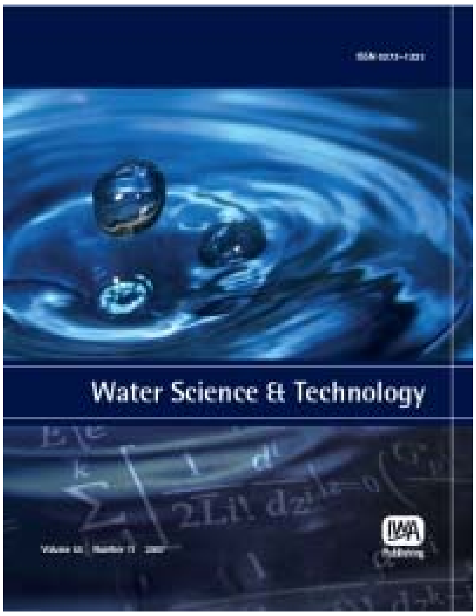
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Oxidation and coagulation of humic substances by potassium ferrate

N. J. D. Graham, T. T. Khoi and J.-Q. Jiang

ABSTRACT

Ferrate (FeO_4^{2-}) is believed to have a dual role in water treatment, both as oxidant and coagulant. Few studies have considered the coagulation effect in detail, mainly because of the difficulty of separating the oxidation and coagulation effects. This paper summarises some preliminary results from laboratory-based experiments that are investigating the coagulation reaction dynamically via a PDA instrument, between ferrate and humic acid (HA) at different doses and pH values, and comparing the observations with the use of ferric chloride. The PDA output gives a comparative measure of the rate of floc growth and the magnitude of floc formation. The results of the tests show some significant differences in the pattern of behaviour between ferrate and ferric chloride. At pH 5 the chemical dose range (as Fe) corresponding to HA coagulation was much broader for ferrate than ferric chloride, and the optimal Fe dose was greater. Ferrate oxidation appears to increase the hydrophilic and electronegative nature of the HA leading to an extended region of charge neutralisation. A consequence of the ferrate oxidation is that the extent of HA removal was slightly lower (~5%) than with ferric chloride. At pH 7, in the sweep flocculation domain, ferrate achieved much greater floc formation than ferric chloride, but a substantially lower degree of HA removal.

Key words | coagulation, ferrate, ferric chloride, humic acid, oxidation, water treatment

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INTRODUCTION

The application of oxidizing chemicals in the treatment of drinking water and wastewater continues to be an active topic of scientific research and an interest to water utility practitioners. This arises from the continuing need to meet higher water quality objectives and to employ treatment chemicals that are cost-effective and which lead to a low level of by-product formation. Of particular interest are those chemicals which are able to contribute to a variety of treatment objectives. In this respect, salts of the ferrate (Fe(VI)) ion, (FeO_4^{2-}), have the ability to act as both oxidant *and* primary coagulant. This arises from the chemical instability of ferrate in aqueous conditions across the normal range of raw water pH and its high reactivity, leading to the chemical reduction of the ferrate to ferric (Fe(III)) species. Whilst considerable study of the application of ferrate to water treatment has been undertaken previously, the subject remains relatively under-researched compared to other oxidants (e.g. permanganate, ozone). Extensive reviews of progress in the preparation and use of ferrate in the field of water treatment has been published previously (Jiang & Lloyd 2002; Sharma 2002; Sharma *et al.* 2008), and the authors have conducted various studies in recent years concerning ferrate reactions with specific contaminants (e.g. Graham *et al.* 2004; Li *et al.* 2008).

Previous studies of ferrate as a water treatment chemical have indicated a superior performance compared to a conventional Fe coagulant in terms of natural organic matter. Thus, White & Franklin (1998) reported that the

