Evaluation of Potassium Ferrate as a Coagulant in Water and Wastewater Treatment

Khoi Tran Tien
MSc.
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DECLARATION

I hereby declare that the work presented in this thesis is my own except where otherwise acknowledged.

Khoi Tran Tien
Ferrate 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 study aims to evaluate the coagulation performance of ferrate together with its oxidation effect in water and wastewater treatment processes, as it has not been studied thoroughly in previous work.

The study involves laboratory-based experiments that investigate the coagulation reaction dynamically via a PDA instrument, between ferrate and a suspension of kaolin powder, and humic acid solution at different doses and pH values, and comparing the observation 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 with kaolin suspension show some similarities and significant differences in the pattern of behaviour between ferrate and ferric chloride. Ferrate demonstrated very similar coagulation characteristics to ferric chloride with regard to the influence of pH and Fe dose. However, the magnitude of floc formation with ferrate was always inferior to that with ferric chloride. The rate of floc growth with ferrate was slower and sometimes less extensive than that with ferric chloride in most cases. It was discovered that the reason for the inferior performance of ferrate was the slow formation of Fe(III) species at neutral to high pH owing to the low degradation rate of ferrate in aqueous solution at these pH values.

The interaction between HA and ferrate was extensively investigated in comparison to ferric chloride in this study. The results reveal that ferrate achieved comparable or better floc formation to ferric chloride over a much broader Fe dose range. However, the degree of organics removal (DOC) was lower than ferric chloride (~5%). The results obtained from model waters containing HA were consistent with those for samples of a natural upland coloured water. Ferrate oxidation appears to increase the hydrophilic and electronegative nature of the HA leading to an extended region of charge neutralization and a consequent slightly lower HA removal compared to ferric chloride.
ACKNOWLEDGEMENTS

The most rewarding achievement in my life so far is, perhaps, the completion of my doctoral thesis as writing a PhD thesis is not an easy task, especially for those who face financial and health problems during the time of study.

In particular, I am deeply indebted to my supervisor, Professor Nigel Graham, for all his enthusiasm, understanding and patience throughout the study. I’d like to thank Dr. Geoff Fowler and Mrs. Carol Edwards for their support to my laboratory experiments. I’d also like to thank Dr. Jia-Qian Jiang, Professor Virender Sharma, and Professor Geoffrey Kelsall for their invaluable advice.

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This thesis is dedicated to my father who worshipped knowledge for all of his life.
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<tr>
<td>ABTS</td>
<td>2,2’-azino-bis (3-ethylbenzothiazoline-6-sulfonate)</td>
</tr>
</tbody>
</table>
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). 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 and Lloyd, 2002, Zhu et al., 2006, Sharma, 2002b) and the authors have conducted various studies in recent years concerning ferrate reactions with specific contaminants (e.g. (Sharma et al., 2006a, Jiang et al., 2006)).

In previous studies, ferrate was found to be a promising coagulant (Waite, 1979), or even much better coagulant compared to traditional coagulants such as FeSO₄·7H₂O and Fe(NO₃)₃ (Waite and Gray, 1984), FeCl₃ and Al₃(SO₄)₃ (Deluca et al., 1992), Fe₂(SO₄)₃·5H₂O (Jiang and Wang, 2003). However, Solo and Waite (1988) reported that ferric chloride was as efficient as ferrate in terms of turbidity removal. Moreover, Farooq and Bari (1986) reported that turbidity removal was not achieved with ferrate in the treatment of secondary effluent.

In addition, 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 removal. Thus, White and Franklin (1998) reported that the removal of organic colour in model waters (tap water spiked with HA) was substantially greater with ferrate compared to ferric sulphate at low equivalent doses (< 1mgFe/l), and Jiang et al. (2001) also found that ferrate performed better than ferric sulphate in treating a natural upland coloured water (reduction in UV₂₅₄ absorbance) at low doses (< 2mgFe/l, pH 5). In a subsequent study involving model waters containing humic and fulvic acids, Jiang and Wang (2003) showed that ferrate could achieve a better performance in removing UV₂₅₄ absorbance and dissolved organic carbon (DOC) in comparison with ferric
sulphate, but with HA the performance was inferior to ferric sulphate at higher doses (> 9mgFe/l with 20mg/l HA at pH 6). However, Wang (2003) and Panagoulopoulos (2004) reported that ferrate was inferior to ferric sulphate in terms of organic removal from model waters containing humic acids. The mechanism of ferrate coagulation has not been reported, thus it was impossible to explain the discrepancy between these studies.

Whilst these and other previous reports have referred to the coagulation performance, there appear to be very few studies that have considered this in detail, particularly the effect of ferrate oxidation on coagulation process; it is assumed that this is mainly because of the difficulty of separating the oxidation and coagulation effects when ferrate is applied.

Therefore, more rigorous work needs to be done to investigate the coagulation performance of ferrate as well as its oxidation effect in water treatment process that could help to better use of the chemical both in research and water treatment applications.

This research project aims to evaluate the coagulation performance of potassium ferrate in water and wastewater treatment and its oxidation effect on the overall treatment efficiency.
2.1 Potassium ferrate

2.1.1 Introduction

Potassium ferrate, an iron (VI) derivative, is a powerful oxidizing agent over a wide pH range with its standard reduction potential varying from +2.2V to +0.7 V in acidic and basic conditions, respectively. Thus in acidic solutions potassium ferrate is a stronger oxidant than chlorine, chlorine dioxide, hydrogen peroxide and ozone, which are used in water and wastewater treatment. Furthermore, during the aqueous oxidation reactions, Fe(VI) is reduced to Fe(III) which is then hydrolysed to form the insoluble iron (III) hydroxide, a conventional coagulant depending on pH and dose. That implies ferrate is a dual – function chemical reagent which will act as an oxidant and a coagulant in a single treatment step. This combined effect in water and wastewater treatment process brings about many benefits such as higher water quality, lower operational and capital costs. Because of its strong oxidising nature, potassium ferrate is also an effective disinfectant, which, together with its oxidation and coagulation nature, becomes a promising multi-purpose water and wastewater treatment chemical.

2.1.1.1 Characteristics

Potassium ferrate is the best-known iron (VI) compound because it is stable (in solid form) and easily prepared (Thompson et al., 1951). In the solid form, it is dark-purple coloured and stable in dry air for up to 1 year.

Potassium ferrate is insoluble in common organic solvents such as benzene, ether and chloroform without rapid decomposition but very soluble in water. Ferrate reduces rapidly and exothermally to Fe(III) and oxygen in strong acidic solutions (Wood, 1958). However, it is stable in strong alkali (3M or above) (Sharma, 2002b). The lowest rate of reduction of ferrate by water occurs between pH 9.4 and 9.7 (Lee and Gai, 1993). The decomposition rate of ferrate at 0.25 mM concentration and different pH values from 7.1
to 11.9 was measured and calculated by Li et al. (2005), the results are shown in Figure 2.1.

![Figure 2.1 Kinetic coefficient (k) of ferrate decomposition at different pH](image)

*Figure 2.1 Kinetic coefficient (k) of ferrate decomposition at different pH (reproduced from (Li et al., 2005))*

The reduction reaction of potassium ferrate in aqueous solutions is as follows:

In acid condition:

\[
FeO_4^{2-} + 8H^+ + 3e \rightarrow Fe^{3+} + 4H_2O \quad \text{E}=2.20 \text{ V}
\]

Neutral and weak basic conditions:

\[
FeO_4^{2-} + 4H_2O + 3e \rightarrow Fe(OH)_3 + 5OH^- \quad \text{E}=0.72 \text{ V}
\]

In aqueous solution, the ion \(FeO_4^{2-}\) is a monomer having a tetrahedral structure with a high degree of four covalent character equivalent Fe – O bonds (Hope et al., 1982). Potassium ferrate was first dynamically characterised by Wood (1958). As a result, the heat of formation of \(FeO_4^{2-}\) (\(\Delta H_f\)) is -115±1 Kcal/mole and the free energy of formation (\(\Delta G_f\)) is -77±2 Kcal/mole.

Carr et al. (1985) studied the spectral and kinetic properties of Fe(VI) as a function of pH in 0.2M phosphate buffer at 25°C. He reported that there existed at least two unstable protonated forms: \(H_2FeO_4\) and \(HFeO_4^-\). However, Rush et al. (1996) found three forms
of Fe(VI) in a similar study with 0.025M phosphate/acetate buffer at 23°C. It can be suggested from the pK values mentioned below that there are four forms of ferrate in a wide pH range.

\[ H_3FeO_4^+ \leftrightarrow H^+ + H_2FeO_4 \]

\[ pK_1 = 1.6 \pm 0.2 \] (Rush et al., 1996)

\[ H_2FeO_4 \leftrightarrow H^+ + HFeO_4^- \]

\[ pK_2 = 3.5 \] (Carr et al., 1985, Rush et al., 1996)

\[ HFeO_4^- \leftrightarrow H^+ + FeO_4^{2-} \]

\[ pK_3 = 7.3 \pm 0.1 \] (Rush et al., 1996)

\[ = 7.8 \] (Carr et al., 1985)

### 2.1.1.2 Synthesis of ferrate

Numerous studies on preparing Fe(VI) as potassium ferrate have been conducted using three basic methods (Jiang and Lloyd, 2002, Jiang and Wang, 2003):

- The dry oxidation method, by which various minerals containing iron oxide are heated under strongly alkaline conditions with oxygen supplement.
- The electrochemical method, by which iron or iron alloy is oxidised in the electrolyte solution of NaOH/ KOH.
- The wet oxidation method, by which an iron (III) salt is oxidised under strongly alkaline conditions using an oxidising agent such as hypochlorite or chlorine.

#### (a) Dry oxidation method

Few studies on this method have been reported in the literature. Generally, a mixture of iron oxides with alkaline and nitrates is heated at the temperature of red heat. The undergoing reactions in this process yield a mixture of ferrate salts, by-products and remaining reactants. For example, potassium ferrate was produced by calcinations of a mixture of ferric oxide and potassium peroxide at 350 – 370°C with continuous flow of
dry oxygen. The product obtained contained $\text{FeO}_5^{2-}$ anions, which were then immediately hydrolysed to generate $\text{FeO}_4^{2-}$ tetrahedral ion when dissolved in water:

$$\text{FeO}_5^{2+} + H_2O \rightarrow \text{FeO}_4^{2-} + 2OH^-$$

The dry oxidation method has become out-of-date because some dry reactions involved are considered to have the risk of explosion or detonation (Jiang and Lloyd, 2002).

**(b) Electrochemical method**

The principle of this method is based on the anodic oxidation of iron electrode during which Fe(III) is oxidized into $\text{FeO}_4^{2-}$ and then KOH is added to form the $K_2\text{FeO}_4$ solid. The reactions in the process are as follows:

Anode reaction:

$$Fe + 8OH^- \rightarrow \text{FeO}_4^{2-} + 4H_2O + 6e$$

Cathode reaction:

$$2H_2O \rightarrow H_2 + 2OH^- - 2e$$

Overall reactions:

$$Fe + 2OH^- + 2H_2O \rightarrow \text{FeO}_4^{2-} + 3H_2$$

$$\text{FeO}_4^{2-} + 2K^+ \rightarrow K_2\text{FeO}_4$$

**(c) Wet oxidation method**

Among the three principal methods, the wet oxidation method has been most investigated by researchers in the past. Foster (1879), Grub and Gmelin (1920), and Thiesse (1930) made ferrate solutions by using various oxidation methods. However, they failed to make the solid ferrate from the solutions which did not precipitate even in saturated NaOH solutions (Ockerman and Schreyer, 1951). Ockerman and Schreyer (1951) developed a method of preparing $Na_2\text{FeO}_4$ by which chlorine gas was bubbled into NaOH solution (30 g NaOH/ 75 ml of water) to generate sodium hypochlorite solution, which was then used to oxidise hydrous ferric oxide, resulting in a solid containing 41.38% $Na_2\text{FeO}_4$. 


Hrostowski and Scott (1950) used a similar method to produce aqueous Na$_2$FeO$_4$. In a further step, potassium ferrate (96.9% purity) was obtained by adding potassium hydroxide to the solution of Na$_2$FeO$_4$ and NaOH so that the potassium ferrate precipitated out of the saturated alkaline solution. However, the yield was as low as 10 - 15% of the theoretical. In 1951, Thompson et al. (1951) improved the yield to 44.1 – 76.4% by using ferric nitrate instead of ferric chloride to prepare hydrous ferric oxide. Potassium ferrate was prepared according to the following scheme:

\[
KMnO_4 + 8HCl \rightarrow MnCl_2 + \frac{5}{2} Cl_2 \uparrow + 4H_2O + KCl
\]

\[
Cl_2 + 2KOH \rightarrow KClO + KCl + H_2O
\]

\[
Fe(NO_3)_3 \cdot 9H_2O + 5KOH + \frac{3}{2} KClO \rightarrow \frac{3}{2} KCl + \frac{23}{2} H_2O + K_2FeO_4 + 3KNO_3
\]

A further purification process gave the final product with purity up to 96.3%. This method has been used widely by many researchers to give a high purity product, e.g. 98.6% (Bielski, 1991), > 99% (Machala et al., 2007). Many modifications have been made in attempt to improve yields and product purity.

In 1974, Williams and Riley (1974) reported a shortened method for preparing potassium ferrate, based on the same principle but different procedure. The most interesting point of this procedure was the shortened washing and drying process, in which ferrate solution was added to 600 ml of ethanol (95%) and stirred for 20 min, then filtered out by using a coarse porosity filter. The resulting precipitate was washed with two 50 ml portions of ethanol (95%) and 50 ml ether. However, the purity of the product was reported as low as 80 – 90%.

