Chapter 17

Evaluating the Coagulation Performance of Ferrate: A Preliminary Study

Khoi Tran Tien[1], Nigel Graham[1,*], and Jia-Qian Jiang[2]

[1]Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, United Kingdom
[2]Centre for Environmental Health Engineering, School of Engineering, C5, University of Surrey, Guildford GU2 7XH, United Kingdom
[*]Corresponding author: n.graham@imperial.ac.uk; fax: 44 207 5946124

Ferrate is cited as having 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 an ongoing laboratory-based project that is investigating the coagulation reaction, dynamically via a PDA instrument, between ferrate and a suspension of kaolin powder 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 similarities and significant differences in the pattern of behaviour between ferrate and ferric chloride. This paper presents and discusses these observations and provides some comparative information on the strength of flocs formed.

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Introduction

Ferrate (Fe[VI]) is widely cited as having a dual role in water treatment, both as a powerful oxidant and as a coagulant, the latter as a consequence of its chemical reduction via Fe[V] to Fe[III]. Among the many studies of ferrate as water treatment chemical, Jiang *et al* (*1*) found that the maximum turbidity removal (almost 100%) was achieved at pH 7.5 for ferrate dosages from 2 to 12 mg/L as Fe and ferrate performed better than ferric sulphate in treating upland coloured water at low doses. In addition, ferrate showed a better performance in removing UV_{254} absorbance and dissolved organic carbon for waters containing humic and fulvic acids in comparison with ferric sulphate (*2*). Ma and Liu (*3;4*) demonstrated that pretreatment with ferrate clearly enhanced the removal of surface water turbidity and algae by coagulation with alum.

Whilst these and other previous reports have referred to the coagulation effect with ferrate, there appear to be very few studies that have considered the effect in detail; it is assumed that this is mainly because of the difficulty of separating the oxidation and coagulation phenomena when ferrate is applied. This paper summarizes some early results from an ongoing laboratory-based project that is investigating the coagulation effect. The study has employed a inert-type particle suspension (kaolin) and organic-free water in order to simplify the nature of the ferrate reaction by minimizing the influence of oxidation effects. The results are compared with those from identical tests using a conventional iron salt (ferric chloride) to observe any differences in behaviour.

Materials and Methods

Chemicals

All water used was deionised RO purified waster from a Purite – Neptune water purification system. Solid potassium ferrate was produced in the laboratory by the wet oxidation method of Li *et al.* (*5*) 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 ≥ 90%, 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 ABTS and an absorption λ of 415 nm (*6*). Ferric chloride stock solution (0.01 M) was made by dissolving 2.71 g $FeCl_3 \cdot 6H_2O$ (from BDH, UK) in 1L deionised water before the commencement of the tests. Kaolin stock suspensions of 5 g/L and 10 g/L were prepared by adding kaolin (light) powder (from Fisher, UK) into 1L deionised distilled water and mixing thoroughly. Bicarbonate buffer solution (0.1 M) was made by dissolving 8.41 g $NaHCO_3$ (from Fisher, UK) in 1L of deionised water. Boric acid/NaOH buffer solution (pH 9.0) was prepared from 50 ml 0.1 M boric acid/0.1 M KCl solution, and 20.8 ml 0.1 M NaOH, then diluted to 100 ml with deionised water.

Apparatus

Conventional jar test methods, as used in coagulation tests, are limited in terms of their sensitivity and practical convenience, although they do sometimes provide a useful visual and semi-quantitative simulation of full-scale performance. In our tests the coagulation process was followed by use of a photometric dispersion analyzer (PDA 2000, Rank Brothers, Cambridge, UK) in a modified jar test procedure. This is a relatively new approach to evaluating coagulation performance which has been found to provide a sensitive and rapid response, although the output of the PDA itself is qualitative in nature. The PDA is an instrument for observing rapidly changing particle suspensions via an optical technique that analyses the light transmitted through a flowing suspension (Figure 1); 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, serves as a relative measure of the change in particle size and density distributions (*7*). The output is referred to as the Flocculation Index (FI).

