity of the
55 reactions of the coagulant with NOM have meant work is usually based on indirect
56 measurements and theoretical calculation of speciation. Nonetheless, the general view is that
57 the maximum charge of the products formed under more acidic conditions is greater for Fe
58 coagulants than for Al (Vilge-Ritter et al., 1999).

59
60 The theoretical relationship between charge and coagulation has been known for many years
61 and was first demonstrated experimentally for potable water treatment in the 1950s (Black
62 and Chen, 1965; Gupta et al., 1975; Packham and Sheiham, 1977). However, direct

correlation between the two has only been made in more recent times due to improvements in instrumentation enabling rapid and regular measurements (Sharp et al., 2006). The correlations demonstrate a range of zeta potential values where residual NOM and turbidity are minimised and importantly identifies a threshold zeta potential value below which the coagulant must operate. Adoption of zeta potential measurement in field situations is becoming more common around the world for Fe and Al coagulants. For instance, in the UK such measurements are used to diagnose coagulation problems and consider changes in operating practice (Sharp et al., 2006) and has been widespread in the US for many years through the application of streaming current devices (Dentel and Thomas, 1989).

However, there is now a strong drive for water treatment processes to be able to provide more DOC removal than that which can be provided by both Fe or Al coagulants. This has primarily been driven by an increase in NOM levels in source waters across the world. This has continued to such an extent that at certain treatment works during periods of elevated NOM flux, coagulant demand is becoming excessive and/or removal is insufficient to maintain a sufficient reduction in disinfection by product (DBP) formation (Mergen et al., 2008). There is also a significant problem associated with a reduction in floc strength when high NOM loads enter the WTWs, resulting in poor removal in solid-liquid separation processes (Jarvis et al., 2008). In such cases, current practice is to pre-treat the source water to reduce the NOM load prior to coagulation with processes such as magnetic ion-exchange (MIEX) (Singer and Bilyk, 2002). The MIEX process in combination with coagulation shows improved removal and substantial reduction in THM formation as well as a significant improvement in particle properties although concerns remain related to treatment and installation costs and the suitability of the process for a range of water types.

A possible solution to both floc strength reduction and inadequate NOM removal has been postulated based around the use of alternative metal ions such as zirconium (Zr) salts which have been investigated for treatment of arsenic removal (Lakshmanan et al., 2008), NOM (Jarvis et al., 2008) and paper and pulp effluent (Ayukawa, 1978). One reason for consideration of Zr as a coagulant lies with its increased positive charge compared with Al and Fe with species bearing a charge of up to 8^+ being reported. However, previous attempts to find highly charged hydrolysis products have not been successful (Veyland et al., 1998). Regardless, a comparative trial of alternatives to traditional coagulants involving Zr, UV/H₂O₂, Fenton's reagent and MIEX+Fe coagulation showed that Zr coagulation gave the largest improvement in both DOC removal and residual THM formation potential (THMFP) reduction (Jarvis et al., 2008). The objectives of the current paper were therefore to provide a more detailed investigation into the potential for Zr as a coagulant in both batch laboratory experiments and continuous pilot scale treatment. This has been achieved by assessing its use against traditional alum and ferric sulphate coagulants with respect to NOM removal and particle properties. These chemicals represent, in the case of alum, the most widely used coagulant across the world (Hammer and Hammer, 2007) and, in the case of ferric sulphate, the most effective coagulant for enhanced NOM removal (Eikebrokk, 1999; Matilainen et al., 2005).

2. MATERIALS AND METHODS

The NOM rich water source used in the jar tests was from a reservoir in the north of the U.K. The coagulants under investigation were Ferripol XL, a ferric sulphate based coagulant (Huntsman Tioxide Europe Ltd, Billingham), aluminium sulphate (Fisher Scientific UK, Loughborough, UK) and a zirconium oxychloride based coagulant (Zr-Coag[®], Water Innovate Ltd, Cranfield, UK). The Zr coagulant contained 20% weight equivalent ZrO₂

consisting of cationic hydroxylated polynuclear zirconium species. The specific gravity of the coagulant was 1.34 and had a pH of <1. After validation of the coagulant performance in laboratory jar tests, the scale of treatment was increased by performing tests on a pilot scale water treatment facility. Due to the duration of the testing, water was taken from the same water source at different points in time so it was necessary to optimise coagulation after each water collection.