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removal of organic colour in model waters (tap water spiked with humic acid (HA)) was substantially greater with ferrate compared to ferric sulphate at low equivalent doses (<1 mg/L as Fe; designated subsequently as, mg Fe/L), and Jiang *et al.* (2001) also found that ferrate performed better than ferric sulphate in treating a natural upland coloured water (reduction in UV_{254} absorbance) at low doses (<2 mg Fe/L, pH 5). In a subsequent study involving model waters containing humic and fulvic acids, Jiang & Wang (2003) showed that in general ferrate could achieve a better performance in removing UV_{254} absorbance and dissolved organic carbon (DOC) in comparison with ferric sulphate, but with HA the performance (ie. removal of DOC) was inferior to ferric sulphate at higher doses (>9 mg Fe/L with 20 mg/L HA at pH 6). Whilst these and other previous studies have referred to the beneficial combination of oxidation and coagulation effects with ferrate, there appear to be very few studies that have considered these effects in detail; it is assumed that this is mainly because of the difficulty of separating the oxidation and coagulation effects when ferrate is applied. Previous studies of the pre-oxidation of natural organic matter by other oxidants (e.g. ozone) have indicated that while there is a definite change in the nature of the organic molecules as indicated by UV_{254} absorbance (decrease) and molecular weight distribution (shift to lower molecular weight), there may be a deleterious effect on their subsequent removal by coagulation. Thus, O'Melia *et al.* (1999) reported that with waters containing moderate to high levels of total organic carbon (TOC) (>4 mg/L), pre-ozonation increased the optimum coagulant dose or reduced the DOC removal at a given coagulant dose. Given that the treatment of humic-type waters are typically undertaken in acidic conditions (such waters naturally have a low pH), where ferrate has a similar oxidation potential to ozone and rate constants for the reaction of ferrate with phenolic-type compounds have been found to be high (e.g. $\sim 10^3\,M^{-1}\,s^{-1}$ for bisphenol A; Li *et al.* 2008), it is expected that similar effects will occur between ferrate and humic substances.

This paper summarizes some new results from a laboratory-based project that has investigated further the comparative oxidation and coagulation effects of ferrate in the treatment of humic substances in model and raw waters.

EXPERIMENTAL METHODS

Chemicals and analytical methods

All water was treated to ultra-pure quality (Purite–Neptune water purification system) before use in the experimental work. Solid potassium ferrate was produced in the laboratory by the wet oxidation method of Li *et al.* (2005) in which ferric nitrate was oxidized with potassium hypochlorite, and solid phase ferrate was precipitated in strong alkaline conditions. The purity of the ferrate, estimated to be 95%, and the concentration of ferrate in solution, were determined by visible light absorbance spectrophotometry; both by the conventional method (at 510 nm, pH 9) and by a novel, indirect spectrophotometric method involving 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate (ABTS) and an absorption wavelength of 415 nm (Lee *et al.* 2005). Ferric chloride (BDH, UK) was prepared as a 10 mM stock solution before the commencement of the tests. Bicarbonate buffer solution (0.2 M) was made from $NaHCO_3$ (Fisher, UK), and pH adjustment was by addition of either HCl or NaOH to test solutions. Humic acid was obtained as commercial reagent grade in solid form (Sigma-Aldrich Company Ltd, UK) and test (model) solutions were prepared in deionised water. The concentration of HA in solution after filtration (0.45 μm) was determined as dissolved organic carbon (DOC) by use of a TOC analyser (Shimadzu Ltd, Japan). Changes in the nature of the organic substances by coagulation (and oxidation) were indicated and determined by chemical and molecular weight fractionation, colloid charge and UV absorbance of solutions at a wavelength of 254 nm. For test solutions, the initial specific UV absorbance (SUVA $= UV_{254}$ absorbance per mg DOC/L) was approximately 10 L/mg m. Chemical fractionation in terms of hydrophilic- and hydrophobic-acids, neutrals and bases was carried out by the method of Croué *et al.* (2000), and mass recovery was 90–95%. The molecular weight distribution of the different chemical fractions was evaluated by size exclusion chromatography (SEC) (Waters 2695 HPLC with photodiode array detection, Waters Corp., UK) following the method described by Zhou *et al.* (2000). Colloid charge was determined using a 'ZetaPALS' zeta potential analyzer (Brookhaven Instruments Corp., New York, USA).

Coagulation tests

Our studies involved observation of the reactions between ferrate and model waters containing HA (10 and 20 mg/L) at different Fe doses (5–500 μM) and pH values (4–7), and comparing the observations with the use of ferric chloride, a typical Fe[III] coagulant, under identical conditions. Further tests were carried out using samples of real water obtained from an operational treatment works located in the north of England that employs an iron salt as coagulant. The raw water was supplied from an upland reservoir and the water quality at the time of sampling had a DOC of 11 mg C/L and a UV_{254} absorbance of 50.8 m^{-1}, giving a SUVA of 4.6 L/mg m. While the SUVA values for the real and model waters were quite different, they both correspond to a highly aromatic, humic type of organic content, which allowed the treatment behaviour of the two waters to be compared.