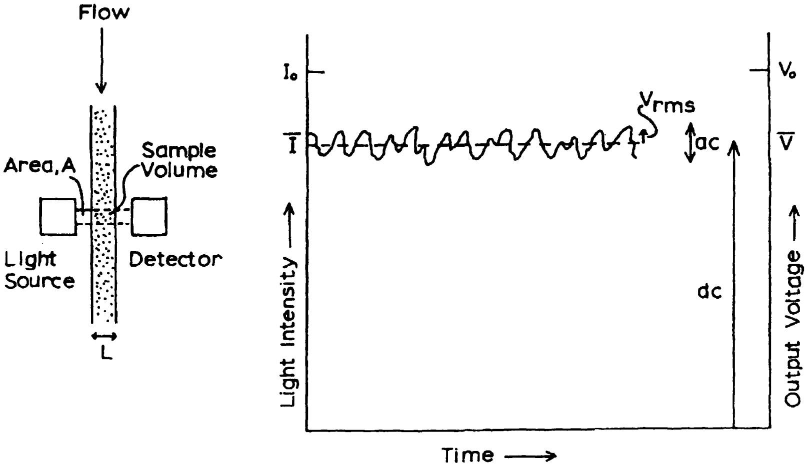

Figure 1. Principle of photometric dispersion analysis (Reproduced from J. Colloid Interface Sci. ***1985***, 105(2). *Copyright 1985.*

Tests were carried out by connecting the PDA to a stirred reactor where the ferrate or ferric chloride is added to the kaolin suspension under defined mixing conditions (Figure 2). The reactor was calibrated so that the mean velocity gradient (G, s^{-1}) of solutions undergoing stirring was directly determined from the rotational speed of the paddle. In the tests a constant flow from the stirred reactor to the PDA optical sensor was maintained by the use of tubing and a peristaltic pump (Matson 505S, UK) operating at about 25 ml/min; the flow passes through the optical sensor where it is illuminated by a narrow light beam (850nm wavelength). The optical data were recorded every second and the results were logged by computer for subsequent spreadsheet analysis. Although inherently qualitative, it is believed that the FI value is correlated with floc size and always increases as flocs grow larger.

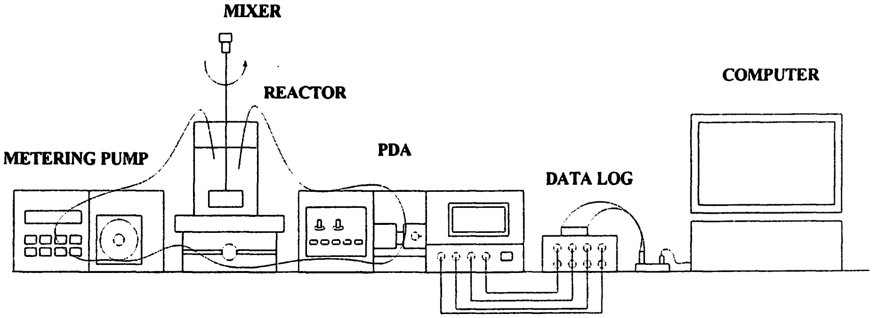

Figure 2. The experimental apparatus.

Experimental Procedures

Coagulation Tests

Our studies involved observation of the reactions between ferrate and an aqueous suspension of kaolin powder (50 mg/L) at different ferrate doses (5 to 200 μM) and pH values (4 to 8), and comparing the observations with the use of ferric chloride (a conventional chemical coagulant) under identical conditions. Kaolin is assumed to be inert to the oxidation effects of ferrate, so the observations of particle (floc) growth are believed to be the result of predominantly coagulation effects by Fe-hydrolysis species. Set pH values were controlled using bicarbonate and boric acid buffers..

Floc Strength Tests

The strength of flocs formed during coagulation depends on many factors, such as the type and amount of coagulant, the nature and quantity of interacting contaminants and the hydrodynamic conditions prevailing during floc formation. An individual floc will break if the stress applied at its surface is larger than the bonding strength within the floc. Gregory (*8*) has observed that when comparing different flocs formed by the same coagulant, the size of the floc (or indirectly the flocculation index, FI) for a given shear rate indicates floc strength. Using the 2L stirred reactor, an indication of relative floc strength can be obtained by applying a sudden increase in shear rate to the formed aggregates and relating velocity gradient applied to the maximum floc size resulting.