2.1 Jar Tests

Coagulation trials were undertaken on a PB-900 jar tester (Phipps and Bird, VA, USA) using cylindrical jars containing 1 L of raw water. Mixing involved a 60 s rapid mix stage at 200 rpm followed by a 15 minute flocculation stage at 30 rpm and a 15 minute settlement period. Settled water samples were analysed for turbidity (Hach 2100N turbidimeter, Manchester, UK) and zeta potential (Zetasizer 2000, Malvern Instruments, Malvern, UK). Measurement of zeta potential assumes sphericity of particles, so it was therefore probable that a small but consistent and repeatable error was evident on the zeta potentials reported for the residual floc particles for the different systems. Further analysis was performed after filtration through a 0.45 µm glass microfibre filter (Fisher Scientific, Loughborough, UK). DOC was measured using a TOC analyser (Shimadzu 5000A, Milton Keynes, UK). The UV₂₅₄ absorbance was measured using a Jenway 6505 UV/Vis Spectrophotometer (Camlab Ltd, UK) with a 40 mm quartz cell supplied by Starna Brand, UK.

Floc size and breakage experiments were performed using an identical experimental setup to Jarvis et al. (2008). The jar tester was connected to the optical unit of a laser diffraction particle sizer (Mastersizer 2000, Malvern Instruments, Malvern, UK) by drawing water through the unit at a flow rate of 1.5 L.h⁻¹ using a peristaltic pump. In each experiment, which

was conducted in duplicate, the rpm of the stirrer in the jar tester was increased following the initial 15 minute flocculation period. Increased stirrer speeds of: 30 (7.4 s^{-1}), 40 (11.4 s^{-1}), 50 (15.9 s^{-1}), 75 (29.3 s^{-1}), 100 (45.2 s^{-1}) and 200 (127.5 s^{-1}) rpm were applied for a further 15 minutes (average velocity gradients, calculated from the Camp equation, in brackets). Floc strength was interpreted from the absolute floc size for a given shear rate and the gradient of the line for the power law relationship between floc size and applied shear rate.

2.2 Pilot plant studies

Comparison of the best performing conventional coagulant with the Zr coagulant was then carried out using a continuous pilot-scale treatment system. Source water was taken from the same source as for the jar tests and transported to Cranfield University's pilot plant hall using a 30 m^3 tanker and was fed directly from the tanker to the pilot plant during experimental runs.

The pilot plant used in the experiments consisted of a rapid mix tank, two flocculator tanks in series, dissolved air flotation (DAF) and sand filtration (Figure 1). This configuration was used as it simulates a typical flowsheet used at full-scale for treating a high organic content water of this type. Raw water was pumped through the plant at 200 L.h^{-1} . The flow through the plant was controlled using a flow meter coupled to a valve positioned before the rapid mixing tank. The flow was calibrated prior to pilot scale testing. The feed water was mixed in the rapid mix stage at 200 rpm at a contact time of 2 minutes. Fresh solutions of coagulants were prepared before the start of each run. NaOH solutions of 0.5 and 0.25 M concentrations were prepared for pH adjustment of coagulation. The coagulant and pH adjusting chemicals were pumped into the coagulation tank using peristaltic pumps. The pH was monitored with a Jenway 2300 pH meter (Fisher scientific, UK) with an epoxy pH electrode (Fisher scientific,