The coagulation behaviour was evaluated by use of a photometric dispersion analyzer (PDA 2000, Rank Brothers, UK) in a modified jar test procedure. The PDA is an instrument for observing rapidly changing particle suspensions via an optical technique that analyses the light transmitted through a flowing suspension; the instrument measures the average transmitted light intensity (dc value) and the root-mean-square (rms) value of the fluctuating component. The output, either the rms or rms/dc ratio, is qualitative in nature and serves as a relative measure of the change in particle size and density distributions (Gregory & Nelson 1986); it is referred to as the Flocculation Index (FI). Tests were carried out by connecting the PDA to a stirred 2 litre acrylic reactor ('Gator jar') where ferrate or ferric chloride was added to the HA solutions under defined mixing conditions (further details given in Fang 2007). The Gator jar was equipped with an overhead, variable speed stirrer and constructed to a standard design (AWWA 2000) with a paddle speed-velocity gradient calibration that could be applied directly. The optimum dosage of coagulant was determined at each pH value in the range of 4–7 and the experiments were performed under ambient conditions in an environmentally controlled laboratory (room temperature was 21 ± 1°C). The dynamic coagulation tests were carried out under standard conditions which involved: the rapid addition of the coagulant to the suspension followed by paddle stirring at 200 rpm (350 s^{-1}) for 30 s; the stirring speed was then reduced to 50 rpm (48 s^{-1}) and held at this value for the required time (10–60 min). Coagulation/flocculation of the humic solution was indicated by a sharp rise in the FI and the maximum steady value of FI was taken for comparison between tests in order to identify the optimum polymer dosage and conditions (Gregory & Nelson 1986); an example of the PDA output is shown in Figure 1. A subsequent 30 min period of quiescent settlement was allowed after the stirring phase, and samples of the solution supernatant were taken for the measurement of UV absorbance (at 254 nm) and DOC.

RESULTS AND DISCUSSION

The interaction between ferrate and HA was investigated extensively in comparison with that of ferric chloride as a reference Fe coagulant under the same conditions. To summarise salient aspects of the coagulation behaviour, the results at pH 5 and 7 are principally described here since they correspond to the two predominant mechanisms of coagulation, these being 'charge neutralisation' and 'sweep flocculation', respectively (Duan & Gregory 2003). While it is well known that the optimal pH for ferric salts is within the range of 3.7–4.2 (e.g. Jiang *et al.* 1996), it is preferable in practice to conduct coagulation at pH values ≥5 in order to reduce residual Fe solubility and the extent of subsequent

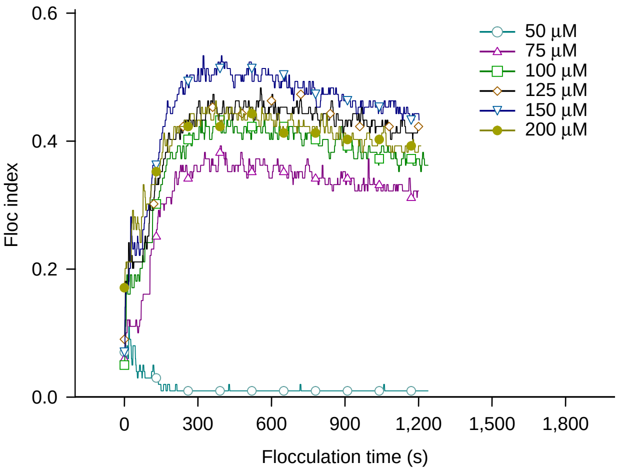

Figure 1 | Temporal variation in flocculation index (FI) for ferrate coagulation of HA (20 mg/L) at pH 5.

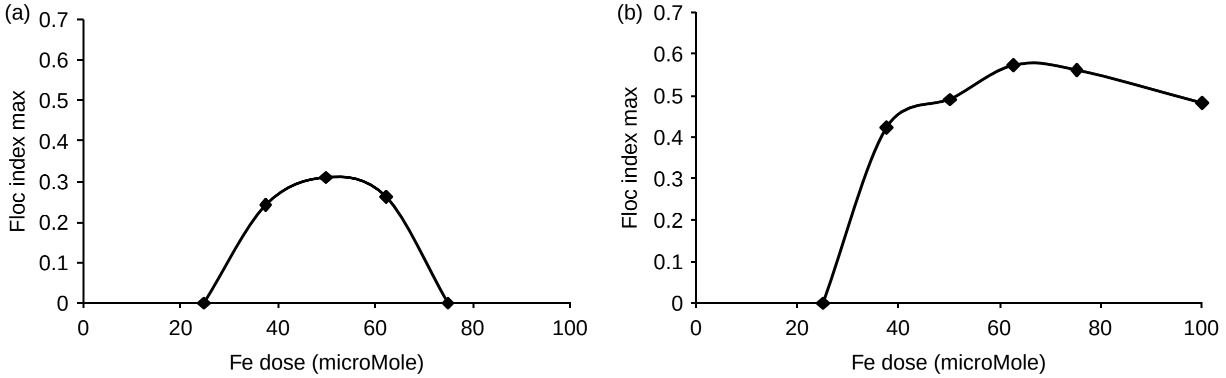

Figure 2 | Coagulation of HA (10 mg/L) in model water by (a) ferric chloride, and (b) ferrate, at pH 5.