In 2001, Jiang et al. (2001) partially revealed a promising method for the preparation of high purity ferrate (99.9%). The preparation procedure was significantly simplified and shortened by employing an oxidant (commercially confidential) instead of producing hypochlorite solution; and freeze drying instead of the complicated washing with solvent. Unfortunately, the method has not been fully published.
In 2005, Li et al. (2005) optimized the procedure by using more appropriate filter media, and modified the washing process to a slightly more complicated one. This method delivered a product of high purity (up to 99%) and a much great yield (50-70%). This appears the best practical procedure so far.

2.1.1.3 Application of ferrate in water and waste water treatment

Potassium ferrate has been shown to be a promising multi-purpose wastewater treatment chemical for coagulation, disinfection and oxidation. Although the role of potassium ferrate as a selective oxidant in water and wastewater treatment has been studied abundantly, only a few articles in the literature have reported on its application as a coagulant.

(a) Use as disinfectant

The first study on the disinfection properties of ferrate was conducted by Murmann and Robinson in 1974 (1974). They studied the effect of ferrate on two types of pure laboratory cultured bacteria and a mixture from river water. It was found the rate of the reaction of Fe(VI) with the bacteria was considerably faster in comparison with the Fe(VI) decomposition rate.

Guilbert et al. (1979) investigated the disinfection effect of ferrate on Escherichia coli; the effectiveness increased remarkably below pH 8.0.

Waite (1979) used ferrate to disinfect the secondary effluent from the North Side Treatment Plant of Chicago Metropolitan Sanitary District and found that a 8 mg/l dose of ferrate could remove 99.9% of total coliform organisms and 97% of total bacteria.

In the recent years, Wang (2003) and Panagoulopoulos (2004) investigated further the disinfection ability of ferrate on model waters and surface waters. They concluded that ferrate was an excellent disinfectant in water and wastewater treatment.

(b) Use as an oxidant

A large number of investigations on the oxidation function of ferrate have been reported in the literature. Williams and Riley (1974), Waite and Gilbert (1978), and Sharma and
Bielski (1991a) were among the first authors who published their research results on the oxidation effect of ferrate.

The oxidation of alcohols (Williams and Riley, 1974), amino-acids (Rush and Bielski, 1995, Sharma and Bielski, 1991a), carboxylic (Bielski et al., 1994), phenol (Rush et al., 1995, Huang et al., 2001), and many other organics have been conducted. It was found that ferrate was a selective oxidising agent in water and wastewater treatment (Jiang, 2000). The oxidation reactions are strongly dependent on the concentration of Fe (VI), the ratios of ferrate to the organics and pH values.

Sharma and his co-workers have published the most papers on ferrate oxidation (Johnson and Sharma, 1999, Sharma, 2002a, Sharma et al., 2006b). They initiated studies on the rates, stoichiometry, and products of the Fe(VI) oxidation of nitrogen and sulphur – containing contaminants in the aquatic environment. They measured the rates of oxidation of ammonia, nitrite, cyanide, aniline, substituted anilines, hydrogen sulphide, thiourea, and thioacetamide with Fe(VI) as a function of pH (8.0 – 12.0) and temperature (15 – 35°C).

Qu et al. (2003) studied the reduction of fulvic acid in drinking water by ferrate using laboratory jar tests and pilot tests. It was reported that ferrate removed 90% of fulvic acid (as UV$_{254}$ absorbance) at the ferrate to FA mass ratio of 12:1. In the presence of turbidity, the FA removal increased to 95% at the same mass ratio.

Graham et al. (2004) investigated the influence of solution pH on the ferrate oxidation of phenol and three chlorinated phenols (potential endocrine disrupters): 4 – chlorophenol (Hrostowski and Scott, 1950), 2,4 – dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP). The degree of the organics oxidation by ferrate was found to be highly pH dependent, and the optimal pH decreased in the order: phenol/CP, DCP, TCP. The removal efficiencies were higher than 80% at the optimal pH and ferrate / organic molar ratio 5:1.

Jiang et al. (2005) studied the degradation of both natural and synthetic EDCs (bisphenol A, oestrone and 17β-estradiol) by using ferrate. The result demonstrated that ferrate can effectively oxidise EDCs to very low levels, ranging between 10 and 100 ng/L. They
obtained the removal percentage of 99.99% at doses between 13 – 17 mg/L as Fe. The optimal EDCs/ ferrate (as Fe) ratios were 0.10 mg: 1mg and 0.06 mg: 1 mg for test solution and primary sedimentation effluents, respectively.

Li el al. (2008) reported the extent of degradation up to 90% of bisphenol A (BPA), a known endocrine disrupting compound, by using aqueous ferrate oxidation. Also in this research, an improved procedure for preparing solid potassium ferrate was developed and demonstrated.

(c) Use as a coagulant

Preliminary studies have demonstrated that ferrate will effectively coagulate turbid water systems. In 1979, Waite (1979) conducted a feasibility study of ferrate in treating secondary effluent using a bench-scale pilot treatment facility. The results showed that ferrate at 10 mg/l as $\text{FeO}_2^{2-}$ removed 85% suspended solid, 53% ortho-phosphate and 86% BOD$_5$ of the secondary wastewater after 45 minutes of flocculation and 4 hours of sedimentation.

Waite and Gray (1984) conducted comparative coagulation jar tests on the lake water and bentonite clay system using ferrate, iron (II) and iron (III) They found that turbidity removal by ferrate was greater than that of Fe(II) and Fe(III) at low coagulant dose (< 10 mg/l as Fe). Increasing ferrate dose beyond the optimum dose (5 mg/l) led to decreases in turbidity removal. However, the pH values, at which these tests were conducted, were not mentioned, thus it is difficult to identify the pH- dose mechanism of the coagulants. In a more detailed experiment, they compared the coagulating performance of 15 mg/l (as Fe) ferrate with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (ferrous sulphate) and $\text{Fe(NO}_3)_3$ (ferric nitrate) at the same dose on removing turbidity of a colloid silica suspension at pH 7. The results showed that turbidity removal of ferrate was greater than that of ferrous sulphate and ferric nitrate. Under those conditions, ferrate achieved the turbidity removal within 1 minute while ferrous sulphate and ferric nitrate did it after 30 minutes. However, after 10 to 30 min of slow mixing, turbidity of the test solution increased substantially, and started to decrease after 10 min of further settling. This suggested that there was a difference in flocculation time between ferrate and Fe(III) and Fe(II). They also studied how the buffer solution...
affected the performance of ferrate as a coagulant. They reported that the turbidity removal efficiency was 95%, 79% and 84%, respectively, when a phosphate buffer, a carbonate buffer and distilled water was applied. The experiment was repeated at the optimum ferrate dose (5 mg/l), but at different concentrations of orthophosphate. The turbidity removal was found to increase with orthophosphate concentration (0 – 10 mg/l as P).

However, ferrate was not always found to be a good coagulant, nor a better one compared to the conventional coagulants in terms of removal of suspended solid and turbidity. Farooq and Bari (1986) carried out batch studies on the tertiary treatment with ferrate of secondary wastewater (COD: 8 - 52 mg/l; turbidity: 6 - 22 NTU) taken from the South Aramco activated sludge sewage treatment plant in Dhahran, Saudi Arabia. Turbidity of the treated effluent was measured after 90 min of settling. They reported that at pH between 7.6 and 7.8, turbidity removal was not achieved with ferrate dose up to 50 mg/l (254 µM). On the contrary, the turbidity of the treated samples increased with the increasing Fe doses because the resulting flocs did not settle well. Better turbidity removal was obtained with samples having higher initial turbidity. A ferrate dose of 15 mg/l (76 µM) was found effective in removing turbidity, COD and coliforms.

Solo and Waite (1988) investigated turbidity removal from well water added with 50 mg/l kaolin (13 NTU) by ferrate and ferric chloride using a direct filtration pilot plant. The results indicated that the turbidity removal by ferric chloride was as efficient as that of ferrate under the experimental conditions. This finding was contrary to previous studies where ferrate was generally found to be a much better coagulant.

Deluca et al. (1992) assessed the use of potassium ferrate in the treatment of combined domestic and industrial wastewater. The wastewater was higher in turbidity (70 -110 NTU) and COD (469 – 612) compared to that in the study of Farooq and Bari (1986). By performing the Jar tests, they recorded the optimum coagulation doses and pH as 50 mg/l - pH 5.5 for ferrate and 125 mg/l- pH 5.5 for FeCl₃, 6H₂O. Under these optimum conditions, ferrate achieved higher turbidity and BOD₅ removal (94% and 70%) than
ferric chloride (89% and 93%) did. However, it should be noted that COD removal with ferrate was lower than that with ferric chloride (viz. 70% and 93% respectively).

Ma and Liu (2002a) investigated the effect of ferrate pre-oxidation on the removal of algae in lake water and cultured solution by coagulation with alum. They found that pre-oxidation with ferrate dramatically increased the algae treatment efficiency, thus, consequently reduced the alum dosages for a certain treatment level. It was believed that the ferrate inactivated algae, produced an aid to the coagulation process from the interaction with algae cells. They argued that the formation of reduced products of ferrate also increased the particle concentration of the solution, thus improving the coagulation process. They also reported in another paper the same year (2002b) that pre-oxidation with 0.5 mg/L ferrate (5µM) significantly enhanced the coagulation of surface waters in terms of turbidity removal at pH between 7.0 – 7.5. They noticed that pre-oxidation with ferrate particularly improved the subsequent coagulation of organic-rich waters.

Jiang et al. (2001) demonstrated that ferrate could act as a dual-function chemical agent for drinking water treatment via a series of jar-test experiments on lake water. The preliminary results indicated that ferrate removed turbidity much more effectively at high pH (7.5) than at lower pH (3.5) while it was reversed for UV254 absorbance removal. They reported that ferrate performed better than ferric sulphate at lower doses in treating upland coloured water (pH 5), and ferrate effectively removed organic matter (as UV254) and turbidity and killed total coliforms at very low doses (< 2 mg/l as Fe). However, the removal of UV254 absorbance and THMFP with ferrate diminished with increasing Fe dose, and became inferior to that of ferric sulphate at doses ≥ 2 mg/l as Fe. The extent of UV254 absorbance removal from the upland water (TOC = 10.2 - 10.1 mg/l) was much greater than the lake water (TOC = 22.5 mg/l) with ferrate.

Jiang and Wang (2003) used ferrate to treat water containing humic and fulvic acids in terms of removing UV254 absorbance and dissolved organic carbon (DOC). The performance of ferrate in terms of the removal of DOC and for UV254 absorbance was superior to that of ferric sulphate over the dose range from 2 to 8 mg/l as Fe (see Figure 2.2). The results indicated that ferrate is a potential water treatment chemical for
Chapter 2: Literature Review

a) Comparative DOC removal at pH 6

b) Comparative UV$_{254}$ removal at pH 6

Figure 2.2 HA removal with ferrate and ferric sulphate at pH 6
(reproduced from (Jiang and Wang, 2003))

Figure 2.3 Remaining SUVA values in treated effluent with ferrate and ferric sulphate at pH 8 – FA model water
(reproduced from (Jiang and Wang, 2003))

Enhanced coagulation. Particularly, the results (shown in Figure 2.3) show that ferrate reduced the SUVA values of model water containing fulvic acid more extensively than ferric sulphate. They argued that this was because the ferrate could degrade the FA first, and the degraded organic matter could be easily removed by coagulation. This seems in
contradiction to their explanation for the decrease in THMFP reduction by ferrate at high doses.

Wang (2003) conducted a broad study on the evaluation of potassium ferrate as an oxidant and coagulant for water treatment. His study was fairly superficial involving disinfection and overall water treatment with crude potassium ferrate (90% purity). He carried out a series of simple jar tests to comparatively assess the coagulation performance of ferrate and ferric sulphate on 3 types of model water (containing 50 mg/l HA + 2 mg/l kaolin, 15 mg/l FA, 5 mg/l FA), lake waters, and river waters. Although the COD parameter is not reliable and accurate, his results show the trend that ferrate performance in terms of organic (UV254 absorbance and COD) removal was inferior in most of the cases for HA model water (see Figure 2.4), comparable for surface waters, and superior for FA model water in comparison to ferric sulphate. However, he did not really look at the treatment mechanism in detail nor try to separate the mechanisms of oxidation and coagulation. Thus, the study aimed to observe and describe the phenomena rather than giving a clear explanation.

![Figure 2.4 Comparative performance between ferrate and ferric sulphate in removing HA from model water (reproduced from (Wang, 2003))](image_url)

a) Residual COD of HA model water treated by Fe(III)  
b) Residual COD of HA model water treated by Fe(VI)
The study of Panagoulopoulos (2004) was similar to that of Wang (2003) apart from the synthesis of ferrate. He conducted the comparative disinfection and coagulation performance of ferrate, aluminum sulphate and ferric sulphate and chlorine on 2 types of model water (high organic content), lake water (UV_{254-abs} = 0.095-0.138 cm^{-1}), river water (UV_{254-abs} = 0.042 - 0.075 cm^{-1}) and wastewater. The ferrate performance (as turbidity, UV_{254} absorbance and UV_{400} absorbance removal) was found to be inferior to ferric chloride in treating both model waters. For river water, compared with ferric sulphate, UV_{254} absorbance removal with ferrate was superior at lower pH (4 and 5), comparable at pH 6, but inferior at pH 7 and 8. The UV_{254} absorbance removal was not reported for lake water. For wastewater, a better quality of final water was found with ferrate in comparison to other coagulants. It appears that the mechanism of ferrate coagulation was not explored in his study.