UK). The coagulation pH was recorded every 5 min and adjustment was made if necessary to keep the pH at the desired level. The coagulated water was then mixed at 5 rpm in the flocculator tanks with a combined contact time of 24 minutes. The DAF unit consisted of a saturator system, an air saturator pump and a cylindrical flotation column leading to an open water tank. The surface overflow of the DAF unit was 3 m.h⁻¹ and the recycle ratio was 18 %. Treated water then went on to a 0.3 m diameter filter column operating at 8 m.h⁻¹, containing 16/30 grade sand (1-0.5 mm diameter) at a depth of 1 m. For each pilot plant experiment, the plant was run in continuous operation for 6 hours. Samples were taken hourly after the DAF unit and after sand filtration. Samples were measured for UV₂₅₄, (DOC), turbidity and zeta potential as before. THMFP was measured using a modified form of USEPA Method 551.1 (Goslan et al., 2002). Filtered samples were chlorinated with excess chlorine and stored at 20 °C for 7 days in the dark. Samples were chlorinated at a dose that was five times greater than the DOC concentration. Samples were buffered at pH 7 to nullify any pH effects. After 7 days exposure to chlorine, samples were quenched using sodium sulphite (100 mg.L⁻¹) and transferred into vials containing a buffer. The buffer was 1% sodium phosphate dibasic (Na₂HPO₄) and 99% potassium phosphate monobasic (KH₂PO₄) and was added to prevent the transformation of other DBPs to THMs. THM4 (trichloromethane, dichlorobromomethane, dibromochloromethane and tribromomethane) were analysed. The total THM concentration was measured using gas chromatography (GC) with micro electron capture detection (μECD) (Agilent 6890).

[Figure 1 here]

Figure 1: Schematic of the pilot plant.

3. RESULTS

3.1 Water characterisation and coagulation tests

The raw water used in the jar tests was typical of a UK moorland water source in terms of the balance of DOC (12.9 mg.L^{-1}) and UV_{254} absorbance (57 m^{-1}) leading to a high specific UV absorbance (SUVA) of $4.8 \text{ L.mg}^{-1}.\text{m}^{-1}$. The water was of low turbidity (3.5 NTU) and low alkalinity of $<10 \text{ mg.L}^{-1}$ as CaCO_3 . Consequently, the source water was regarded as being typical of the type being treated at a water treatment works (WTWs) where they are considering upgrading its treatment facilities with MIEX technology to reduce load demand (Singer and Bilyk, 2002; Jarvis et al., 2008).

The comparison of the three coagulants was determined for three doses that were representative of the range of operational coagulant doses applied at the WTWs for removal of NOM ($5, 10, 15 \text{ mg.L}^{-1}$ as M^+) representing dose ratios of 2.58, 1.29 and $0.86 \text{ mg}_{\text{DOC}}.\text{mg}_{\text{M}^+}^{-1}$ respectively (Figure 2). In all cases, the Zr systems generated more positive zeta potentials and a higher isoelectric point (IEP) than Fe or Al, demonstrating that the Zr coagulant provided more charge neutralising power than the other coagulants on a mass basis. The zeta potential of the NOM-coagulant complexes switched from positive to negative charge as the pH was increased. The IEP of the Zr-NOM system increased from pH 5.3 to 6.3 as the dose ratio decreased from 2.58 to $0.86 \text{ mg}_{\text{DOC}}.\text{mg}_{\text{Zr}}^{-1}$.

Minimum DOC residuals at a dose of 5 mg.L^{-1} were 1.3 mg.L^{-1} for Zr at a pH of 4.5; 1.9 mg.L^{-1} for Fe at a pH of 4.5-5 and 3 mg.L^{-1} for Al at a pH of 5. Increasing the dose decreased the DOC residual for each coagulant such that at the highest coagulant dose of 15 mg.L^{-1} , the DOC residual was 0.6, 1.5 and 2.4 mg.L^{-1} for Zr, Fe and Al respectively. The difference in removal between Fe and Al is consistent with other reported comparative trials and can be