In these tests, the samples were prepared identically to those corresponding to the optimum performance for the coagulation tests at pH 7, where the optimum Fe dose was 200 μM. The kaolin suspension after the addition of the ferrate or $FeCl_3$ was initially mixed at 200 rpm ($G = 350\ s^{-1}$) for 60 seconds, and then the stirring was reduced and maintained at 50 rpm ($G = 50\ s^{-1}$) for an appropriate period of time so as to obtain the maximum flocculation (about 400 seconds). A sudden rise in the shear rate was then applied by increasing the stirring speed to 400 rpm ($600\ s^{-1}$) for 120 seconds, followed by a reduction/return in the speed to 50 rpm for the remainder of overall test period. The flocculation index was observed and recorded continuously during the test so that semi-quantitative values, corresponding to a *strength factor* and *recovery factor* could be determined and used for comparison. These terms are defined later.

Results and Discussion

The output from the PDA, although qualitative in nature, gives a comparative measure of the rate of floc growth and the magnitude of floc formation. Two examples of the output of the PDA are given in Figures 3 and 4; in these figures the PDA response, the Floc Index (RMS), is an optical index quantified on the y-axis, with time from the beginning of the test on the x-axis. The particular results shown in Figures 3 and 4 summarise the observed variation in PDA response with pH, at a given dose (200 μM) of ferric chloride and potassium ferrate, respectively. Additional results have been obtained with different doses of the chemicals.

Interpretation of the overall results is complicated, partly by the well-established dependence of coagulation performance on both chemical dose and pH, and partly by the qualitative nature of the PDA response. With the latter, to provide a quantitative basis for comparison, two values can be extracted from

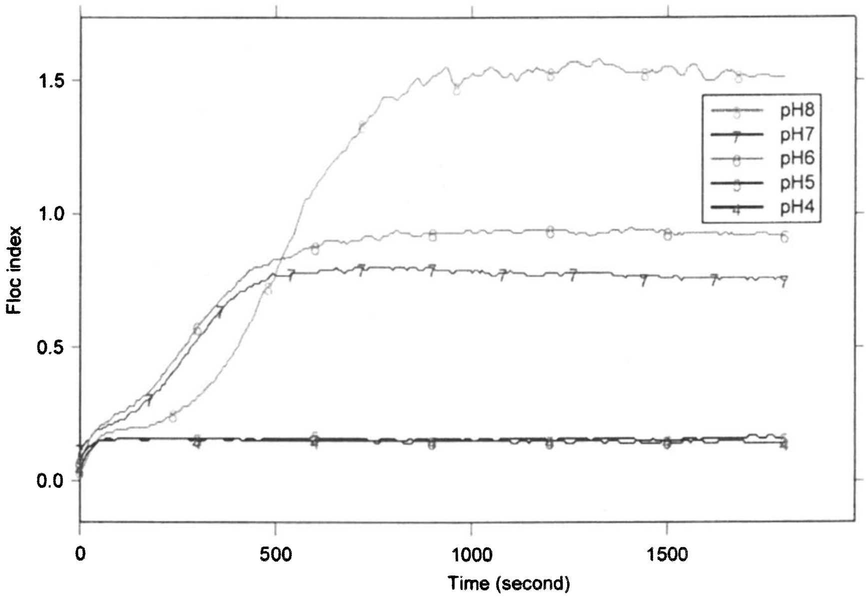

Figure 3. Coagulation of 50mg/L kaolin with 200μM $FeCl_3$ (1mM $NaHCO_3$ buffer solution).