In good agreement with the finding of Panagoulopoulos (2004), ferrate was later reported to be an effective coagulant and disinfectant in treating sewage (Jiang et al., 2006), even at very low doses, viz. 0.005 -0.04 mg/l as Fe (Alsheyab et al., 2009).

Ferrate also gave a high effectiveness for removing metal ions, such as cadmium (Deganello et al., 2008), lead (63%), copper (Deganello et al., 2008) and chromium (88%). In addition, Murmann and Robinson (1974) reported that potassium ferrate could remove a range of metals (e.g., Fe^{2+}, Fe^{3+}, Mn^{2+}, Cu^{2+}) and toxic heavy metals (e.g., Pb^{2+}, Cd^{2+}, Cr^{3+}, and Hg^{2+}) to a low level, whereas it had no significant effects on removing Cr^{6+} and Zn^{2+}.

### 2.1.1.4 Oxidation - coagulation effects

It is clear from the foregoing that ferrate is a dual function chemical, both as an oxidant and coagulant, and the latter is caused by the reduced product of the first process. Thus, oxidation with ferrate leads to subsequent coagulation. The precipitate from coagulation instantly interferes with the optical monitoring of the reaction or contributes to the reduction of the study reactant, confusing the results.
Various tactics have been used by the researchers in order to avoid the interference of coagulation effects of ferrate on the oxidation research. Williams and Riley (1974) dissolved the precipitated Fe(III) after the reaction by adding acetic acid. Instead of re-dissolving the precipitate, Bielski and Thomas (1987) chelated the Fe(III) ions with adding DTPA (diethylenetriaminepentaactic acid) to avoid the interference during their study on the decay of ferrate in aqueous solution. Sharma and Bielski (1991b) used a phosphate buffer to prevent precipitation from generating. All the tested solutions were buffered with phosphate because they believed that phosphate, beside its buffering effect, served as a complexing agent for Fe(III), resulting in soluble complexes. They prepared the ferrate stock solution in 0.005 M Na₂HPO₄/0.001 M borate, pH 9.0, as it was believed to be most stable under these conditions. Although the nature of this effect of phosphate is not known since it was first mentioned in January 1991 by Bielski (1991), phosphate buffer (5-25 mM) has been widely used afterwards by Sharma and his coworkers in all of their studies (Sharma, 2002b), and many other researchers, e.g. Johnson and Hornstein (1994), Read et al. (1998), Johnson and Sharma (1999) Hua Huang (2001), Lee et al. (2005a).

However, in the oxidation of Lake Zurich water spiked with a phenolic endocrine disruptor (Gunten et al., 2005), 10 mM phosphate did not completely prevent the precipitation of the complexes of Fe(III), phosphate and NOM in the water. Thus, the treated samples were further acidified to pH below 2.5 with concentrated HClO₄. Similarly, Qu et al. (2003) acidified the reacted samples with 1 ml of composite acid (H₂SO₄: H₃PO₄ at ratio 1:1) before measuring the concentration of residual fulvic acid. They claimed that it was solely an oxidation process because the Fe(OH)₃ precipitation from reduced ferrate was re-dissolved, thus the influence of co-precipitation of FA with adsorption on Fe(OH)₃ was avoided.

In contrast to the oxidation studies, the oxidation process is inevitable in investigating the coagulation performance of ferrate. Thus, no attempt to look at the sole oxidation effects has been seen in studies of ferrate coagulation.
2.2 Mechanism of coagulation by hydrolysing metal salts

2.2.1 General

Natural waters contain a wide variety of particulate impurities. These consist of inorganic substances, such as clays and metal oxides, various organic colloids and microbes such as viruses, bacteria, protozoa and algae. Among these, particulate matter, colloidal particles, which have average diameters in the range of $10^{-4}$ to $10^{-6}$ mm, and soluble substances bring about undesirable properties to the water, for example, turbidity, colour, taste, odour and present a challenge for water treatment technology. Fundamentally, coagulation refers to the removal of soluble and colloidal particles by aggregation. It is a unit process in water purification during which chemicals are added to water in order to destabilise and aggregate these contaminants into larger sizes that may be removed after flocculation by separation processes, such as settling or filtration. This process is also called destabilisation of colloidal systems.

2.2.2 Mechanism

Normally, in natural waters, colloids are predominantly negatively charged because of a variety of negative functional groups on the surface of the particles. Therefore, the colloid systems may be stable as a result of electrical repulsion. The addition of positively charged species in appropriate quantities to neutralise the charge on colloidal particles will destabilise the system by overcoming the electrical repulsion and subsequently cause the aggregation with the assistance of van der Waal’s forces. Hydrolysing metal salts, based on aluminium or iron, are widely used as coagulants because they are predominantly cationic and so can interact strongly with negative colloids, causing destabilisation and subsequent coagulation. The most common forms are aluminium sulphate (called alum) and ferric sulphate or chloride and pre-hydrolysed metal salts such as polyaluminium chloride.

All metal cations are hydrated to some extent in water to form the primary hydration shell in which water molecules are in direct contact with the central metal ion. It is known that the primary hydration shell of $\text{Al}^{3+}$ and $\text{Fe}^{3+}$ consists of six water molecules in octahedral
co-ordination (Richens, 1997). Depending on the solution pH, the water molecules in the shell are progressively replaced by hydroxyl ions, via the oversimplified scheme as follows, shifting from left to right with the increasing of pH:

\[ Me^{3+} \rightarrow Me(OH)^{2+} \rightarrow Me(OH)_2^+ \rightarrow Me(OH)_3^- \rightarrow Me(OH)_4^- \]

The uncharged metal hydroxide of both aluminium and iron is of very low solubility and forms an amorphous precipitate, which is very important in the coagulation process, at intermediate pH values. At higher pH values, the soluble anionic form \( MeOH^- \) becomes dominant. The hydrolysis process is considered to involve successive de-protonation reactions as follows:

\[ Me^{3+} + H_2O \leftrightarrow Me(OH)^{2+} + H^+ \]

\[ Me(OH)^{2+} + H_2O \leftrightarrow Me(OH)_2^+ + H^+ \]

\[ Me(OH)_2^+ + H_2O \leftrightarrow Me(OH)_3^- + H^+ \]

\[ Me(OH)_3^- + H_2O \leftrightarrow Me(OH)_4^- + H^+ \]

The dissolution equation of metal hydroxides is as follows:

\[ Me(OH)_3^- \leftrightarrow Me^{3+} + 3OH^- \]

It can be seen that both aluminium and iron metals are amphoteric, that is, cationic and anionic complexes are formed. The complexes exist in equilibrium with the dissolution products of \( Me(OH)_3 \). In addition, it is known that there exist many other possible polynuclear forms such as \( Me_2(OH)_2^{4+} \), \( Me_3(OH)_5^{4+} \), \( Al_{13}O_4(OH)_{24}^{7+} \), etc. Martin (1991) pointed out the difference in the hydrolysis behaviour of aluminium and iron, which can be clearly seen in Figure 2.5.

According to Duan and Gregory (2003), there are two distinct mechanisms associated with the coagulation process of hydrolysing metals: charge neutralisation and sweep coagulation.
Figure 2.5 Proportion of dissolved hydrolysis products in equilibrium with amorphous hydroxides (reproduced from (Martin, 1991))
2.2.2.1 Charge neutralisation

At very low dosages of metal salts, only soluble species, the hydrated metal ion and various hydrolysed species are present. The hydrolysed cationic species (e.g. \((OH)_2^+\)) tend to adsorb strongly on negative surfaces of many type of particles, including bacteria and clays, and as a result, neutralise their negative charge and bring about coagulation. Generally, charge neutralisation with aluminium salts occurs at rather low metal concentration and at around low to neutral pH. At higher pH values, the optimum dosage increases because of the decreased positive charge of the adsorbed species.

The coagulation with aluminium and iron involves three steps according to the Precipitation Charge Neutralisation (PCN) model introduced by Dentel (1991):

- Destabilisation begins when the coagulant concentration in the solution exceeds the operational solubility limit of aluminium (or iron) hydroxide.
- The hydrolysed species are then deposited onto the colloidal surfaces by several possible pathways.
- The positively charged species neutralise the charge of the colloidal surfaces.

2.2.2.2 Sweep coagulation

At higher dosages, rapid and extensive hydroxide precipitation occurs and optimum removal of particles is achieved. This is known as sweep coagulation since the particles are swept out of water by the amorphous precipitate.

Sweep coagulation achieves higher particle removal effectiveness than charge neutralisation. This is partly because sweep coagulation increases the solids concentration, causing the greatly increased rates of aggregation. The rather open structure of hydroxide precipitates gives a large effective volume for capturing other particles and possibly produces stronger aggregates. The optimum pH zone for sweep coagulation is between 6 and 8 (Willy, 1992) and the solubility of amorphous iron(III) hydroxide is lowest over this pH range (see Figure 2.6).
Increasing the coagulant dosage in the sweep region improves the coagulation performance, however, there is little improvement beyond the operational optimum dosage (Gregory, 2001). The speciation of iron at 25°C is shown in Figure 2.7. The correlation between mechanism and dosage of iron salt is shown in Figure 2.8.
Figure 2.7 Iron speciation at 25°C
(provided by Professor Geoff Kelsall\(^1\) via personal communication)

Figure 2.8 Relation of dosage-mechanism of ferric chloride in coagulation
1: sweep coagulation zone; 2: charge neutralisation zone; 3: re-stabilisation zone
(reproduced from (Willy, 1992))

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\(^1\) Professor of Electrochemical Engineering, Department of Chemical Engineering, Imperial College London
2.3 Coagulation of humic substances

2.3.1 Natural organic matter (NOM)

NOM (aquatic) exists ubiquitously in all surface waters as a highly heterogeneous mixture of anionic polyelectrolytes that vary with regards to acidity, molecular weight and charge density (Collins et al., 1986), (Edzwald, 1993). This mixture also varies with place (location) and time (season) in terms of concentration and composition (Owen et al., 1993), (Scott et al., 2001). NOM contains a mixture of hydrophobic and hydrophilic organic compounds within a wide range of molecular weights, consisting of humic substances, proteins, amino acids, polysaccharides, carbohydrates, aldehydes, ketones and alcohols, where humic substances (HS) is the dominant fraction (Eikebrokk et al., 2007). NOM can be broadly divided in to humic substances (humic acid and fulvic acid) and non-humic compounds, such as carbohydrates, lipids, and amino acids (Eikebrokk et al., 2007). Humic materials constitute a skeleton of alkyl/aromatic units cross-linked mainly by oxygen and nitrogen groups being composed of a set of active chemical groups that give humic substances their unique chemical behaviour. These functional groups are carboxylic acid, phenolic and alcoholic hydroxyls, ketone, and quinone groups (Kim, 2003). The carboxyl (-COOH) and phenolic groups give to the humic substances their weak acidity. These carboxyl groups dissociate their H atoms at pH 3 - 6 giving HS a negative charge in surface water (Kim, 2003); with zeta potential ranging from -12 mV to -40 mV (Chandrakanth et al., 1996, Duan et al., 2002). Charge densities of HS have been reported in the range of 2 – 15 mequ.g\(^{-1}\) DOC (Tiller and O'Melia, 1993, Kam et al., 2001, Scott et al., 2001).

HS are divided into fulvic acids and humic acids according to their aqueous solubility, with fulvic acids being more soluble than humic acids. Fulvic acids are predominant in most waters and have lower molecular weight in comparison to humic acids, ranging from 500 to 2000 daltons. The molecular weight of humic acids are larger, from a few thousand daltons to greater than 100,000 daltons (Duan and Gregory, 2003). A hypothetical structure of humic acids is shown in Figure 2.9.
2.3.2 Coagulation of humic substances

Many studies have reported that HS can be effectively removed from water coagulation by hydrolyzing coagulants. According to Duan and Gregory (2003), HS are believed to be removed by hydrolyzing metal coagulants via two likely mechanisms as follows:

- Charge neutralization: metal hydrolysis species act as polycations, which bind to anionic sites of HS, thus neutralizing their charge and reducing their solubility. The resulting metal-humix complexes then precipitate or aggregate to form larger particles that can be removed by sedimentation or filtration.

- Co-precipitation: HS are removed by incorporation or sorption of humic material into or onto amorphous metal hydroxides precipitate.

It has been reported that there is a stoichiometry in the relation between the organic content (DOC) and the required coagulant dosage. Optimum pH for removal is usually lower (typically pH 5-6) than that for removal of suspended solids. Coagulant overdosing may result in a charge reversal, consequently leading to destabilization. This can be
attributed to the charge neutralization mechanism of the coagulation of HS (Amy et al., 1985).

2.4 Conclusions

The method of preparation of ferrate developed by Li et al. (2005) has been, so far, the one that gives highest purity and yield. Therefore, it was considered necessary to check whether this method was reproducible and could be further improved.

Of particular importance is that phosphate buffer (pH 9.1) was mainly used in previous studies to prepare ferrate stock solution, because it was believed to keep the ferrate stable for a relatively long time. Phosphate buffer was used to prevent the precipitation of Fe(III) in order to avoid particle interference (from ferric products) in the measurement of ferrate concentration in aqueous solutions using spectrophotometry. Although it is believed that phosphate can prevent the formation of amorphous Fe(OH)$_3$ by forming strongly soluble complexes with Fe ions, no literature about the nature of this effect has been reported. It was expected that phosphate could prevent the coagulation of a colloidal system by Fe coagulants, including ferrate. Thus, it is necessary to investigate further the effect of phosphate buffer on the coagulation process by ferrate and the use of phosphate buffer to achieve the solely oxidation effects by ferrate on organic matter.