further extended to show that Zr provides additional removal of NOM above that of Fe. For Zr it was apparent that the lowest residual turbidity was not seen over the same pH conditions as for the lowest residual DOC (Figure 2). At 5 mg.L⁻¹, Zr gave the lowest turbidity between pH 5-6 (0.25 NTU). Below pH 5, residual turbidity rapidly deteriorated. At 10 mg.L⁻¹ the lowest turbidity for Zr shifted to higher pH between 6-7 (0.31-0.38 NTU). At pH <6.0, residual turbidity deteriorated. At 15 mg.L⁻¹, the lowest turbidity residual was seen between pH 6-8 (0.63-1.28 NTU). For the three coagulants investigated based on combined DOC removal and turbidity removal, it can be seen that Zr operates over a wider range of zeta potentials for optimum removal, but has more specific pH requirements than the other coagulants for a given dose to reach the required zeta potential range (Table 1). The results agree with previous work treating similar waters showing that as long as coagulation is carried out within the correct zeta potential range, optimum particle and NOM removal will be achieved (Sharp et al., 2006).

[Figure 2 here]

Figure 2: Performance comparison of the Zr, Fe and Al coagulants at 5-15 mg.L⁻¹.

Table 1. Optimum conditions for coagulation of NOM with the three coagulants.

[Table 1 here]

3.2 Floc properties

Floc characteristics were measured for coagulation conditions that represented optimised treatment within the previously determined operational zeta potential windows (Table 1). These were doses and pH levels of 5 mg.L⁻¹ at pH 5.5 (-1 mV) for Zr; 8 mg.L⁻¹ at a pH of 4.5 (-3 mV) for Fe; 10 mg.L⁻¹ at a pH of 6 (-4 mV) for Al. Comparison of the floc size was made using the median equivalent volumetric diameter (d₅₀). Analysis of the floc growth profiles

showed significant differences for the average steady state d_{50} floc sizes for the three different coagulants across the 7 duplicated runs (Figure 3). In the case of Zr flocs, the d_{50} floc size ranged between 870-990 μm with an average of 930 μm . In contrast, Fe flocs were considerably smaller with a range of 670-790 μm and an average of 710 μm and Al flocs were smaller still with a range between 430-490 μm and an average of 450 μm . In comparison, application of a pre-treatment with MIEX resin followed by Fe coagulation (MIEX+Fe) on water from the same source water during a different trial yielded large flocs with a median size of 1020 μm (Jarvis et al., 2008) indicating that Zr flocs approach those obtained when using pre-treatment. The three systems also showed differences in growth profiles with the growth rates being fastest for the Al flocs at around 520 $\mu\text{m}.\text{min}^{-1}$ compared to 220 $\mu\text{m}.\text{min}^{-1}$ for Zr and 190 $\mu\text{m}.\text{min}^{-1}$ for the Fe flocs. After a spike in floc size, the fast growing Al flocs reached a steady state size after 3 minutes, whilst it took 4 minutes for the Zr flocs and 5 minutes for the Fe flocs.

Once the flocs had reached a steady state size during the slow stir phase, they were exposed to increased shear rates. The breakage pattern for the Fe and Al flocs followed a classical response composed of two components: at elevated shear levels above 75 rpm ($G_{\text{av}} = 29.3 \text{ s}^{-1}$) a rapid decrease in floc size was observed within the first minute after the increased shear rate had been introduced followed by a more gradual change in floc size (Figure 3d). This was ascribed to a fragmentation breakage mechanism causing a large change in floc size distributions followed by an erosion breakage mechanism as small particles erode from the parent floc. Below 75 rpm only a gradual decline in floc size occurred as the shear conditions erode the flocs rather than cause large-scale fragmentation. To illustrate, in the case of Fe, upon exposure to an elevated shear rate of 50 rpm (15.9 s^{-1}) the median floc size initially decreased from 680 to 620 μm ; whereas at 75 rpm (29.3 s^{-1}) the median floc decreased from