pH correction. At pH 5 the interaction between hydrolysed Fe species and HA is nevertheless predominantly charge neutralisation which is characterised in terms of an optimal Fe dose, and a well defined Fe:HA mass stoichiometry. These phenomena can be seen in Figures 2(a) and 3(a) in terms of the FI response (maximum floc index), where a clear optimal Fe dose of 0.28 mg/mg HA was evident for ferric chloride with the model HA water. This corresponds to a dose stoichiometry at pH 5 of 1.4 mg Fe/mg C removed. For the upland water samples (Figure 4(a)), the optimal dose stoichiometry at pH 5 was slightly greater at approximately 1.7 mg Fe/mg C removed, which compares closely to corresponding values reported in other studies with Fe salts and river derived humic substances (e.g. 1.76 by Jiang *et al.* 1996; 1.8 by Eikebrokk 1999).

The comparative FI results for ferrate were substantially different to those for ferric chloride (see Figures 2 and 3). For both HA concentrations the optimal dose of ferrate, as equivalent Fe for maximum FI, was greater (20–50%) than with ferric chloride and the Fe dose range corresponding to significant HA coagulation was much broader, principally for Fe doses greater than the optimal dose (ie. for the charge restabilisation region). While the value of the FI is not an absolute quantity, it is a relative measure of the size and density of coagulant flocs and the results showed a much greater degree of coagulation/flocculation for ferrate at Fe doses greater than (up to double) the optimal Fe dose for ferric chloride.

In contrast to the observed behaviour in terms of maximum apparent floc growth, the resulting HA removal

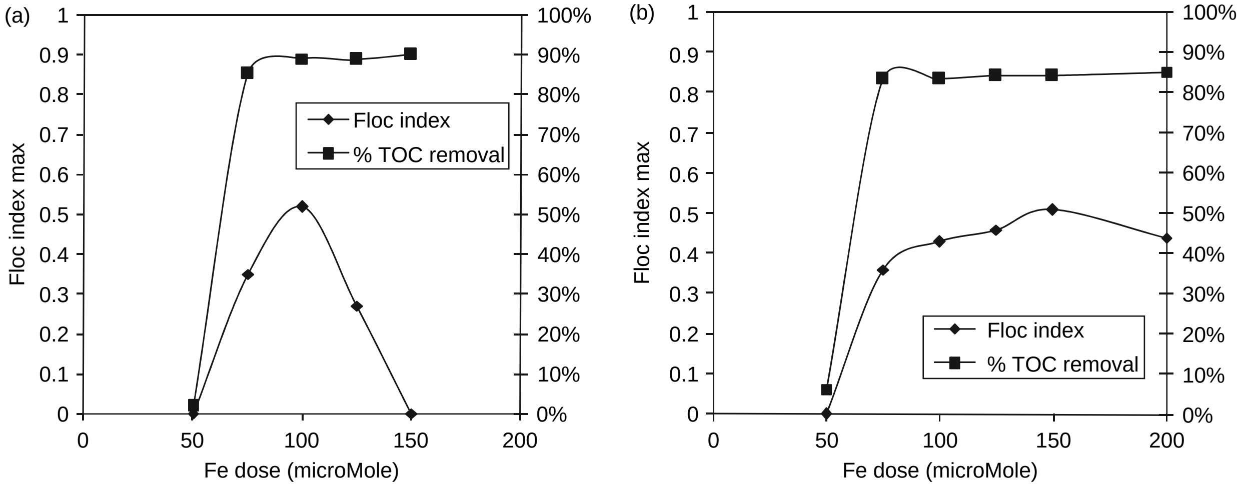

Figure 3 | Coagulation of HA (20 mg/L) in model water by (a) ferric chloride, and (b) ferrate, at pH 5.