Although a large number of studies have been conducted to investigate the oxidation effect of ferrate, there appear to be only a few studies that have considered the coagulation effect and none that have investigated the coagulation effect in detail. In most of the studies, which referred to the coagulation effect, the mechanism of the coagulation process was not considered, and in particular the flocculation process and floc characteristics. Generally, the overall turbidity and colour removal were used as an indicator to evaluate the coagulation performance of the coagulant via simple jar tests. It has not been clear about the coagulation performance of ferrate on humic substances as Jiang et al. (2001) reported that ferrate was superior to ferric sulphate in terms of removing organic matter, whereas opposite results were found by Wang (2003) and Panagoulopoulos (2004).
2.5 Aim and objectives of this study

This study aims to evaluate the coagulation performance of ferrate together with its oxidation effect in water and wastewater treatment processes, as it has not been studied thoroughly in previous work. The whole study includes the following objectives:

- Evaluate, and possibly improve, the method described by Li. et al (2005) to prepare high purity solid ferrate for using in this study;
- Cross check the method for analysis of ferrate concentration in aqueous solution using ABTS developed by Yunho et al. (2005a) with the spectrophotometric measurement at 510 nm; subsequently determine the standard curve to use in this study;
- Ascertain the use of phosphate buffer (5mM) to prevent precipitation of Fe(III) hydrolyzing species, thus suppress the coagulation of colloid by Fe coagulants;
- Investigate the coagulation performance of potassium ferrate with model waters containing different types of colloids, such as ‘inert’ suspensions, humic substances, and real waters over typical pH ranges and Fe dosages to understand the relative importance of oxidation and coagulation mechanisms; compare the performance of ferrate with that of ferric chloride as a reference coagulant under the same conditions;
- Investigate solely the oxidation effects on the target colloid (humic acids) and its consequent effects on the overall treatment efficiency (organic removal); investigate the impact of ferrate oxidation on the organics by studying the nature of changes in characteristics of the residual organics, for example molecular weight, molecular size distribution and chemical properties.
CHAPTER 3: MATERIALS AND METHODS

3.1 Introduction

This chapter has been structured so as to broadly reflect the general materials and methods that were used in the experimental sequence of this study.

The controlling ideas of this study is to compare the coagulation performance of potassium ferrate to ferric chloride, a conventional coagulant used in water and wastewater treatment, in terms of removing DOC and colloidal particles from water. Potassium ferrate was prepared in the laboratory and ferric chloride was obtained from a UK chemical supplier (Fisher Scientific, UK).

The coagulation experiments consisted of three main parts conducted on three different aqueous colloidal systems: kaolin suspension as an inert inorganic colloid, model water containing humic acids as organic colloid, and an upland coloured water as a natural colloid system. Generally, the coagulation performance was assessed based on a floc growth index and the removal percentage of colloids. The flocculation process was observed by using a photometric dispersion analyser (PDA) which generates a flocculation profile that shows the development of the floc with time (1 second interval) based on a relative floc size called the floc index (FI). The coagulation performance of the two coagulants was evaluated by comparing the floc index and the floc growth time.

The removal of colloids was assessed by using the parameters that are directly proportional to their concentration in the water: turbidity in the case of kaolin; UV$_{254}$ absorbance and total organic carbon (TOC) in the case of humic acids and NOM of upland water.

Hence, the first section describes the general analysis methods. The second section presents the experiment for preparation and characterisation of ferrate. The next section delineates the experimental procedures that were used to evaluate the coagulation performance of ferrate in comparison with ferric chloride. The final section describes further investigations in detail.
3.2 General materials

3.2.1 Deionised Water

Deionised water (~ 18 mΩ) was used to prepare stock solutions, buffers, and model waters in all experiments. It was purified by reverse osmosis membrane and then deionised through a water purification unit (Purite - Neptune).

3.2.2 Reagents and chemicals

All the reagents and chemicals used in this study (except ferrate) were purchased from chemical suppliers in the UK. These reagents and chemicals were all analytical grade and were used as supplied.

3.2.3 Filter paper and membranes

The paper and membranes of all kind used in this study were bought from Whatman (Germany).

3.2.4 Phosphate buffer

Phosphate buffer (5mM phosphate/ 1mM borate: pH 9.1) was used to make ferrate stock for determining ferrate concentration. Furthermore, phosphate buffer was used in oxidation tests to prevent coagulation being occurred. This buffer was prepared by adding 25 ml of 0.2 M sodium phosphate (NaH$_2$PO$_4$·2H$_2$O) stock solution and 40 ml 0.025 M sodium borate (Na$_2$B$_4$O$_7$·10H$_2$O) stock solution to deionised water and made up to 1 litre.

3.2.5 Boric acid/ NaOH buffer

Boric acid buffer (pH 9.0) was used extensively in this study to make the ferrate stock solution for all the coagulation tests by ferrate. This buffer was made by adding 50 ml of 0.1 M H$_3$BO$_3$ and KCl solution, and 20.8 ml 0.1 M NaOH then diluting to 100 ml with deionised water.
3.2.6 Ferrate

Ferrate was prepared in the laboratory following the wet oxidation method (see section 3.4.2). It had high purity (95 – 97%) and was in the form of a purple coloured powder. The chemical was kept in a dessicator at room temperature (20 - 22 °C) for a maximum time of one month. Because of its instability in an aqueous solution, ferrate solutions were prepared from solid ferrate weighed and diluted into 10 ml of buffer for use immediately before the tests instead of making a stock solution in advance for all experiments.

3.2.7 Ferric chloride

Ferric chloride hexahydrate (FeCl₃.6H₂O) was used as a comparative ferric coagulant. It was purchased from BHD (Dagenham, Essex, UK) in the form of a yellow - brown solid. Ferric chloride stock solutions were prepared at a concentration of 0.01 M before the commencement of the tests.

3.2.8 Kaolin suspension

The kaolin suspension used in this study was model water made by adding kaolin light powder (Fisher, UK) to deionised water. Stock suspensions of 5 g/l and 10 g/l were prepared by adding 5 g/ 10 g kaolin light powder into 1 litre of deionised water and the obtained suspensions were mixed thoroughly for 12 hours. The suspension showed good dispersion and stability. The geometric mean size of the kaolin was 4.85 μm as determined by the use of a laser diffraction particle size analyzer (Coulter S Series, Beckman Coulter Ltd., UK). The working suspension of 50 mg/l kaolin had a turbidity of 44 ± 1 NTU (see section 3.3.4). Although the surface potential of the test suspensions were not determined, it is known that kaolin clay has a net negative charge in natural water.

3.2.9 Humic Acid (HA)

Humic acid (Sodium salts, 42.2 % carbon content) was obtained as commercial reagent grade in solid form from Sigma-Aldrich Company Ltd. (UK). Stock solution was
prepared by dissolving 1 g of dry humic acid into 1 litre of deionised water and the solution was vigorously mixed for 12 hours and then filtered through a 0.45 \( \mu \text{m} \) pore size filter membrane. Stock solutions were kept refrigerated in an amber glass bottle for a maximum time of 1 week.

### 3.2.10 Model water containing humic acid

Test (model) solutions were obtained by diluting HA stock solution to deionised water to the desired concentration (10 mg/l and 20 mg/l). The concentration of HA in solution after filtration (0.45 \( \mu \text{m} \)) was determined as non-purgeable organic carbon (NPOC) by use of a TOC analyser (Shimadzu Ltd., Japan). For the test solutions, the mean initial specific UV absorbance (SUVA\(^2\)) was 9.7 l/mg.m (see Table 3.1), and the UV-visible absorbance is presented in Figure 3.1.

Based on the results in Table 3.1, two calibration curves of HA were built and displayed in Figure 3.2 and Figure 3.3.

### Table 3.1 UV\(_{254}\) absorbance, DOC and SUVA of HA solutions

<table>
<thead>
<tr>
<th>HA concentration (mg/l)</th>
<th>UV(_{254}) absorbance (cm(^{-1}))</th>
<th>DOC (mgC/l)</th>
<th>SUVA (l/mg.m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.039</td>
<td>0.457</td>
<td>8.6</td>
</tr>
<tr>
<td>4</td>
<td>0.084</td>
<td>0.877</td>
<td>9.6</td>
</tr>
<tr>
<td>6</td>
<td>0.128</td>
<td>1.212</td>
<td>10.6</td>
</tr>
<tr>
<td>8</td>
<td>0.172</td>
<td>1.770</td>
<td>9.7</td>
</tr>
<tr>
<td>10</td>
<td>0.213</td>
<td>2.091</td>
<td>10.2</td>
</tr>
<tr>
<td>20</td>
<td>0.435</td>
<td>4.600</td>
<td>9.5</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td>9.7</td>
</tr>
<tr>
<td>Standard deviation</td>
<td></td>
<td></td>
<td>0.7</td>
</tr>
</tbody>
</table>

\(^2\) SUVA = UV\(_{254}\) absorbance per mg DOC/l
Chapter 3: Materials and Methods

Figure 3.1 UV – visible absorbance of HA solutions

Figure 3.2 UV$_{254}$ absorbance – HA concentration calibration curve
3.2.11 Upland coloured water

Upland coloured water was obtained from an operational treatment works located in the north of England. The raw water was supplied from an upland reservoir and the water quality at the time of sampling had a DOC of 11 mgC/l and a UV\textsubscript{254} absorbance of 50.8 m\textsuperscript{-1}, giving a SUVA of 4.6 l/mg.m. While the SUVA values for the real water 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.

3.3 Analytical methods

3.3.1 Analysis of ferrate concentration in aqueous solutions by direct spectrophotometry

$\text{K}_2\text{FeO}_4$ dissolves in water as $\text{FeO}_4^{2-}$ and protonated species (e.g. $\text{HFeO}_4^-$) which have a distinctive UV-visible light absorbance spectrum. The absorbance spectrum of $\text{FeO}_4^{2-}$
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has a peak at 510 nm (Jiang and Wang, 2003). The molar absorption coefficient ($\varepsilon$) at 510 nm was determined as 1150 M$^{-1}$cm$^{-1}$ by Bielski and Thomas (1987) and this value has been used as a reference in many studies. However, this coefficient is not only relatively low but also varies significantly with pH; for example, $\varepsilon = 520$ M$^{-1}$cm$^{-1}$ at pH 6.2 and $\varepsilon = 1,150$ M$^{-1}$ cm$^{-1}$ at pH 9.1 (Jiang and Lloyd, 2002). Moreover, Jiang and Wang (2003) reported the coefficient as being equal to 1,185.2 M$^{-1}$ cm$^{-1}$ at pH 9.1 which is greater than the value of 1,070 M$^{-1}$ cm$^{-1}$ (in 4 M NaOH) found previously by Wood (1958).

3.3.2 Analysis of ferrate concentration in aqueous solutions by indirect spectrophotometry

A new method for the determination of low concentrations (0.03 – 35 μM) of aqueous ferrate has been developed by Lee et al. (2005b). The method is based on the reaction of Fe (VI) with 2, 2'-azino-bis (3-ethylbenzothiazoline - 6 - sulfonate) (ABTS) which has a stoichiometry of 1:1 in excess of ABTS. The reaction generates a green radical cation with respect to Fe(VI) at pH 4.3 (acetate buffer) that can be measured by spectrophotometry at 415 nm. The molar absorption coefficient at 415 nm was reported as 34,000 ± 500 M$^{-1}$ cm$^{-1}$ and it was independent of the pH of the water because all the samples were prepared at pH 4.3 using acetate buffer.

(a) Chemicals

Stock solutions of 1 g/l ABTS were made by dissolving 0.1 g of diammonium –ABTS (Sigma-Aldrich Company Ltd., UK) in to 100 ml deionised water and stored at 4°C. Acetate buffer (pH 4.1) was prepared by adding 34.3 ml CH$_3$COOH, 7.8 g NaH$_2$PO$_4$.2H$_2$O and 53.7 g Na$_2$HPO$_4$.12H$_2$O into deionised water and diluting to 1 litre. Primary stock solutions of ferrate (100 μM) were prepared in phosphate buffer at the start of the tests and were used within 10 min after preparation. Ferrate samples were made by diluting the primary stock solutions with deionised water.
(b) Experimental procedure

5 ml of acetate buffer reagent and 1 ml of ABTS reagent were added to a 25 ml volumetric flask. A ferrate sample was then added under shaking and the resulting volume was made up to 25 ml with deionised water. The volume (≤19 ml) and concentration of the ferrate sample were carefully estimated in order to keep the final concentration of Fe(VI) in the flask below 35 μM.

After the reaction was completed (less than 1 second) and the solution became green in colour, the solution was transferred into a 10 mm cell to measure the absorbance at 415 nm. A blank sample was prepared by the same procedure, but without Fe(IV).

The ferrate concentration of a sample was calculated from the absorbance using the following equation:

\[
[Fe(VI)]_{\text{sample}} = \frac{\Delta A_{415}^{\text{final}} V_{\text{final}}}{\varepsilon l V_{\text{sample}}}
\]

Where:

- \(\Delta A_{415}^{\text{final}}\): the absorbance at 415 nm after correcting for blank sample,
- \(V_{\text{final}}\): the final volume of the sample (25 ml)
- \(\varepsilon\): absorption coefficient 34,000± 500 M\(^{-1}\) cm\(^{-1}\)
- \(l\): cell path length (1 cm),
- \(V_{\text{sample}}\): the volume of the original ferrate sample added to the flask (ml).