730 to 550 μm and at 200 rpm (127.5 s^{-1}) from 755 to 397 μm . Thereafter the floc size decreased in an approximate power law relationship, reaching final median sizes of 535, 389 and 245 μm respectively. In contrast, the Zr floc system did not exhibit such an initial rapid decrease in floc size upon exposure to any level of elevated shear. Instead, the median floc size decayed with a power law coefficient of -0.51, -0.90, -2.49 at elevated shear rates of 50, 75 and 200 rpm respectively. No difference could be observed between the breakage profiles at 150 rpm (86.2 s^{-1}) and 200 rpm (127.5 s^{-1}) indicating that the flocs had reached a stable response against exposure to elevated shear rate beyond 150 rpm (86.2 s^{-1}).

Overall comparison of the strength of the flocs through a plot of final steady state size against shear rate (Figure 3d) indicated that whilst the Zr flocs were initially larger, all three systems approached a similar median floc size of 245-277 μm at very high levels of elevated shear rate (200 rpm, 127.5 s^{-1}). The strength of the flocs can be described in two ways from the figure. The initially higher size of flocs formed during the initial slow stir phases indicates a clear sequences of floc strength as $\text{Zr} > \text{Fe} > \text{Al}$. This is because larger flocs grown at any given shear rate indicate a greater resistance to breakage (Yukselen and Gregory, 2004). The gradient of the log-log plot, defined as the stable floc size exponent (γ), can be used to define the relative strength of the floc to exposure across the whole elevated shear spectrum. Observed gradients of -0.69, -0.53 and -0.29 for the Zr, Fe and Al systems indicated a clear difference, with Zr and Fe more affected by exposure to elevated shear rate. The MIEX+Fe line shown in Figure 3d had a gradient of -0.54, indicating that these flocs were more resistant to breakage than for the Zr coagulant.

3.3 Pilot plant studies

The improved performance of Zr in laboratory tests was then assessed in a continuous pilot plant environment. Tests were carried out using the best performing conventional coagulant (ferric sulphate) in comparison with the Zr coagulant. This also enabled a direct link to be made between floc properties as measured from the mixing experienced in a jar tester to the removal of the flocs in flotation and filtration clarification processes.

As the water used in these trials was collected at a different point in time to the bench scale jar testing experiments, it was necessary to carry out separate preliminary jar tests to establish optimum dosing conditions for the new water. The water DOC and UV_{254} were 8.7 mg.L^{-1} and 45.1 m^{-1} respectively. Coagulant doses of 9 mg.L^{-1} at pH 4.5 were established for optimum DOC removal for both Fe and Zr coagulants based on these tests. Coagulation zeta potentials were well within the optimum operational ranges for charge minimisation of NOM for both coagulants (-7 mV for Fe and $+2.5 \text{ mV}$ for Zr). As seen in the jar tests, comparison of direct Fe and Zr dosing showed there to be a significant difference in the removal of NOM and the operation of the plant which was in close agreement with the bench scale testing (Figures 4 and 5). Residual DOC (Figure 4) and turbidity (Figure 5) were found to be significantly lower for Zr in comparison to the Fe coagulant (Mann-Whitney U-Test, $P < 0.05$). After flotation, DOC removal was 80.5 % after treatment with Fe (residual DOC of $1.7 \pm 0.3 \text{ mg.L}^{-1}$) and 86.2% using Zr (residual DOC of $1.2 \pm 0.1 \text{ mg.L}^{-1}$). The improved DOC removal when using Zr also resulted in a lower THM-FP for the final treated water. The THM-FP of water sampled after the filter was $163.1 \pm 36.7 \text{ } \mu\text{g.L}^{-1}$ after treatment with Fe and $100.7 \pm 15.0 \text{ } \mu\text{g.L}^{-1}$ after treatment with Zr. The amount of THMs formed per mg DOC was $75.6 \pm 5.5 \text{ } \mu\text{g.mg}^{-1}$ and $68.2 \pm 8.2 \text{ } \mu\text{g.mg}^{-1}$ for Fe and Zr respectively, indicating no preferential removal of DBP forming organic compounds by either coagulant.