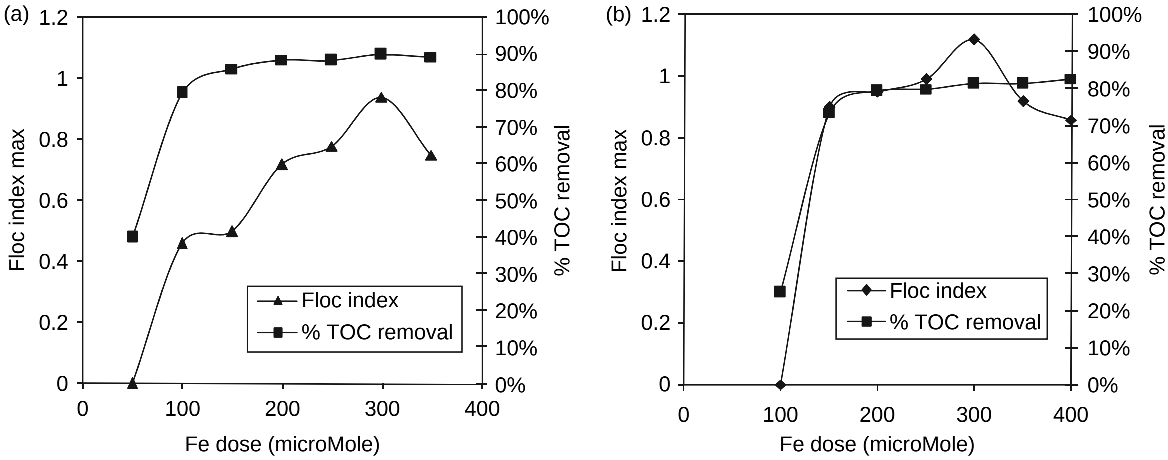

Figure 4 | Coagulation of upland coloured water (DOC 11 mg/L) by (a) ferric chloride, and (b) ferrate, at pH 5.

(as % TOC removal) with ferrate was found to be slightly inferior to that with ferric chloride (see Figure 3). While the absolute removal of organic carbon was high in both cases (viz. 90% for ferric chloride; 85% for ferrate) the ferrate performance was consistently less than ferric chloride over the complete range of Fe doses studied. This behaviour was also observed with the upland coloured water (Figure 4) where a similar degree of organic carbon was removed. Eikebrokk (1999) also reported a high removal (~80%) of TOC by ferric chloride sulphate at pH 5 for a low alkalinity, high humic raw water. The difference in the coagulation behaviour of ferric chloride and ferrate is believed to be the result of the oxidation effects of ferrate. In previous studies of the direct effects of ozone on humic substances (HS), Graham (1999) summarised the following changes that may be caused by ozone oxidation: a strong and rapid decrease in colour and UV absorbance due to a loss of aromaticity and depolymerisation; a small reduction in TOC (eg 10% at 1 mg O_3/mg C); a slight decrease in the high apparent molecular weight fractions, and a slight increase in the smaller fractions; a significant increase of the carboxylic functions; and the formation of ozonation byproducts. Ferrate treatment is believed to cause similar effects, given that its nominal oxidation strength (E^0 2.20 V; Jiang & Lloyd 2002), is equivalent to ozone (E^0 2.07 V). Thus, Table 1 shows the direct oxidation effect of ferrate on humic substances, expressed as the percentage reduction in DOC. These tests were carried out in phosphate (5 mM) and bicarbonate buffers whereby reduced Fe, principally as Fe(III), was prevented from forming insoluble coagulation products with HA through Fe-phosphate complexation. The results show that HA degradation by ferrate increased with ferrate dose and decreased with pH. The impact of ferrate on reactive substrates is complex in view of the aqueous instability of ferrate which decreases with pH, while the oxidation potential also decreases with pH. Overall, it can be seen that at pH 5, and at near optimal ferrate doses (100–200 μM), the extent of direct oxidation was substantial with a DOC reduction of approximately 20% (Table 1). A similar, but greater, effect was observed with samples of the upland coloured water (~35%; Table 1). In both types of test waters, the magnitude of the change in DOC appeared to be similar, or possibly, greater than that reported for ozone.

In addition to organic mineralisation, it was expected that ferrate would modify the size and nature of the humic substances. Some evidence of a general reduction in the molecular size was indicated from size exclusion chromatography (SEC) analysis, but this was tentative owing to the

Table 1 | DOC reduction (% C mass) by direct ferrate oxidation

Ferrate dose (μM)	pH 5	pH 6	pH 7
Model water (20 mg/L HA)			
100	19.3	14.4	1.0
200	18.1	14.9	3.0
300	30.7	25.2	6.5
Upland coloured water			
200	35.5	22.9	13.3

Table 2 | Comparative change in HA fractions (% C mass) with ferric chloride and ferrate treatment (20 mg/L HA, pH 7)