3.3.3 Analysis of total dissolved organic carbon (DOC)

The organic content of test samples was determined by using a total organic carbon analyser, TOC-Vws (Shimadzu, Japan). The non-purgeable organic carbon (NPOC) was chosen in which the sample is automatically acidified to pH 2 to 3 by adding orthophosphoric acid and then sparging with high purity nitrogen to strip the dissolved carbon dioxide out of the sample solution. The carbon remaining after sparging is considered to
be organic carbon. The sample is then injected with a pre-set volume along with the oxidizing agent (sodium persulphate and phosphoric acid) into a reactor in which the organic carbon is completely oxidised to form carbon dioxide under heat (80°C) and UV radiation conditions. This carbon dioxide is swept out of the reactor by carrier gas to a dehumidifier for dehydration, then to a halogen scrubber for removing halogen, and finally to a non-dispersive infrared detector where the carbon dioxide is quantified. The carbon content is converted from the carbon dioxide peak area using the correlation derived from a calibration curve.

All the samples were filtered with 0.45 μm membrane filter before being analysed. A calibration curve was made once a month or after any maintenance to avoid systematic errors caused by the change of the analyser condition with time.

3.3.4 Analysis of turbidity of aqueous solutions

The turbidity of test samples was determined using a turbidity meter (model 2100A, HACH, UK). The meter was calibrated before measurement using standard turbidity tubes of 1 NTU, 10 NTU and 100 NTU.

3.3.5 Analysis of residual iron

An atomic absorption spectrometer (Model 3300, PerkinElmer Inc., USA) was used to determine the residual iron concentration of test samples. An iron stock solution of 1000 mg/l was purchased from Fisher Chemical (UK). Standard solutions (1 – 5 mg/l) were precisely prepared by spiking 1 – 5 ml of primary stock solution into 0.01 N HNO₃ and making up to the volume of 1 litre with 0.01 N HNO₃. A calibration curve in a range of 1 to 5 mg/l was performed using the standard solutions at the beginning of the measurement. Test samples were prepared in the same matrix as the standard solutions.

3.3.6 Analysis of molecular weight

In this study, the molecular weight distribution of humic acids and NOM samples before and after treatment were analysed by the use of size exclusion chromatography (SEC) following the method described by Zhou et al (2000).
SEC is a powerful technique that has been used to determine the molecular mass distribution of natural and synthetic polymers. A gel-permeation column was used to separate the sample components on the basis of their molecular size. Large molecules move through the column faster because they can diffuse into fewer of the stationary pores, while small molecules stick in more pores of the porous beads of the gel and are retarded. Therefore, the high molecule weight components elute from the column first. The elution time data can be easily converted to molecular weight through a calibration curve. From the mass distribution curve, the average molecular weight can be derived.

(a) Chemicals

Sodium polystyrene sulfonate (PSS) standards with known molecular weight of 4230, 6530, 14900 and 32900 daltons were obtained from Sigma – Aldrich (UK). All the PSS standard samples were prepared at a concentration of 100 mg/l, and filtered through 0.2 µm pore size filters. Acetone HPLC grade (99.99 %, Sigma-Aldrich, UK) was used as a 58 daltons standard and salicylic acid (99.99 %, Sigma-Aldrich, UK) as a 138 daltons standard. The mobile phase was phosphate buffered at pH 6.8, prepared by dissolving 0.272 g KH₂PO₄ (BHD, UK), 0.456 g K₂HPO₄·3H₂O (BHD, UK) and 5.85 g NaCl (BHD, UK) into deionised water, and then the solution was filtered using a 0.2 µm pore size membrane filter.

(b) Mode of analysis

SEC analysis was performed by using an HPLC (Waters 2695, Waters Corporation, UK) coupled with a photodiode array detector (Waters 2696, Waters Corporation, UK). The instrument’s accompanying computer software (Empower) was used to control the analysis process. It was used to set up the analysis mode and process the data obtained, for example to extract a chromatograph, provide an analysis report and extract raw data.

All the test samples were filtered through 0.2 µm pore size syringe filters (Whatman, Germany). The SEC injection volume varied depending on the sample concentration. A maximum volume of 100 µL was selected when the sample concentration was low (e.g. for treated solutions). The mode of analysis is presented in Table 3.2.
After the analysis, the data were processed in order to get the raw data of absorbance over elution time which was converted to logari t of molecular weight using the following equation:

\[ \log MW = -0.3203Et + 6.3634 \]  (see Figure 3.5 )

where :

MW : molecular weight (dalton) ; Et : evolution time (min)

**Table 3.2 Mode of SEC analysis**

<table>
<thead>
<tr>
<th>Column</th>
<th>Protein – Pak 125</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>230</td>
</tr>
<tr>
<td>Mobile phase</td>
<td>Phosphate buffer at pH 6.8 (0.002 M KH₂PO₄, 0.002 M K₂HPO₄ and 0.1 N NaCl)</td>
</tr>
<tr>
<td>Runtime (min)</td>
<td>25</td>
</tr>
<tr>
<td>Flow-rate (ml/ min)</td>
<td>1</td>
</tr>
<tr>
<td>Injection volume (μl)</td>
<td>25 (standard sample), 100 (test samples)</td>
</tr>
</tbody>
</table>

(c) **Calibration**

Standard compounds of known molecular weight were analysed. Based on the data obtained, a semi-log calibration curve was built to determine the correlation between elution time and molecular weight. A chromatogram of the standard compounds is shown in Figure 3.4 and the calibration curve is presented in Figure 3.5. Using this correlation, a sample of 20 mg/l HA was analysed and its molecular weight distribution is shown in Figure 3.6.

(d) **Assumption**

The results are based on the calibration with PSS which may not be the absolute representation of the molecular weight of humic substances. Thus the molecular weight values can be considered to be nominal.
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Figure 3.4 The chromatogram of standard compounds

Figure 3.5 Molecular weight calibration curve
3.3.7 Fractionation of humic substances

There are various chemical and physical methods available for fractionating humic substances. The chemical methods are conducted on the basis of the differences in some physico-chemical properties, for example, solubilities in a chemical reagent, charge characteristics, adsorption affinities, density, particle size, and molecular weight. The main physical methods consist of filtration and centrifugation. Whereas, resin exchange is one of the fractionation techniques based on differences in adsorption properties. There are many alternative types of resins (XAD-8, XAD-4,...) and the choice of any of them depends on the purpose of fractionation. Among them, the XAD-8 resin is widely used for the isolation of humic substances from natural water and the fractionation of them. In this study, XAD-8 resin was used because the targeted fractions were hydrophobic and hydrophilic.
(a) **Amberlite XAD-8 resin**

The amberlite XAD-8 resin was purchased from Supelco (AWWA, 2000). It is available as an industrial – grade preparation in the form of 20 – 40 mesh beads. This resin is a macro porous methylmethacrylate copolymer that has an average surface area of 450 m²/g and an average pore size of 250 Å.

XAD-8 resin was sieved with a 500-µm sieve to remove the large beads. It was then mixed with 0.1 M NaOH, the fine beads were decanted, and the remainder was stored in 0.1 NaOH for 24 hours. The organic contaminants in the resin were removed by sequential 24-h Soxhlet extractions with acetone and hexane. The clean resin was slurred in methanol and pumped to a glass column (80 ml). The column was then cleaned by pumping methanol through until free of hexane. Finally, the column was washed with deionised water until the effluent TOC was less than 1mg/l. The XAD-8 column was rinsed with 0.1 M NaOH, 0.1 M HCl, and deionised water immediately prior to application.

(b) **Fractionation procedure**

The fractionation method here was based mainly on the version of Leenheer (1981) except the procedure in step 5 was modified adopting the method described by Croue et al. (1999).

The column used in this test had a bed volume (V_B) of 80 ml. The maximum flow rate was 2.4 l/h or 40 ml /min (30V_B /h). The sample flow rate was selected as 20 ml /min. All the samples were carefully filtered with 0.45 µm pore size membrane filters. The whole process is shown schematically in Figure 3.7.

(i) **Step 1:**

1 litre of filtered sample was pumped through the XAD-8 column at a flow rate of 20 ml/min. This was followed by 200 ml (2.5 V_B) of deionised rinse water. The effluent is denoted as S_1.
(ii) **Step 2:**

The influent and effluent tubings of the column were then reversed and the hydrophobic base fraction was backflush eluted with 20 ml (0.25 V_B) of 0.1 M HCl, followed by 120 ml (1.5 V_B) of 0.01 M HCl. The pH was carefully monitored to detect the initial desorption of the hydrophobic base fraction. About the first 50 ml (0.6 V_B) of backflush effluent was rinse water and this volume (S_2) was recombined with the sample effluent (S_1).

(iii) **Step 3:**

The sample effluent from step 2 (S_1+S_2) was acidified to pH 2 with HCl and filtered through the column again at a flow rate of 20 ml/min. The column was then rinsed by 80 ml (V_B) of 0.01 M HCl. The total effluent is denoted as S_3.

(iv) **Step 4:**

The hydrophobic-acid fraction was backflush eluted with 20 ml (0.25 V_B) of 0.1M NaOH, followed by 120 ml (1.5 V_B) of deionised water. The initial desorption point was determined by observing the effluent pH. The first 50 ml of 0.01 M HCl rinse before the desorption occurred was added to S_3 to obtain the hydrophilic-base fraction.
(v) Step 5:

After the hydrophobic – acid elution, the XAD-8 column was eluted by the mixture of 75% acetonitrile and 25% water. The effluent was vacuum evaporated at 40°C and 0.1
Torr to remove acetonitrile. The remaining solution contained the hydrophobic – neutral fraction.

### 3.4 Preparation and characterisation of potassium ferrate

$\text{K}_2\text{FeO}_4$ with a purity of up to 97% was successfully prepared by the oxidation of ferric nitrate with hypochlorite, which had been produced by bubbling chlorine gas through a potassium hydroxide solution. The basic reactions are as follows:

$$\text{KMnO}_4 + 8\text{HCl} \rightarrow \text{MnCl}_2 + \frac{5}{2}\text{Cl}_2 \uparrow + 4\text{H}_2\text{O} + \text{KCl}$$

$$\text{Cl}_2 + 2\text{KOH} \rightarrow \text{KClO} + \text{KCl} + \text{H}_2\text{O}$$

$$\text{Fe}^{3+} + 4\text{OH}^- + 2\text{ClO}^- \rightarrow 2\text{Cl}^- + 2\text{H}_2\text{O} + \text{FeO}_4^{2-}$$

#### 3.4.1 Preparation of aqueous potassium ferrate

Liquid phase potassium ferrate was prepared by the wet oxidation method as described by Panagoulopoulos (Panagoulopoulos, 2004).

##### 3.4.1.1 Chemicals

The main chemicals used were ferric nitrate ($\text{Fe(NO}_3\text{).9H}_2\text{O}$, Fisher Scientific, UK), potassium hydroxide ($\text{KOH}$, Fisher Scientific, UK), hydrochloric acid 36% ($\text{HCl}$, Fisher Scientific, UK) and potassium permanganate ($\text{KMnO}_4$, Sigma - Aldrich Company Ltd., UK). These chemicals were all analytical grade and used without any further purification. All the solutions were prepared with deionised water.

##### 3.4.1.2 Experimental procedure

Beforehand, pre-chilled KOH solution was prepared by adding 60 g of KOH into 100 ml of deionised water and kept refrigerated for 2 hours. 165 ml of 37% HCl was placed into the funnel and dripped onto 26.7 g $\text{KMnO}_4$ in the flask below to generate chlorine. The freshly generated chlorine was then bubbled through pre-chilled KOH solution in an impinger for 2 hours. The solution was stirred continuously by a magnetic stirrer and cooled by inserting the impinger into an ice bath (see Figure 3.8). 90 g of KOH was then
added to the resulting hypochlorite solution. The suspension obtained was cooled and filtered through a GF/C filter paper to remove the KCl precipitate. The filtrate, a concentrated and strongly alkaline solution of potassium hypochlorite, was chilled at 0°C. This hypochlorite solution was then stirred rapidly while 37.5 g of pulverized Fe(NO₃)₃·9H₂O was added slowly for over 1 hour under cooling conditions (< 5°C). In these conditions, the Fe(III) ion was readily oxidized to Fe(VI) and the solution became dark purple in colour. The final suspension was centrifuged at 4,500 rpm for 15 minutes, leaving the supernatant as a pure ferrate solution which was kept refrigerated prior to use.

Figure 3.8 An apparatus for preparation of ferrate
3.4.2 Preparation of solid phase potassium ferrate

The preparation of solid potassium ferrate was very similar to that of aqueous potassium ferrate but some extra steps were needed with the final suspension obtained before the centrifuge step. The procedure mainly followed the approach of Li et al. (2005) who reported an improved method of preparing solid phase potassium ferrate with high purity and yield.

(a) Chemicals

The main chemicals were identical to those used for the preparation of aqueous ferrate. Extra solvents, methanol (Fisher Scientific, UK), diethyl ether (Fisher Scientific, UK), n-hexane (Rathburn Chemical Ltd., Scotland) and n-pentane (Rathburn Chemical Ltd., Scotland), were used to dry-wash the ferrate precipitate. 1 M KOH and KOH saturated solutions (~ 97 g/100 ml deionised water) were prepared and chilled in a refrigerator for at least 4 hours.

(b) Experimental procedures

The initial experiments were carried out in the same manner as the preparation of aqueous ferrate to obtain the solution containing ferrate and by-products.