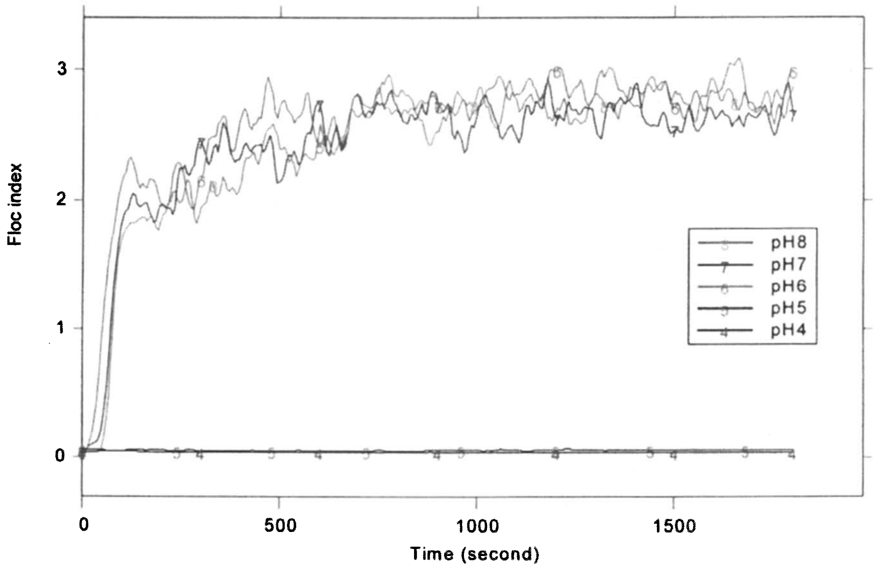

Figure 4. Coagulation of 50mg/L kaolin with 200μM Ferrate (1mM $NaHCO_3$ /Boric acid buffer solution).

each PDA response; these are the T_{50} and FI_{max} (RMS_{max}). The T_{50} is the time elapsed since the start of the test for the RMS value to reach 50% of its maximum value (RMS_{max}). Thus, good coagulation is demonstrated by a low T_{50} (i.e. rapid destabilization and floc growth) and a high FI_{max} (RMS_{max}) (ie. large, voluminous floc particles).

The results of the tests with ferrate and ferric chloride show some similarities and significant differences in the coagulation behaviour. In general, substantial floc formation was observed with both chemicals at the highest Fe concentrations (50, 100 and 200 μM), at pH 6, 7 and 8 (see Figures 3 and 4). This is consistent with the so-called 'sweep flocculation' mechanism whereby particles (kaolin) are incorporated within amorphous ferric hydroxide precipitates.

The solubility of amorphous ferric hydroxide has been reported to be a minimum at pH 8, and with only a minor increase in the range of 6 to 8. With ferric chloride the lowest T_{50} value was 66 s, corresponding to 200 μM Fe at pH 6; whilst for ferrate the lowest T_{50} value was 258 s, corresponding to 200 μM Fe at pH 7. However, the FI_{max} values for the two cases were quite different (viz. 3.09 ferric chloride, 0.95 ferrate), indicating significant differences in the nature of the flocs, and the conclusion that overall coagulation performance by ferrate was inferior to that with $FeCl_3$.

As can be seen from Figure 5 and 6, coagulation effects with both ferrate and ferric chloride were observed at doses from 5 to 200 μM at pH 6. Under these conditions it is believed that coagulation occurs by a combination of 'sweep flocculation' via ferric hydroxide precipitation *and* charge interaction between the kaolin and soluble cationic iron species. Good coagulation occurred under conditions of higher pH (6-8) and high dose (50 to 200 μM), which corresponds to the sweep floc region, and relatively poor coagulation occurred at low pH (4-5) and low dose (5, 10 and 15 μM). The performance increased proportionally with Fe dose. Overall, the coagulation performance of ferrate was not as good as ferric chloride, with generally higher values of T_{50} and lower values of FI_{max} observed with ferrate.

At lower pH values, 4 and 5, and [Fe]>15 μM, no or very little floc formation was evident with both chemicals. This is consistent with previous studies (*9*) which suggest that under these conditions the coagulant exists primarily as charged Fe(III) hydrolysis species (e.g. $Fe(OH)^{2+}$, $Fe(OH)_2^+$) that re-stabilize the kaolin suspension. However, at lower Fe doses (5, 10 and 15 μM), the balance of charges is such that some degree of destabilization occurs, leading to coagulation. At pH 5, and with 10 μM Fe dose, the ferrate coagulation performance was superior to the ferric chloride (see Figure 7). Some tests at pH 4 and 5 were repeated with a higher concentration of kaolin suspension and evidence of a dose stoichiometry (Fe:kaolin ratio) was found, with both ferrate and ferric chloride, supporting the assumption that charge neutralization is the predominant coagulation mechcanism under these pH—dose conditions.