Organic fraction	Untreated HA	$FeCl_3$ (0.2 mM)	Ferrate (0.2 mM)	Ferrate (0.3 mM)
Hydrophobic base	0.7	2.0	0.4	5.1
Hydrophobic acid	81.5	89.5	66.9	38.3
Hydrophobic-neutral	3.0	2.5	4.5	12.1
Hydrophilic	11.1	8.4	20.1	37.9

inherent interference of Fe in the UV detection of the SEC separated molecular fractions. However, the results shown in Table 2 provide evidence that the humic macromolecular structures are cleaved into more hydrophilic (electronegative) fractions by the effect of ferrate oxidation, and as a consequence the extent of charge interaction and adsorption of organic fractions to the resulting iron hydrolysis flocs is substantially altered, leading to differences in organic removal. Thus, it is speculated that the increase in electronegativity with ferrate causes the equivalent Fe dose for maximum FI, corresponding to charge neutralisation, to increase. Similarly, the Fe dose range for effective coagulation increases substantially with ferrate dose beyond the charge neutralisation dose, since greater ferrate doses causes greater electronegativity, and thus, avoids charge restabilisation. However, at very high relative ferrate doses the extent of increased electronegativity is not as great as the amount of cationic Fe(III) species present, thereby causing reduced coagulation through charge restabilisation (e.g. Figure 3(b), for $[Fe] > 200\,\mu M$). An attempt was made to obtain supporting information from colloid charge measurements, and Figure 5 shows the zeta potential of colloids formed 3 min after coagulant addition. The results, although preliminary in nature, indicate significant differences in behaviour between ferrate and ferric chloride, and are broadly consistent with the mechanism described above. Thus, with ferric chloride there is a clear charge reversal with increasing dose, while with ferrate the colloid charge remains close to zero with increasing ferrate dose; thus, there is no charge reversal as the increasing Fe dose is matched by increasing HA electronegativity from ferrate oxidation.

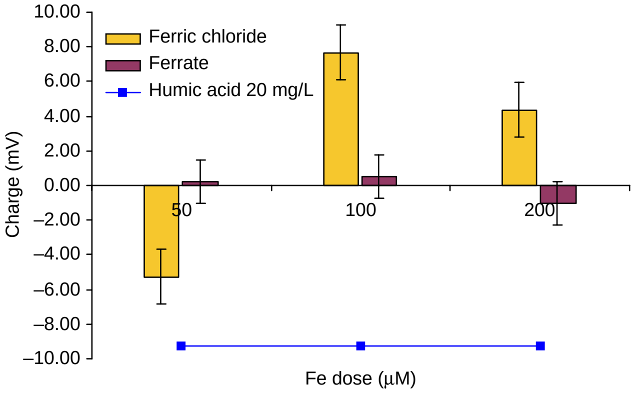

Figure 5 | Variation of colloid zeta potential with ferric chloride and ferrate dose for HA (20 mg/L) at pH 5 (3 min after coagulant addition).

The results of the tests carried out with upland coloured water showed that ferrate and ferric chloride had a very similar optimal Fe dose corresponding to a maximum FI value, and both chemicals displayed a charge restabilisation region for Fe doses above the optimal concentration. However, ferrate was able to achieve a greater degree of floc formation at doses above and below the optimal dose. This difference may be important practically in terms of the performance of subsequent separation processes (e.g. flotation, sedimentation, filtration) and the resulting final water quality. Also, for waters containing turbidity as well as HS, the enmeshment of turbidity by more voluminous flocs may be a considerable advantage in their removal. In contrast to the greater floc formation, the degree of organics removal (DOC) with ferrate was clearly inferior to ferric chloride in the laboratory tests which suggests that in practice there may be a greater quantity of smaller molecular weight, hydrophilic organic compounds present in final waters by applying ferrate instead of a conventional ferric salt.

The results of the model water tests conducted at pH 7 were different in various respects to those at pH 5. At pH 7 the coagulation of NOM by iron salts is well known to be less effective than at pH 5, since the principal mechanism is believed to be adsorption of HS on to iron hydroxide precipitates rather than charge neutralisation and precipitation of iron-humate complexes (Duan *et al.* 2002); thus, coagulation requires much greater Fe concentrations in order to precipitate sufficient quantities of $Fe(OH)_3$. Comparing the results for ferric chloride at pH 5 (Figure 2(a)) and pH 7 (Figure 6(a)) it can be seen that a much greater Fe dose ($>300\,\mu M$) was required to achieve the maximum FI at pH 7 than at pH 5 ($50\,\mu M$), and the