Then, 30 g of KOH was added in portions to the Fe(VI) solution and the mixture was stirred for 20 min and the resulting solution was allowed to stand for a further 40 min. The subsequent dark purple slurry was filtered with a P-0 glass filter (500 ml capacity), after which the filtrate was discarded, and the precipitate was washed six times with a 25 ml quantity each time of cold 1 M aqueous KOH solution. The filtrate from the washings was collected and added to a flask containing 300 ml of a chilled saturated KOH solution. The solution was then mixed, allowed to stand for 10 min, and then filtered initially with a P-3 glass filter (500 ml capacity), followed by double filtering with GF/A filter papers. The precipitate was carefully flushed with n-hexane (4 x 25 ml), n-pentane (4 x 25 ml), methanol (4 x 10 ml), and diethyl ether (2 x 10 ml).

The final product, solid potassium ferrate (black in color), was collected and stored in a vacuum desiccator prior to further use.
To determine the quality of the solid ferrate, a specific amount of ferrate (~ 10 mg) was dissolved into 500 ml phosphate buffer (pH 9.1) and immediately analysed using both direct and in-direct methods. The purity of the solid ferrate was calculated as the ratio of the measured concentration (M) over the theoretical concentration (sample weight concentration/MW).

### 3.4.3 Effect of phosphate buffer on ferrate precipitation

Of particular importance is that phosphate buffer (pH 9.1) was mainly used in previous studies to prepare ferrate stock solution, because it was believed to keep the ferrate stable for a relatively long time. Phosphate buffer has been used to prevent Fe(III) precipitation in order to avoid the particle interference in the measurement of ferrate concentration in aqueous solutions using spectrophotometry (Sharma, 2002b, Gunten et al., 2005). Although it is believed that phosphate can prevent the formation of amorphous Fe(OH)$_3$ by forming strongly soluble complexes with Fe ions, no literature about the nature of this effect has been reported. Moreover, a probable effect of coagulation, as a result of Fe(III) precipitate, in oxidation experiments has not been considered accordingly. Thus it is necessary to investigate further the effect of phosphate buffer on the coagulation process by ferrate and the use of phosphate buffer to conduct a ‘pure’ oxidation reaction.

#### 3.4.3.1 Determine the precipitate quantity at pH 9

A specific weight of ferrate was diluted into 1 litre of phosphate buffer (section 3.2.4) to maintain solution pH around 9.1. The samples were filtered promptly after dilution to remove impurities using 0.2 µm pore size nylon filter membrane. The filtrate solutions were allowed to stand in laboratory conditions for 5 days and then filtered (0.2 µm) again. The filter papers was dried at 105°C for 1 hour and weighed before and after filtration to calculate the precipitate quantity.

#### 3.4.3.2 General effects of phosphate buffer on ferrate solution

Stock solutions of 100 µM ferrate were prepared in phosphate buffer. 10 volumes (1 litre each) of this stock were taken and their pH was adjusted to desired values (from 4 to 9) by adding 1 M HCl solution. These samples were halved and the first half was then
filtered by 0.2µm pore size membrane filter to determine the precipitate quantity. The filtrate was taken for SEC analysis, residual iron measurement and UV-visible scanning. UV-visible scanning was carried out with the second half of the samples as non-filtered solutions.

3.5 Coagulation experiment

3.5.1 The gator jar

A specially designed ‘gator’ jar was used as a reactor instead of a commercial glass beaker for the coagulation tests since the gator had been calibrated previously for velocity gradient in relation to the mixing rate. It is a 2L square, acrylic vessel of 21 cm height and 11.5 cm square side built to a standard design recommended by AWWA (AWWA, 2000). The calibration included a rectangular flat paddle of 2.5 cm x 7.6 cm connected to a vertical mounted motor. The correlation between impeller speed and velocity gradient is shown in Figure 3.9.

The square acrylic jar has a number of advantages over glass beakers:

- Lower vortex because of the reduced rotation of the water during mixing,
- Stable temperature due to thicker wall and lower heat conductivity of acrylic material,
- Less fragile than glass beakers
Figure 3.9 The mean velocity gradient – impeller speed calibration for the flat paddle in the gator jar (reproduced from (AWWA, 2000))

3.5.2 The photometric dispersion analyser

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 this study, the coagulation process was followed by the use of a photometric dispersion analyzer (PDA2000, Rank Brothers, Cambridge, UK) in a modified jar test procedure. This is a relatively new
approach to evaluate coagulation performance which has been found to provide a sensitive and rapid response, although the output 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 3.10). The principle of this instrument is based on the fact that there are small-scale, local variations in particle composition in any suspension or emulsion. These variations cause fluctuations in the intensity of the transmitted light when a narrow light beam illuminates the flowing suspension. The light intensity is recorded by a sensitive photodiode and converted to a voltage proportional to the intensity. The output voltage average component (dc value) corresponds to the average transmitted light intensity. The fluctuation component (ac value) denotes the change of transmitted light intensity caused by the variation of particle composition. The output, either the root-mean-square of the fluctuating component (RMS) or RMS/dc ratio, is a relative measure of the change in particle size and density distribution. The output is referred to as the Flocculation Index (FI).

![Figure 3.10 Principle of photometric dispersion analysis](reproduced from (Gregory, 1985))

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. An example of the output of
the PDA is given in Figure 3.11; in this figure the PDA response (floc index) is an optical index, quantified on the y-axis, with time from the beginning of the test on the x-axis. To provide a quantitative basis for comparison, two values have been extracted from each PDA response; these are the $T_{50}$ and $F_{I_{\text{max}}}$. The $T_{50}$ is the time elapsed since the start of the test for the floc index value to reach 50% of its maximum value (Ratio max or $F_{I_{\text{max}}}$). Thus, good coagulation is demonstrated by a low $T_{50}$ (rapid destabilization and floc growth) and a high $F_{I_{\text{max}}}$ (large, voluminous floc particles).

Figure 3.11 Example of the output of the PDA

(The symbols are not data points, but distinguish the different curves – Applied for all graphs which show the flocculation process with time, SEC results and UV scan results in this thesis)
3.5.3  The coagulation test

The coagulation test is the main test used in this study to evaluate the coagulation performance of the research chemical. The apparatus is shown in Figure 3.12 and Figure 3.13. The experiment was based on the principle of the jar test but the coagulation process was observed by use of the PDA. The gator jar was used as the reactor where the test solution and chemicals were mixed by a flat paddle driven by an overhead motor to maintain the flocculation process. The peristaltic pump circulated the test sample in the gator through the PDA via 3 mm diameter tubing. The PDA output was logged by a Pico data logger which was connected to a computer to record the output data. The test process was observed and controlled by use of accompanying software that allowed to record data as spreadsheets and online graphs. The two ends of the tubing were kept stable at the same depth above the paddle in all tests so that the results were not affected by the stratification of flocs and particles due to sedimentation.

![Figure 3.12 Schematic of the coagulation test apparatus](image-url)
3.5.4 Floc strength test

Floc strength is an important parameter in the process of developing and separating floc during water treatment as good strength minimizes the floc breakage and increases the removal efficiency because large aggregated particles generally are more easily removed. It is believed that higher density floc has greater strength (Gregory, 2004), and therefore floc strength is used as an indicator to assess the floc quality.

An empirical measure of floc strength was obtained by observing the response of floc index to a sudden increase in mean velocity gradient (shear rate) within the Gator reactor. At selected conditions (generally optimum dose and pH), the coagulation test was repeated. When the floc reached steady state at its peak FI, a sudden increase in shear rate (300 rpm, 600 s⁻¹) was applied for 1 or 2 min and regular (50 rpm) mixing rate was re-applied so that the floc broke and reformed (if possible). The floc strength can be
expressed quantitatively in terms of the ratio of the floc index after the sudden increase in shear (FI₂) to the floc index before (FI₁). A measure of the ability of the coagulated flocs to re-form after breakage can be expressed as a recovery factor determined as (FI₃ - FI₂)/(FI₁ – FI₂) where FI₁, FI₂ and FI₃ are illustrated in Figure 3.14.

![Figure 3.14 Define of floc strength factors](image)

**3.6 Coagulation test with kaolin suspensions**

**3.6.1 Coagulation test with 50 mg/l kaolin suspension**

The experiment aimed to compare the coagulation performance of potassium ferrate with ferric chloride, using kaolin as an ‘inert’ colloid in blank solution. The experiments were conducted using the method described in section 3.5.3.

(a) Chemicals

Solid potassium ferrate was produced in the laboratory by the wet oxidation method, described earlier in this chapter, and kept in a desiccator. Ferric chloride stock solution (0.01 M) was made by dissolving 2.71 g FeCl₃.6H₂O (BHD, UK) in 1 litre deionised water immediately before the tests. Bicarbonate buffer solution (0.2 M) was made by
dissolving 16.82 g NaHCO₃ (Fisher Scientific, UK) in 1 litre deionised water. Boric acid/NaOH pH 9.0 buffer (section 3.2.5) solution was used to make ferrate stock solution.

(b) Experimental procedure

The experiments were carried out with different dosages (5, 7.5, 10, 12.5, 15, 50, 100 and 200 μM as Fe) of coagulants in a range of pH from 4 to 8. The coagulation pH was controlled by adding an appropriate amount of 0.1 M HCl or 0.1 M NaOH prior to the coagulant, that had been determined in a pH adjustment test.

Firstly, 10 ml (0.2 M) of bicarbonate and 20 ml of kaolin stock (5 g/l) were added to the gator jar and diluted to 2 l (including the volume of coagulants) with deionised water. The reactor was then placed under the overhead stirrer, and connected to the PDA via the tubing and pump systems (see and Figure 3.13). A pre-determined volume of 0.1 M HCl or 0.1 M NaOH was added by pipette to adjust the pH values of the test solution to the desired point. The stirrer was started at an initial mixing rate of 200 rpm (G = 350 s⁻¹).

Secondly, an appropriate volume of FeCl₃.6H₂O stock solution (according to the desired dose) was added to the gator jar. In the case of potassium ferrate, an appropriate amount of ferrate was dissolved in 10 ml of boric acid buffer immediately before adding to the reactor.

Finally, 1 minute after adding the coagulant, the mixing rate was reduced to 50 rpm (regular mixing, 50 s⁻¹) to maintain a mild turbulence until the end of the test (normally 30 minutes). The coagulation and flocculation processes were observed and recorded by the PDA and computer logger system. The recording was started immediately after adding the coagulants.

After the test was finished, the solution was left to settle out for 1 hour and the supernatant was taken to measure its turbidity and residual iron concentration.
3.6.2 Coagulation tests with 50 mg/l kaolin suspension and with sodium sulphite ($\text{Na}_2\text{SO}_3$)

The assessment of the performance of potassium ferrate versus ferric chloride with model waters containing kaolin suspension showed some similarities as well as differences in the performance of both coagulants. It appeared that the performance of ferrate in terms of $\text{FImax}$ and $\text{T}_{50}$ (qualitative PDA parameters) was inferior to ferric chloride in the case of inert suspensions. This might be because of the slow formation of ferric species (cationic species and ferric hydroxide formation) from the ferrate decomposition in the water. The addition of a reducing agent (e.g. sodium sulphite) in identical tests with kaolin suspension may answer the question of whether the ferrate decomposition rate is the reason for the inferior performance of ferrate. When added to the reaction mixture at slightly higher than the stoichiometric level, sodium sulphite reacts immediately with all the ferrate in the mixture and hence quickly produces reduced ferric species, which are the target coagulant. Thus the presence of sodium sulphite should improve the flocculation process, and possibly produce a very similar behaviour to ferric chloride.

(a) Chemicals

Sodium sulphite stock solution was prepared at a concentration of 1 M. Other chemicals and stocks were identical to those described in section 3.6.1.

(b) Procedure

20 ml of kaolin stock (5 g/l), 10 ml of sodium sulphite solution, and 10 ml of bicarbonate buffer were added to the gator jar to make the total volume of 2 litres; the coagulant was added immediately before starting the test. Reagents for pH adjustment were then added in the reactor to achieve the desired pH value. The solution was mixed at 200 rpm (350s$^{-1}$) for 1 min and then reduced to 50 rpm (48s$^{-1}$) for 30 mins. The reactor was removed from the apparatus and left for settle for 1 hour.

Besides the measurement of the turbidity removal, the floc formation and its time dependences were observed continuously by using the PDA 2000, so that floc response indicators such as $\text{FImax}$ and $\text{T}_{50}$ were detected.
3.6.3 Investigating the effects of phosphate buffer on the coagulation performance

This experiment aimed to investigate the effect of phosphate buffer on the coagulation performance of iron-based coagulants, in this case, potassium ferrate and ferric chloride. Phosphate is commonly added to prevent coagulation and particle interference with spectroscopy analysis, particularly in ferrate studies, as it is believed that phosphate can prevent the formation of amorphous Fe(OH)₃ by forming strongly soluble complexes with Fe(III) ions (Sharma, 2002b).

(a) Chemicals

The chemicals used were similar to those, which were used in the test described in section 3.6.1, except phosphate buffer was used instead of boric acid buffer.

(b) Experimental procedures

The experiment was carried out with different dosages (5, 10, 15, 50, 100 and 200 µM) of coagulants in a range of pH from 4 to 8. The pH values of the samples were pre-set before doing the experiments by adding 0.1 M HCl or 0.1 M NaOH.

An appropriate volume of FeCl₃.6H₂O stock solution (according to the desired dose), 20 ml of bicarbonate and 20 ml of kaolin were added to the 2-litre reactor and diluted to 2 litres with deionised water. A pre-determined volume of 0.1 M HCl or 0.1 M NaOH was added to the mixture to adjust its pH to the desired value. In the case of potassium ferrate, an appropriate amount of ferrate was dissolved in 10 ml of boric acid buffer (pH = 9.1) immediately before doing the test.