The resultant removal of floc in the clarification stages matched the observations seen in the laboratory experiments, with the larger and more robust Zr flocs being better removed in clarification stages. The residual turbidity values observed were somewhat higher than those typically seen on a full-scale water treatment facility. This was thought to be as a result of scaling difficulties resulting in less effective DAF performance than when compared to a full scale plant. The optimum reaction zone for bubble attachment to particles was difficult to achieve using a single nozzle in the pilot plant when compared with how multiple numbers of nozzles operate in a full scale system. This resulted in high particle loads onto the filters. Nevertheless, as the conditions used were constant, the results obtained were very useful for comparing the performance of the Zr and Fe coagulants. Following flotation, residual turbidity was 6.4 ± 4.8 NTU after treatment with Fe while Zr treatment resulted in a lower turbidity of 2.3 ± 0.3 NTU. After filtration, the results matched the observations seen following DAF, with the Zr coagulant resulting in significantly improved residual turbidity: 1.2 ± 0.5 NTU for Fe and 0.4 ± 0.1 NTU for Zr (Mann-Whitney U-Test, $P < 0.05$).

[Figure 3 here]

Figure 3: Comparison of floc strength of Zr, Ferric and Alum flocs.

[Figure 4 here]

Figure 4: Residual DOC measured after DAF and after the filter during pilot plant treatment with Fe and Zr coagulants under optimum conditions (the bars represent the maximum and the minimum values, the box the 25th to 75th percentile values and the data point the mean).

[Figure 5 here]

Figure 5: Turbidity measured after DAF and after the filter during pilot plant treatment with Fe and Zr coagulants under optimum conditions (the bars represent the maximum and the minimum values, the box the 25th to 75th percentile values and the data point the mean).

4. DISCUSSION

The results presented in this work show a definite improvement in performance when using a Zr based coagulant for the treatment of NOM compared to the more traditional Fe and Al salts at both laboratory and pilot scale. When optimised for combined DOC removal and low residual turbidity, Zr out-performed the other coagulants tested. Improvements were demonstrated in terms of the achievable residual, lower THMs and the floc properties formed. Analysis of the jar testing data indicated that the best conditions for coagulation of NOM using Zr was between pH 5-6 for doses of between 5-15 mg.L⁻¹. Below this pH, floc properties rapidly deteriorated which was coincidental with an increased residual turbidity and an increase in the positive charge of the system. These data indicate that particle re-destabilisation occurs as a result of the high positive charge added by the Zr coagulant compared with the Fe and Al coagulant. The consequence of which is the necessity for careful control of coagulation conditions when using Zr to ensure the successful operation of solid-liquid separation processes at full scale WTWs.

For Fe and Al coagulants, dose minimisation occurs under acidic conditions as more highly charged hydrolysis species exist enhancing the neutralising power of the coagulant. The improved NOM removal performance for Zr over conventional coagulants was comparable to that seen for treatment systems that utilise MIEX+Fe (Singer and Bilyck, 2002) whilst also producing similar quality flocs in terms of physical characteristics (Jarvis et al., 2008). Consequently, the practical significance of using Zr coagulation is as a direct replacement for

Fe or Al in instances where additional NOM removal is required and may negate expensive installation of new treatment technology such as AOPs or ion-exchange systems. The explanation for the improved NOM removal by Zr is not easily elucidated from these results or from the literature. Some authors have proposed very highly charged cationic hydrolysis species being formed when Zr is dissolved in water, such as $[\text{Zr}_3(\text{OH})_3]^{8+}$ (Baes and Mesmer, 1976). Other workers have identified $[\text{Zr}(\text{OH})(\text{OH}_2)_7]^{3+}$ and a cyclical tetramer of $[\text{Zr}_4(\text{OH})_8(\text{OH}_2)_{16}]^{8+}$ (Rose et al, 2003). However, other authors have only found species with a +1 charge (Veyland et al, 2008). Whilst the distribution of hydrolysis products remains unclear, the higher zeta potential and IEP for the Zr coagulant demonstrates that it provides more charge than the alternative coagulants. The improvements may therefore relate to increased charge on precipitated Zr solids, which have been demonstrated to be important for alum coagulants (Letterman and Iyer, 1985; Dentel 1988).