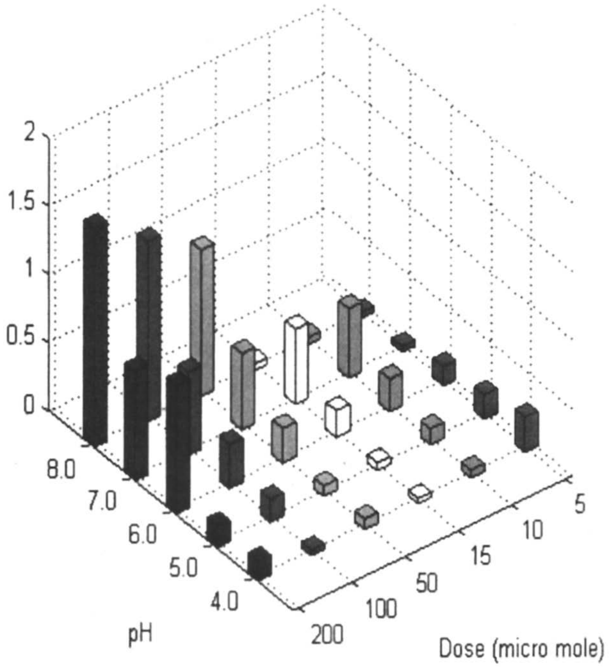

Figure 5. Variation of FI_{max} with dose and pH for Ferrate.

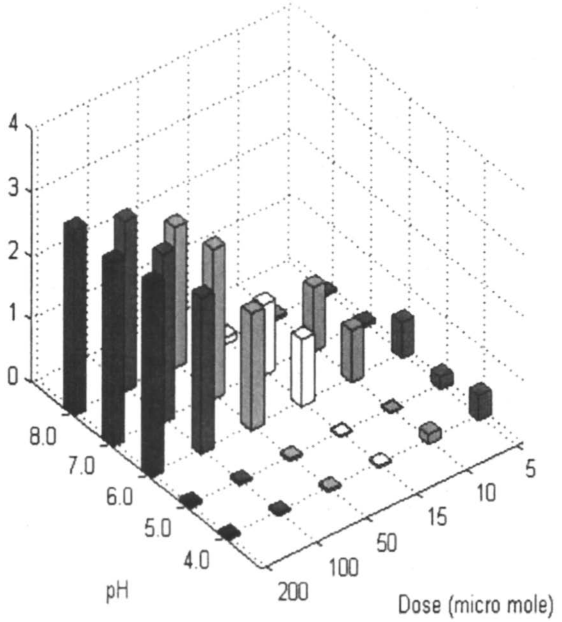

Figure 6. Variation of FI_{max} with dose and pH for Ferric Chloride.

Figure 8 presents the results of the floc strength tests with ferrate and ferric chloride under common optimal coagulation conditions (ie. 200 μM at pH 7). From Figure 8, it can be seen that by increasing the stirring rate from 50 rpm (50 s^{-1}) to the higher rate of 400 rpm (600 s^{-1}), there is an immediate and rapid decrease in FI, corresponding to a rapid breakage of flocs. When the stirring speed was reduced back, after 120 s, to 50 rpm (50 s^{-1}) there was no real evidence of a recovery or re-growth of flocs; in other coagulation systems limited re-growth of flocs is often observed. Thus, in these limited tests the results have indicated complete and irreversible floc breakage with both chemicals.

In general, semi-quantitative values, or indices, can be determined from the FI response curves in order to compare alternative coagulation conditions. Representative Flocculation Index values for the initial (FI_1), broken (FI_2) and reformed (FI_3) flocs can be used as surrogates for floc size in order to determine indices for the floc strength. These are as follows, as defined by Gregory and Yukselen (*10*) as:

$$\textit{Strength factor} = (FI_2 / FI_1) \cdot 100$$

$$\textit{Recovery factor} = [(FI_3 - FI_2) / (FI_1 - FI_2)] \cdot 100$$

It is believed that the higher the value of the strength factor, the stronger the flocs, since they are less sensitive to breakage as a result of the increased shear rate. The recovery factor is a measure of the capability of the floc to re-form and is of particular relevance to coagulation performance in practice, where floc disturbance due to flow irregularities is typical.

The results shown in Figure 8 indicate similar floc strengths for the two coagulants (strength factors: 0.3 for ferrate and 0.35 for ferric chloride), with ferrate flocs being slightly weaker than those from ferric chloride. The generally similar response suggests that the flocs could have similar physical structures arising from the aggregation of the insoluble Fe hydrolysis products and kaolin particles; this aspect will be investigated further. With both coagulants it is apparent that an irreversible breakage (recovery factor = 0) occurred when the shear rate increased. This is consistent with the well known effect in practice that flocs formed by hydrolysing coagulants tend to be weak and not fully reversible when formed in the sweep coagulation range (*7*); the zero recovery factor may be a consequence of the use of organic-free model water.