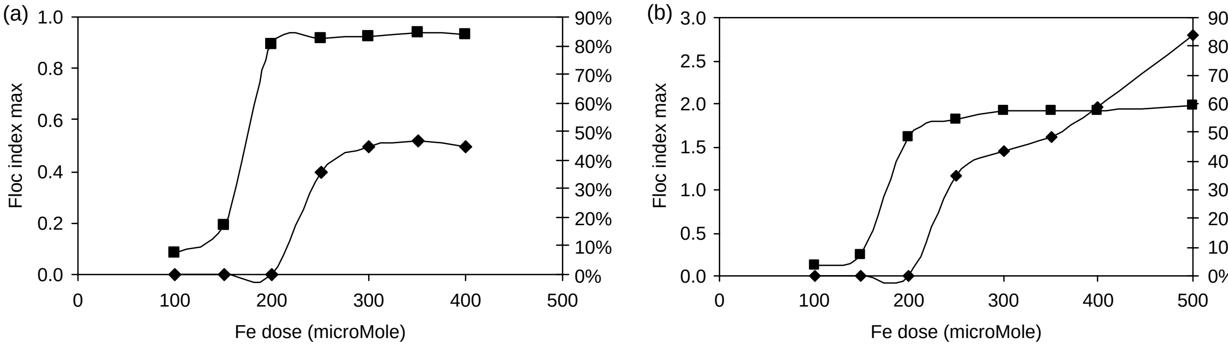

Figure 6 | Coagulation of HA (10 mg/L) in model water by (a) ferric chloride, and (b) ferrate, at pH 7 (■ % TOC removal; ◆ Floc Index).

narrow Fe dose range for coagulation at pH 5 was not evident at pH 7. Comparison of the coagulation of HA by ferrate with ferric chloride at pH 7 (Figure 6(a,b)), showed a similar minimum Fe dose required for coagulation, ~250 μM, but ferrate achieved a much greater extent of coagulation (FI max) which increased with Fe dose up to 500 μM. In contrast, the performance of ferrate in terms of HA removal was substantially lower than ferric chloride, with the extent of removal approximately 58% compared to 85%, respectively. Furthermore, this reduced effectiveness in HA removal by ferrate was much greater at pH 7 than at pH 5. The reason for this is unclear, but may be concerned with the greater stability of ferrate at pH 7 than at pH 5, where the generation of Fe(III) from the chemical reduction of ferrate is time dependent, in contrast to the instantaneous presence of Fe(III) in the dosing of ferric chloride. At pH 5 the ferrate self-decomposition rate is believed to be very rapid (ie. chemical reduction in seconds), while at pH 7 the rate has been determined and a half-life of approximately 3 min has been reported (Yang & Doong 2008). It is possible that the delayed generation of Fe(III) from ferrate, and weaker oxidation effects on HS at pH 7, lead to less effective adsorption of HS on to iron hydroxide precipitates. This aspect is complex in view of the inter-related processes of ferrate oxidation, Fe(VI) chemical reduction, Fe(III) hydroxide precipitation and HS adsorption/enmeshment; further investigation is required to consider this in detail.

CONCLUSIONS

Previous studies concerned with the treatment of upland coloured water by ferrate have indicated that its performance was superior to conventional ferric salts (e.g. ferric sulphate) in reducing colour, UV_{254} absorbance, and trihalomethane formation potential (THMFP) when the Fe dose was less than 2 mg/L. A further investigation using model waters containing humic and fulvic acids (Jiang & Wang 2003) also reported that the performance of ferrate was superior to that of ferric sulphate in the dose range of 2–8 mg/L Fe (35.7–142.8 μM Fe) for TOC and UV_{254} absorbance removal; the study concluded that ferrate can degrade the organics first and the degraded organic matter could be removed easily by coagulation. From this previous work and the results presented in this paper, which display some differences to the previous studies, it is evident that the nature of the interaction between ferrate and humic acids is complex and depends on many factors. In addition to the variability in the properties of the natural organic matter, the pH and coagulant metal ion dose are known to be key factors that affect the coagulation performance. With the application of ferrate the coagulation behaviour will be affected by the kinetics and extent of oxidation and charge interaction between cationic Fe hydrolysis species and $Fe(OH)_3$ precipitation.

The results of this study have shown that ferrate achieved comparable, or better, floc formation to ferric chloride over a much broader Fe dose range at both pH 5 and 7. However, associated with this was a lower degree of organics removal (as DOC) than ferric chloride, which was minor at pH 5 (~5%), but much greater at pH 7. The results obtained from model waters containing HA were consistent with those for samples of a natural upland coloured water. Experimental evidence showed that the organic macromolecules are cleaved into smaller, more hydrophilic fractions from the oxidation effects of ferrate which are more difficult to remove by coagulation, and require greater amounts of Fe species to achieve their removal. Similar phenomena were reported by O'Melia *et al.* (1999) for the pre-oxidation of water containing moderate/high TOC concentrations where ozonation was shown to have an adverse effect on coagulation and TOC removal. They explained that there is a shift in the distribution of NOM toward smaller, more oxygenated compounds caused by the oxidation process. The smaller compounds typically have a higher negative charge, thus a more reactive surface area of coagulant (alum, in their study) is needed to obtain the same TOC removal.