The observation that the Zr coagulant had a much narrower pH range of operation when compared with the Fe and Al coagulants may be linked to the ion associated with the metal coagulant. Sulphate has been shown to be a strongly adsorbing anion which can destabilise systems in which coagulant has been overdosed, effectively extending the operational pH range over which the coagulant may operate (Letterman and Vanderbrook, 1983). Oxychloride is a less well adsorbed ion and therefore does not produce the same effect, further indicating that more precise control of the Zr coagulant's operational range is required.

The parameter of floc strength is difficult to both define and measure leading to a number of approaches. However, irrespective of approach, it is accepted that the strength of the aggregate relates to the combination of the number and strength of the bonds formed (Bache,

2004). In the analysis performed here, it was shown that Zr flocs formed under optimised conditions for combined NOM removal and residual turbidity were larger and better removed than for the conventional coagulants for laboratory and pilot scale systems. In pilot plant experiments, it was demonstrated that the flocs formed by the Zr coagulant were better removed in flotation and filtration processes meaning that solids loading onto filters was reduced with the potential for offering longer filter run times. The reasons for this improved removal in DAF and filtration are two-fold: 1) as a result of the increased strength of Zr flocs and 2) increased electrostatic attraction between bubbles and floc for Zr systems. Given that bubbles are negatively charged in DAF applications (Dockko and Han, 2004), the more positively charged Zr flocs will have a strong affinity for the oppositely charged bubbles, improving the overall floc removal.

Whilst the Zr-NOM floc size was most affected by changing rpm, the median floc size was able to remain larger than that of the other coagulants throughout, indicating that the Zr flocs had greater inherent strength than for the flocs formed from the other coagulants. The increased breakage of the larger flocs was expected as they are exposed to micro-scale energy dissipating eddies which smaller flocs can get entrained into rather than being broken by (Boller and Blaser, 2004). Overall the strength of the connection points in a floc is based on a force balance including steric, van der Waals, polymer bridging and electrostatic forces (Gregory, 1989). Zeta potential provides a suitable means of considering the role of electrostatic effects and provides the most convenient way to control floc properties in practice (Sharp et al., 2006), such that when these forces are minimised floc strength is maximised. The current work continues this development with the identification of a zeta potential window of -10 to +10 mV for the Zr coagulant, compared with -8 to +5mV for Fe and -8 to 0 mV for Al for combined NOM removal and strong floc properties. A final

consideration for the application of a Zr based coagulant in drinking water treatment is its toxicity. Zirconium is generally thought to be nontoxic as an element or in its compounds and exists mostly in a physiologically inert dioxide form at pH levels associated with biological activity (Blumenthal, 1976; Kroschwitz and Howe-Grant, 1999). Zirconium has hence not shown any potential to be harmful to humans, but this still needs to be verified in future work.

5. CONCLUSIONS

- The results from this work have established that Zr offers improved NOM removal over that of conventional coagulants when using conditions optimised for DOC removal and strong floc properties.
- The improved removal of NOM using Zr also resulted in lower THM formation, however there was not a preferential removal of organic compounds with a high DBP-FP, as reflected by the similar normalised THM-FP results.
- The Zr coagulant requires careful control of the coagulation conditions before charge reversal and re-stabilisation is observed causing a poor quality floc to be formed.
- The Zr coagulant produced strong, robust flocs which showed better clarification than conventional coagulants in sedimentation systems (jar tests) and flotation processes (pilot scale) when coagulation conditions had been selected for optimised NOM and turbidity removal.

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