In some studies concerning the oxidation performance of ferrate the complicating influence of coagulation effects are minimized by the use of a phosphate buffer and high pH (e.g. ref *11*). It is assumed that Fe(III) forms soluble complexes with phosphate, and this phenomenon was briefly studied here. Figure 9 shows the effect of 5mM phosphate on the ferrate interaction with the kaolin. The results showed that the effectiveness of the phosphate in preventing coagulation effects at all pH values, with the exception of pH 4 where

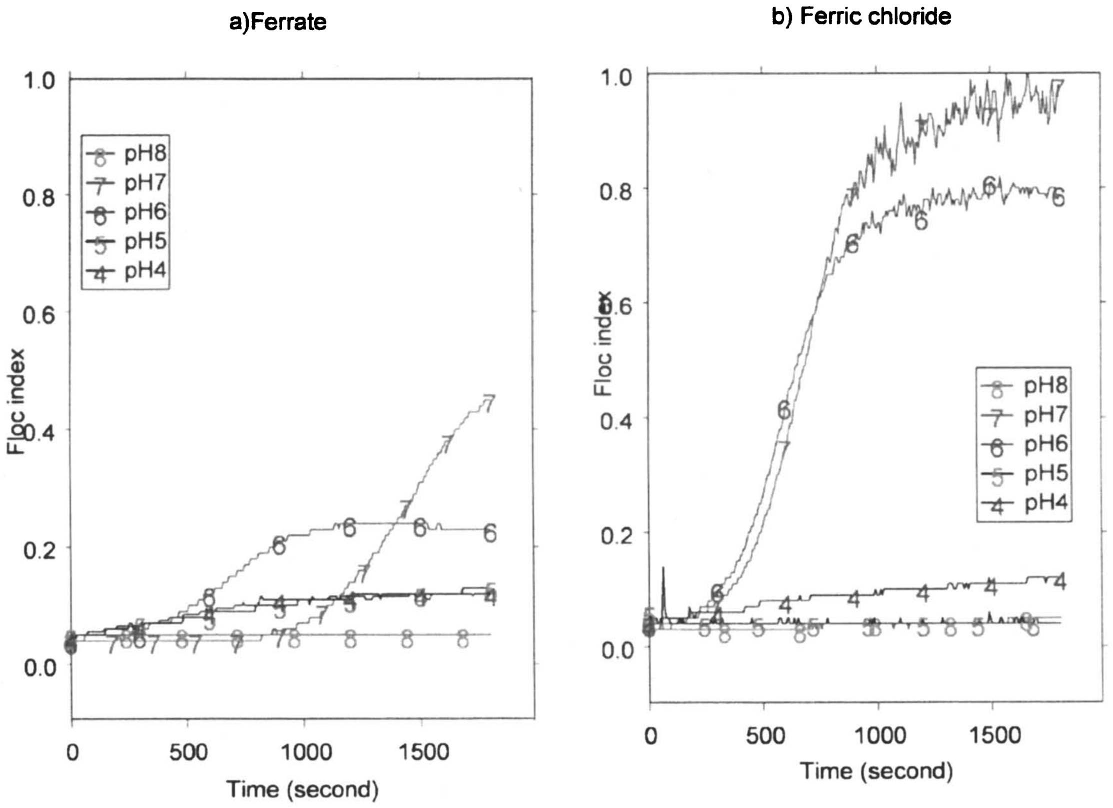

Figure 7. Coagulation of 50mg/L kaolin with 10μM Ferrate and $FeCl_3$.