The reactor was then connected to the PDA via the tubing and pump systems. The solution was stirred at the speed of 200 rpm (350 s⁻¹) for 1 min and then reduced to 50 rpm (48 s⁻¹) until the end of the test (normally 30 min). The coagulation and flocculation process were detected and measured by the PDA.
3.7 Coagulation tests with humic acid colloidal systems

3.7.1 Coagulation tests with HA model water

The interaction between ferrate and HA was investigated extensively in comparison with ferric chloride as a reference Fe coagulant under the same conditions. These experiments were conducted at various pH values and at two different concentration of HA: 20 mg/l and 10 mg/l.

(a) Chemicals

Solid potassium ferrate was produced in the laboratory by the wet oxidation method, described earlier in this chapter, and kept in a desiccator. Ferric chloride stock solution (0.01 M) was made by dissolving 2.71 g FeCl₃.6H₂O in 1 litre deionised water right before the tests. Humic acid stock solution (1g/l) was made by dissolving 1g humic acid into 1L of deionised water, mixed well for 24h and then filtered by 0.45 μm pore size membrane filter. Bicarbonate buffer solution (0.2 M) was prepared by dissolving 16.82 g NaHCO₃ (Fisher) in 1 litre deionised water. Boric acid buffer was used to prepare ferrate solution.

(b) Experimental procedures

The experiments were carried out with different Fe dosages from 5 to 300 μM around the optimum points in a range of pH from 4 to 7 (4, 5, 6 and 7). The sample pH was pre-set before doing the experiments by adding an appropriate amount of 0.1 – 0.25 M HCl or 0.1 – 0.25 M NaOH that had been determined in a pH adjustment test.

Firstly, 10 ml of bicarbonate and 40 ml (20 ml) of humic acid stock were added to the gator and diluted to 2 litres (including the volume of coagulant stock added later) using deionised water. The reactor was then connected to the coagulation test apparatus shown in and Figure 3.13. A pre-determined volume of 0.1 – 0.25 M HCl or 0.1 – 0.25 M NaOH was added to adjust pH of the test solution to the desired values. The stirrer was started at an initial mixing rate of 200 rpm (350 s⁻¹).
Secondly, an appropriate volume of FeCl$_3$.6H$_2$O stock solution (according to the desired dose) was added to the gator jar. For potassium ferrate, 10 ml of ferrate stock, which had been prepared by dissolving an appropriate amount of ferrate into 10 ml of boric acid buffer immediately before doing the test, was added to the test solution.

Finally, 1 min after adding the coagulant, the mixing rate was reduced to 50 rpm (regular mixing, 50 s$^{-1}$) to maintain a mild turbulence until the end of the test (normally 20 min). The coagulation and flocculation process were observed and recorded by the PDA and computer system. The recording was started immediately after adding coagulants.

After the test was finished, the solution was left to settle for 1 hour and a sample of the supernatant was taken to measure its turbidity. A further sample of the supernatant was filtered by 0.45 μm pore size membrane filter and then taken to analyse the DOC content, UV$_{254}$ absorbance, and residual iron concentration.

Besides the measurement of DOC and UV$_{254}$ absorbance (directly relating to the concentration of humic substances), the floc formation and its time dependence was observed continuously by using the PDA, so that floc response factors such as FI$_{max}$ and T$_{50}$ were detected.

The flocs generated in the experiments mentioned above were characterised by using a floc strength test (described in section 3.5.4), in which the flocs were selected at optimum conditions for both coagulants and the strength was evaluated by exposing the flocs to a sudden rise and then reduction in shear stress to observe their breakage and reformation.

The changes in the nature of the organics were detected by measuring the change in their molecular weight distribution using the SEC method (see section 3.3.6).

### 3.7.2 Fractionation of treated HA

The change in chemical fractions of HA after treatment by ferrate and ferric chloride at pH 7 was determined by using the XAD – 8 column (see section 3.3.7). A volume of 2 litres of 20 mg/l model HA was brought into reaction with either the ferrate or ferric chloride at pH 7 and the chosen Fe doses (200, 300 μM) using the Gator jar. It was decided to carry out the experiments under these conditions because no coagulation had
been observed. The reaction was maintained for 30 min under a sequence of rapid and then slow mixing rate, and was observed by the PDA. The PDA outputs showed that no flocculation had occurred (FI ~ 0) as expected. A volume of 1 litre of treated HA was filtered through a 0.45 μm pore size membrane filter and pumped through an XAD-8 resin column (V_{bed} = 80 ml). Because there was residual inorganic iron in the treated HA solution, between each filtration step the column was carefully washed by an appropriate solution (0.01 M NaOH, 0.01 M HCl or deionised water) until the effluent was free of iron to ensure that there was no inorganic iron in the solution of organic fractions obtained by elution in the next step. The obtained hydrophobic and hydrophilic fractions were analysed to determine their DOC, iron content and molecular weight distribution.

### 3.7.3 Oxidation tests with HA model water

The test was carried out with HA model water in comparison with upland coloured water. This experiment was conducted in the same manner as the coagulation tests but using phosphate buffer instead of boric acid/ NaOH buffer. After 30 min reaction, test solutions were taken for filtration (0.45 μm pore size) and DOC analysis.

### 3.7.4 Colloid Potential measurement

Changes in colloid potential by adding different doses (50, 100, 200 μM) of ferrate and ferric chloride at pH 5 was determined using a ‘ZetaPALS’ zeta potential analyser (Brookhaven Instruments Corp., New York, USA). The tests were prepared and carried out as for the coagulation test, however, at 3 min after initial mixing (200 rpm) a volume of 10 ml of test solution was taken and placed into a cuvette to measure the colloid zeta potential.

### 3.8 Coagulation tests with upland water

Finally, 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 11mgC/l and a UV$_{254}$ absorbance of 50.8 m$^{-1}$, giving a SUVA of 4.6 l/mg.m.

(a) Chemicals

The chemical used were the same as those described in of section 3.7.1 but using samples of real water instead of model water.

(b) Procedure

The test procedure was similar to that described in section 3.7.1.

Turbidity, UV$_{254}$ absorbance, NOM (DOC) removal, $F_{\text{max}}$ and $T_{50}$ were detected. The change in the nature of the organics was observed by measuring the change in molecular weight distribution of the organics using the SEC method. The change in chemical fractions of the organics was also investigated.
4.1 Introduction

This chapter summarises the results from the experiments concerning the preparation and characterization of ferrate, including preparation of aqueous and solid potassium ferrate by wet oxidation methods, analysis of ferrate concentration in aqueous solutions and investigation of the effect of phosphate buffer on the precipitation of reduced Fe(III) in ferrate solutions.

4.2 Preparation of potassium ferrate

4.2.1 Preparation of aqueous potassium ferrate

Following the method described in section 3.4.1, 120 ml of ferrate solution was achieved from 1 experiment. The obtained solution was analysed to determine the ferrate concentration on the same day of preparation and 1 week later by direct spectrophotometry at the wavelength of 510 nm using the SP8-100 ultraviolet spectrophotometer. The absorption coefficient of 1150 M\(^{-1}\) cm\(^{-1}\) at 510 nm (Carr et al., 1985) was assumed in order to calculate the concentrations via the Beer’s law equation. The measurement of ferrate concentration was conducted in duplicate, and the results are shown in Table 4.1

As can be seen in Table 4.1, the average concentration of the freshly made ferrate solution was 0.037 M. However, after being kept refrigerated (at around 4°C) for 1 week, the ferrate concentration had decreased by 56.6 % from 0.037 M to 0.016 M.

In addition, the ferrate solution was strongly alkaline (pH = 13), thus when added to the test solution, it made the pH adjustment of the system very difficult. Therefore, the ferrate solution was not used in this study.
**Table 4.1 Ferrate concentration in the prepared solution**

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<th>Sample</th>
<th>Dilution ratio</th>
<th>UV\textsubscript{510} absorbance (cm\textsuperscript{-1})</th>
<th>Concentration (M)</th>
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<td></td>
<td>1</td>
<td>1:100</td>
<td>1.201</td>
<td>0.038</td>
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<td>1:250</td>
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<td>0.036</td>
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<tr>
<td></td>
<td>Mean</td>
<td></td>
<td></td>
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<tr>
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<td>Mean</td>
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</tbody>
</table>

**4.2.2 Preparation of solid potassium ferrate**

Following exactly the method described by Li. et al. (2005), it took almost 8 hours to prepare and carry out the preparation of a quantity of solid potassium ferrate. The first experiment was not successful because the P-0 filter used (100 ml capacity) was too small as its capacity was not stated in the paper. When using an inadequate capacity filter, the filtration rate was slow and consequently a large amount of Fe(VI) was reduced during the prolonged filtration process. It could be seen in the experiment that the slurry changed from dark purple to yellowish brown.

The subsequent experiments yielded about 8 – 10 g of ferrate per batch with a purity of between 85 – 90%. Under careful observation, it was visible that the colour of the solid ferrate obtained from the final filtration step (using P-3 fritted glass filter) changed from dark purple to yellowish brown when it was washed with methanol. This phenomenon suggested that there was interaction between methanol and ‘wet’ ferrate, in other words, ferrate reacted with methanol in the presence of water. Therefore, extra care was taken with the washing process and it was found that double the number of washing by n-
hexane and n-pentane improved the quality of the ferrate. Using the modified drying process (shown in Table 4.2), the highest purity of 97 ± 0.5 % was achieved.

Table 4.2 Modified drying process (solvent washing sequence)

<table>
<thead>
<tr>
<th>Process report by Li et al. (2005)</th>
<th>Modified process</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 x 25 ml n-hexane</td>
<td>8 x 25 ml n-hexane</td>
</tr>
<tr>
<td>4 x 25 ml n-pentane</td>
<td>8 x 25 ml n-pentane</td>
</tr>
<tr>
<td>4 x 10 ml methanol</td>
<td>4 x 10 ml methanol</td>
</tr>
<tr>
<td>4 x 10 ml diethyl ether</td>
<td>4 x 10 ml diethyl ether</td>
</tr>
</tbody>
</table>

All the quantities of ferrate were kept in a desiccator at room temperature. Further analysis showed that solid ferrate was stable in these conditions for up to 40 days (see Figure 4.1). Therefore, this method was used to produce the ferrate for this study because of its reliability, and all the prepared ferrate was used within 40 days.
Chapter 4: Preparation and characterisation of ferrate

4.3 Characterisation of ferrate

4.3.1 Analysis of ferrate concentration in aqueous solution

The concentration of potassium ferrate in aqueous solutions was determined by UV-visible absorbance using a Shimadzu spectrophotometer. Both direct and indirect analysis methods were used to determine the concentration of ferrate samples.

Firstly, the concentration of a ferrate sample was determined by the indirect method and the results are presented in Table 4.3. Secondly, based on the estimated purity of 91.2 %, a calibration curve was built by correlating the UV\textsubscript{510} absorbance of standard samples with their concentration.

The calibration curve achieved is shown in Figure 4.2. The absorption coefficient obtained was 1,146.7 M\textsuperscript{-1}.cm\textsuperscript{-1} which is almost the same as the commonly used value of 1,150 M\textsuperscript{-1} cm\textsuperscript{-1} (Bielski and Thomas, 1987, Jiang and Lloyd, 2002).
### Table 4.3 Results of ferrate concentration analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>(C_0) (M)</th>
<th>(V_{\text{sample}}) (ml)</th>
<th>Abs</th>
<th>(C) (M)</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.54E-05</td>
<td>5</td>
<td>0.220</td>
<td>3.24E-05</td>
<td>91.5%</td>
</tr>
<tr>
<td>2</td>
<td>4.80E-05</td>
<td>3</td>
<td>0.178</td>
<td>4.36E-05</td>
<td>90.9%</td>
</tr>
<tr>
<td>Mean</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>91.2 ± 0.3 %</td>
</tr>
</tbody>
</table>

**Note:**
- \(C_0\) is the concentration estimated by dividing the weight of solid ferrate by the volume of the sample.
- \(C\) is the concentration calculated from the absorbance at the wavelength of 415 nm.
- Purity is the percentage ratio of \(C\) and \(C_0\).

![Figure 4.2 Calibration curve of ferrate at the wavelength of 510 nm](image)

\[ y = 1146.7x \]
\[ R^2 = 0.9999 \]
4.3.2 Effect of phosphate buffer on ferrate

4.3.2.1 Determining the precipitate quantity at pH 9.3

The purpose of measuring the precipitate of Fe(III) was to ascertain whether a phosphate buffer would be able to prevent Fe(III) precipitation.

The weight of precipitate from a specific amount of ferrate diluted (after 5 days in laboratory) in 1 litre of phosphate buffer (pH 9.3) was determined using 3 duplicate samples. The results are given in Table 4.4. In this table, the column entitled ‘theoretical Fe(OH)₃ concentration’ presents the amount of Fe(OH)₃ in the sample if all the reduced Fe(III) ions exist as Fe(OH)₃. The percentage of the measured precipitate to the theoretical Fe(OH)₃ value is presented in the column ‘percentage of precipitate’, simply verifying whether Fe(III) precipitates are in the form of Fe(OH)₃.

It can be seen from Table 4.4 that the amount of precipitate was almost zero at pH 9.3. It suggested that at this pH, all the reduced Fe(III) existed in soluble forms, perhaps Fe – phosphate complexes or Fe(OH)₄⁻. This finding therefore strongly supports the general assumption that Fe³⁺ ions are not precipitated in a phosphate buffer environment at pH 9.3.