REFERENCES

AWWA 2000 Operational control of coagulation and filtration processes. In: *Manual of Water Supply Practices-M37*, 2nd edition, AWWA, Denver, USA.

Croué, J. P., Korshin, G. V. & Benjamin, M. M. 2000 *Characterization of Natural Organic Matter in Drinking Water*. AWWA Research Foundation, American Water Works Association, USA.

Duan, J. & Gregory, J. 2003 Coagulation by hydrolysing metal salts. *Adv. Colloid Inferface Sci.* **100–102**, 475–502.

Duan, J., Graham, N. J. D. & Wilson, F. 2002 Coagulation of humic acid by ferric chloride in saline (marine) water conditions. *Water Sci. Technol.* **47**(1), 41–48.

Eikebrokk, B. 1999 Coagulation-direct filtration of soft, low alkalinity humic waters. *Water Sci. Technol.* **40**(9), 55–62.

Fang, G. 2007 Evaluation and performance of a tannin-based polymer as a coagulant in water treatment. PhD Thesis, Imperial College London, UK.

Graham, N. J. D. 1999 Removal of humic substances by oxidation/biofiltration processes–a review. *Water Sci. Technol.* **40**(9), 141–148.

Graham, N., Jiang, C., Li, X.-Z., Jiang, J.-Q. & Ma, J. 2004 The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate. *Chemosphere* **56**(10), 946–956.

Gregory, J. & Nelson, D. W. 1986 Monitoring of aggregates in flowing suspensions. *Colloid Surf.* **18**(2–4), 175–188.

Jiang, J. Q. & Lloyd, B. 2002 Progress in the development and use of ferrate(VI) salt as an oxidant coagulant for water and wastewater treatment. *Water Res.* **36**, 1397–1408.

Jiang, J.-Q. & Wang, S. 2003 Enhanced coagulation with potassium ferrate(VI) for removing humic substances. *Environ. Eng. Sci.* **20**(6), 627–633.

Jiang, J.-Q., Graham, N. J. D. & Harward, C. 1996 Coagulation of upland coloured water with polyferric sulphate compared to conventional coagulants. *J. Water SRT–Aqua* **45**(3), 143–154.

Jiang, J.-Q., Lloyd, B. & Grigore, L. 2001 Preparation and evaluation of potassium ferrate as an oxidant and coagulant for potable water treatment. *Environ. Eng. Sci.* **18**(5), 323–328.

Lee, Y., Yoon, J. & von Gunten, U. 2005 Spectrophotometric determination of ferrate (Fe(VI)) in water by ABTS. *Water Res.* **39**(10), 1946–1953.

Li, C., Li, X. Z. & Graham, N. 2005 A study of the preparation and reactivity of potassium ferrate. *Chemosphere* **61**(4), 537–543.

Li, C., Li, X. Z. & Graham, N. 2008 The aqueous degradation of bisphenol A and steroid estrogens by ferrate. *Water Res.* **42**, 109–120.

O'Melia, C. R., Becker, W. C. & Au, K.-K. 1999 Removal of humic substances by coagulation. *Water Sci. Technol.* **40**(9), 47–54.

Sharma, V. K. 2002 Potassium ferrate (VI): an environmentally friendly oxidant. *Adv. Environ. Res.* **6**, 143–156.

Sharma, V. K., Li, X. Z., Graham, N. & Doong, R.-A. 2008 Ferrate (VI) oxidation of endocrine disruptors and antimicrobials in water. *J. Water SRT–Aqua* **57**(6), 419–426.

White, D. A. & Franklin, G. S. 1998 A preliminary investigation into the use of sodium ferrate in water treatment. *Environ. Technol.* **19**, 1157–1160.

Yang, S. & Doong, R. 2008 Preparation of potassium ferrate for the degradation of tetracycline. In: Sharma, V. K. (ed.) *Ferrates-Synthesis, Properties and Applications in Water and Wastewater Treatment*, *ACS Symposium Series 985*. American Chemical Society, USA, pp. 404–419.

Zhou, Q., Cabaniss, S. E. & Maurice, P. A. 2000 Considerations in the use of high-pressure size exclusion chromatography (HPSEC) for determining molecular weights of aquatic humic substances. *Water Res.* **34**(14), 3505–3514.