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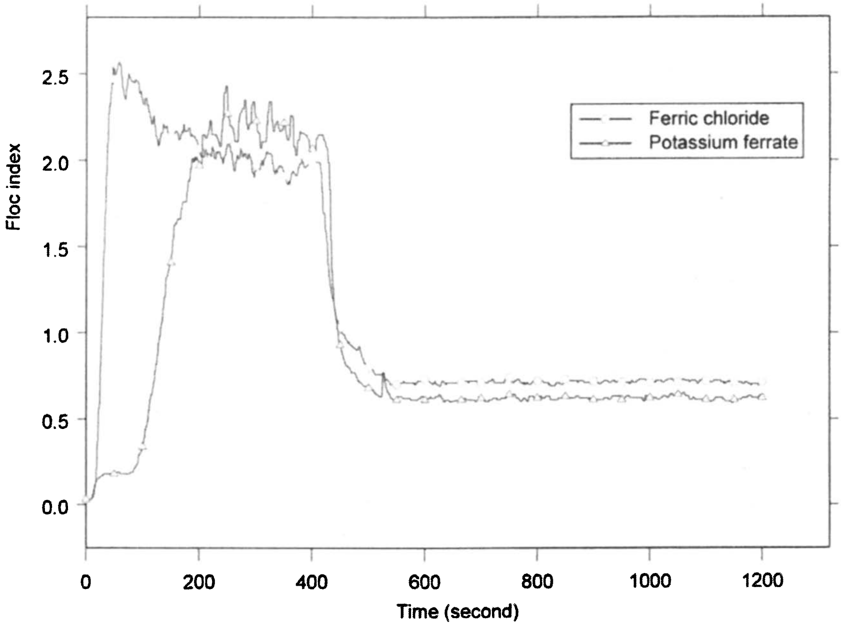

Figure 8. Variation of FI response during floc strength test (pH 7; Fe dose 200 μM).

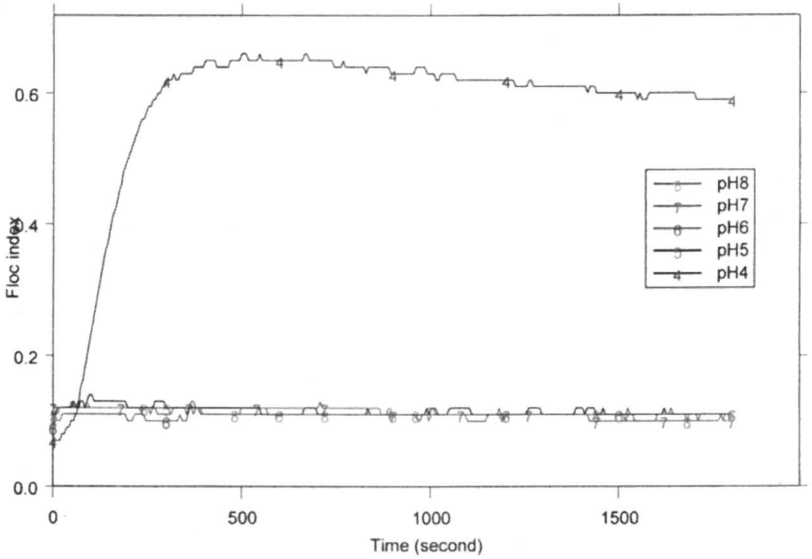

Figure 9. Coagulation of 50mg/L kaolin with 100μM Ferrate with 5mM phosphate/ 1mM borate buffer.

some solid phase precipitation is evident. A very similar behaviour was observed with the use of ferric chloride. The precise nature of the precipitate formed at pH 4 is unclear at present, as is the nature of the Fe-phosphate complex that is assumed to be formed.

Conclusions

A preliminary study has been undertaken to compare the coagulation performance of potassium ferrate in direct comparison with ferric chloride, a conventional coagulant chemical. A special test methodology was used to exclude simultaneous oxidation effects of ferrate, and to monitor the rapid formation of floc particles. The former was achieved by use of kaolin suspensions as the reacting substrate, which was assumed to be inert to the influence of ferrate oxidation. Floc formation was monitored by use of an on-line PDA light obscuration instrument.

In general, the ferrate demonstrates very similar coagulation characteristics to ferric chloride with regard to the influence of pH and Fe dose. Thus, floc formation with ferrate was relatively rapid and substantial at neutral pH and moderate Fe concentrations, corresponding to 'sweep coagulation', while at low pH there was some evidence of charge destabilisation and charge stoichiometry. In addition, there was no significant difference in the strength of flocs formed by each coagulant under optimal conditions.

The principal differences between ferrate and ferric chloride as coagulants was that the magnitude of floc formation with ferrate was always inferior to that with ferric chloride, and that in most cases the rate of floc growth with ferrate was slower than with ferric chloride. However, there was some evidence of a superior coagulation effects with ferrate at pH 4 and 5 at low Fe doses (5-15 μM). The reasons for the difference in the magnitude and rate of floc growth are not clear at present and will be considered in further work. Subsequent studies will also consider the comparative performance of ferrate and ferric chloride with humic substances, and will focus in particular on the separate roles of oxidation and coagulation in the case of ferrate.

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