Table 4.4 Results of precipitate determining test at pH 9.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ferrate concentration (µM)</th>
<th>Theoretical Fe(OH)₃ concentration (mg/l)</th>
<th>Measured Precipitate (mg/l)</th>
<th>Percentage of precipitate as Fe(OH)₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
<td>(d)</td>
<td>(e)</td>
</tr>
<tr>
<td>1</td>
<td>88.9</td>
<td>9.5</td>
<td>0.2 ± 0.1</td>
<td>2.1</td>
</tr>
<tr>
<td>2</td>
<td>88.9</td>
<td>9.5</td>
<td>≤ 0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>90.9</td>
<td>9.7</td>
<td>≤ 0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>90.9</td>
<td>9.7</td>
<td>0.1 ± 0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>182.8</td>
<td>19.6</td>
<td>0.2 ± 0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>182.8</td>
<td>19.6</td>
<td>≤ 0.1</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Note: value(e) = [value(d) ÷ value(c)] × 100
4.3.2.2 General effect of phosphate buffer with ferrate solution

The main purpose of this experiment was to investigate the effect of phosphate buffer on the precipitation of Fe(III) from ferrate solution at different pH values by measuring the amount of precipitate formed, observing the UV-visible absorbance of the solution and the molecular weight distribution of iron complexes in the phosphate buffer as well as determining the residual iron concentration.

The results of the quantification of Fe precipitate with pH are presented in Table 4.5, which is constructed in a similar layout to Table 4.4. The residual iron concentration is shown in Table 4.6 together with the UV254 and UV510 absorbance.

Figure 4.3 and Figure 4.4 display the UV-visible absorbance of non-filtered and filtered reduced samples of ferrate in phosphate buffer over the pH range from 4 to 9.3, respectively.

The molecular weight distribution of ferrate in phosphate buffer is shown in Figure 4.6 and its close-up look at pH 4 and 5 in comparison with HA is displayed in Figure 4.7.

Table 4.5 Precipitate from 100 μM ferrate in phosphate buffer

<table>
<thead>
<tr>
<th>pH</th>
<th>Measured Precipitate (mg/l)</th>
<th>Theoretical Fe(OH)₃ concentration (mg/l)</th>
<th>Theoretical FePO₄.H₂O concentration (mg/l)</th>
<th>Percentage as Fe(OH)₃ (%)</th>
<th>Percentage as FePO₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3</td>
<td>0.2 ± 0.1</td>
<td>10.7</td>
<td>16.9</td>
<td>1.9</td>
<td>1.3%</td>
</tr>
<tr>
<td>8.0</td>
<td>0.4 ± 0.1</td>
<td>10.7</td>
<td>16.9</td>
<td>3.7</td>
<td>2.6%</td>
</tr>
<tr>
<td>7.0</td>
<td>0.4 ± 0.1</td>
<td>10.7</td>
<td>16.9</td>
<td>3.7</td>
<td>2.6%</td>
</tr>
<tr>
<td>6.0</td>
<td>0.4 ± 0.1</td>
<td>10.7</td>
<td>16.9</td>
<td>3.7</td>
<td>2.6%</td>
</tr>
<tr>
<td>5.0</td>
<td>15.6 ± 0.1</td>
<td>10.7</td>
<td>16.9</td>
<td>145.8</td>
<td>103.3%</td>
</tr>
<tr>
<td>4.0</td>
<td>16.4 ± 0.1</td>
<td>10.7</td>
<td>16.9</td>
<td>153.3</td>
<td>108.6%</td>
</tr>
</tbody>
</table>

Note: value(e) = [value(b) ÷ value(c)] × 100; value(f) = [value(b) ÷ value(d)] × 100
Table 4.6 UV-visible absorbance at 254 and 510 nm, and residual Fe

<table>
<thead>
<tr>
<th>pH</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
<th>7.0</th>
<th>8.0</th>
<th>9.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV$_{254}$ (cm$^{-1}$)</td>
<td>0.003</td>
<td>0.004</td>
<td>0.392</td>
<td>0.437</td>
<td>0.358</td>
<td>0.369</td>
</tr>
<tr>
<td>UV$_{510}$ (cm$^{-1}$)</td>
<td>0</td>
<td>0</td>
<td>0.001</td>
<td>0.002</td>
<td>0.002</td>
<td>0.015</td>
</tr>
<tr>
<td>Fe (mg/l)</td>
<td>0</td>
<td>0.005</td>
<td>5.393</td>
<td>5.208</td>
<td>5.401</td>
<td>5.459</td>
</tr>
</tbody>
</table>

Table 4.5 shows that the quantity of Fe(III) precipitate was very low at pH 6 – 9.3 but substantial at pH 4 and 5. The calculated quantity of the theoretical precipitate indicates that Fe(III) may precipitate in the form of FePO$_4$ rather than Fe(OH)$_3$. The precipitate was almost zero at pH 9.3, which is consistent with the results shown in Table 4.4, and was a maximum at pH 4 (16.4 ± 0.1 mg). In conjunction with Table 4.6, it can be seen that at pH 4, all Fe ions were precipitated and filtered out of the solution. As a result, the residual Fe concentration was zero. Similarly, most of the Fe ions precipitated at pH 5, but were soluble at pH 6 to 9. This is confirmed by comparing Figure 4.3 and Figure 4.4, where the absorbance fell to zero by filtration at pH 4 and 5, but it was unchanged at pH between 6 and 9.

It is apparent that reduced Fe ions and complexes in the solution, either in the form of soluble or dispersed particles, had UV-visible light absorbance between 190 and 400 nm and their spectra (shown in Figure 4.3 and Figure 4.4) are analogous to that of HA (see Figure 3.1) and ferric chloride (see Figure 4.5). This implies that the assessment of treated HA concentration (by ferric coagulants) by UV$_{254}$ absorbance can be difficult owing to interference by residual Fe.

Figure 4.6 reveals that the molecular weight of Fe compounds in phosphate solution broadly ranged between 1,000 and 10,000 daltons at pH 7, 8 and 9, being comparable to that of HA. In contrast, at pH 4, 5 and 6 the molecular weight was concentrated at two distinct narrow ranges around 600 and 20,000 daltons, where the peak at pH 6 was obviously the highest. Thus, it is clear from these results that the use of UV absorbance to
observe changes in MW distribution of treated HA will suffer from interference by residual Fe (e.g. Figure 4.7).

Figure 4.3 UV-visible absorbance of reduced ferrate (100 µM) in phosphate buffer (non-filtered)
Figure 4.4 UV-visible absorbance of reduced ferrate (100 µM) in phosphate buffer (filtered)

Figure 4.5 UV-visible absorbance of 300 µM ferric chloride solution at pH 5
Figure 4.6 MW distribution of 100 µM ferrate in phosphate buffer compared to HA

Figure 4.7 MW distribution of 100 µM ferrate in phosphate buffer compared to HA
(close-up look at pH 4 and 5)
4.4 Chapter summary

- Phosphate buffer can prevent coagulation – precipitation of amorphous Fe(OH)$_3$ for a Fe dose up to 100 µM (5.6 mg Fe/l) at pH 6 – 9.

- At pH 4, Fe(III) was effectively insoluble and Fe precipitate can be filtered out by 0.2µm pore size membrane filter.

- At pH 5, Fe (III) was mostly precipitated.

- The molecular weight (MW) of Fe complexes in phosphate buffer mainly ranged from 1,000 to 10,000 daltons, which is similar to that of humic acid (HA). Thus the use of phosphate buffer can interfere in the measurement of the MW distribution of treated HA when Fe exists in the solution.

- The shape of the UV- visible spectrum of Fe(III) in both phosphate and non-phosphate buffer is similar to that of HA in the wavelength range between 190 to 590 nm, thus the use of phosphate buffer may invalidate the measurement of residual HA using UV$_{254}$ absorbance when Fe exists in the solution.
CHAPTER 5: RESULTS - COAGULATION OF KAOLIN SUSPENSION

5.1 Introduction

This chapter presents the outcome of the work undertaken to evaluate the coagulation performance of ferrate, in comparison to ferric chloride, with inert colloidal particles by dynamically observing the flocculation with kaolin suspension. The experiments were described in section 3.6, and included coagulation tests with 50 mg/l kaolin suspension, a repeat of this test in the presence of sodium sulphite, stoichiometric tests, a floc strength examination, and an investigation of the effect of phosphate buffer on the coagulation by ferrate.

5.2 Coagulation of 50 mg/l kaolin suspension

Using the apparatus combining a PDA and a gator jar, the coagulation of kaolin suspension for a given pH in the range of 4 to 8 was carried out for both ferrate and ferric chloride. The flocculation process was dynamically observed by the PDA and recorded to a computer via a data logger. The outputs are presented graphically in Figures 5.1 – 5.5, where the x-axes denote the elapsed time from the start of the test and y-axes represent the floc index of the process.

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 have been extracted from each PDA response; these are the FI max and T50. The variation of FI max with pH and Fe dose is illustrated in Figure 5.6 and the values of T50 are summarized in Table 5.1 and Table 5.2.

In addition to this qualitative assessment, turbidity removal (%TR) was used as a quantitative parameter to evaluate the process. In order to visualize the correlation of
Chapter 5: Coagulation of kaolin suspension
	hese two parameters, the combined charts of floc index and turbidity removal at a given pH for both coagulants were constructed and they are shown in Figures 5.7 – 5.16.

Generally, it can be seen from the Figures 5.1 - 5.5 that floc index and flocculation time were well related, whereby the higher the floc index, the shorter the $T_{50}$. Near the optimum doses, the floc index rose more sharply to reach the steady maximum values.

The results of the tests with the two chemicals show some similarities and significant differences in the coagulation behaviour between ferrate and ferric chloride.

Overall, good coagulation occurred at the high pH (6 – 8) and high dose (50 to 200 μM) region and poor coagulation was evident at low pH (4-5) and low doses (5 – 15 μM). The performance increased proportionally with dose. The coagulation performance of ferrate was not as good as ferric chloride, with generally higher values of $T_{50}$ (see Table 5.1 and Table 5.2) and lower values of FI max observed with ferrate (see Figure 5.6).
Looking at Figures 5.1 – 5.5, it is first apparent that substantial floc formation was observed with both chemicals at the highest Fe concentrations (50, 100, and 200 μM), at pH 6, 7 and 8. This is consistent with the so-called ‘sweep flocculation’ mechanism whereby kaolin particles are incorporated within amorphous ferric hydroxide precipitates. It appears, rather, that at lower pH values, 4 and 5 (in Figure 5.4 and Figure 5.5), and [Fe]>15 μM, no floc formation was evident with both chemicals. This is consistent with previous studies (Amirtharajah and O'Melia, 1990), which suggested that under these conditions the coagulant exists primarily as charged iron hydrolysis species (e.g. Fe(OH)\(^2^+\), Fe(OH)\(_2^+\)) that re-stabilize the kaolin suspension. However, at lower doses (5, 10 and 15 μM), the balance of charges is such that some degree of destabilization occurs, leading to coagulation. Flocculation was seen over the whole range of low dose (5 -15
µM) for ferrate, but the range was narrower (pH 4: 5 – 10 µM; pH 5: 5 – 7.5 µM) for ferric chloride. These two coagulation zones can be seen clearly in Figure 5.6.

**Figure 5.2 Influence of chemical dose on floc growth at pH 7**

In the ‘sweep’ coagulation zone, it is first apparent that coagulation tends to occur at a broader range of doses for ferric chloride compared to ferrate; for example at pH 7, coagulation was evident at the lower concentration of 7.5 µM for ferric chloride compared to 15 µM for ferrate (Figure 5.2). It appears, also, that the maximum floc index values of ferric chloride were a great deal larger (see Figures 5.1 -5.3), and T50 values were considerably shorter than ferrate (shown in Tables 5.1 and 5.2). With ferric chloride the lowest T50 value was 66 s, corresponding to 200 µM Fe at pH 6, whilst for ferrate the lowest T50 value was 240 s, corresponding to 200 µM Fe at pH 7. Moreover, the FI max values for the two cases were quite different (viz. 4.91 ferric chloride, 1.44 ferrate), indicating significant differences in the nature of the flocculation process, and the
conclusion that overall coagulation performance by ferrate was inferior to that with ferric chloride.

As it can be seen from Figure 5.3, coagulation effects were observed for both ferrate and ferric chloride at almost all doses (5 μM to 200 μM) at pH 6, except for ferrate at 5 and 7.5 μM. 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. However, the floc formation by ferrate was insignificant in comparison to ferric chloride as most maximum floc index values were less than 1 for ferrate, whilst those of ferric chloride were greater than 1 and up to 4.90.

Figure 5.3 Influence of chemical dose on floc growth at pH 6
Clear re-stabilization due to an overdose effect can be seen in Figure 5.4b as no floc formation was found at doses higher than 5 µM of ferric chloride at pH 5. This is consistent with the dosage-mechanism in coagulation of ferric chloride which is illustrated in Figure 2.8. However, with ferrate, the over dose effect occurred at a higher dose (15 µM) as the highest FI max was found at the dose of 12.5 µM (see Figure 5.4a).
In Figure 5.5, it can be seen that at pH 4 flocculation occurred for both coagulants in the range of low doses and their performances were similar to each other in terms of FI max and T₅₀. For ferric chloride, flocculation was evident at the dose of 5 and 7.5 µM, and negligible at 10µM. A max FI was found at 5 µM and an over dose effect appeared at 7.5 µM. In contrast, the overdose effect was observed at 10 µM for ferrate and floc formed over a wider range of doses (5 – 15 µM). The optimum FI max with ferric chloride was slightly greater that with ferrate (viz. 0.44 ferric chloride and 0.40 ferrate), conversely the optimum T₅₀ with ferric chloride was larger than ferrate (viz. 411 s ferric chloride and 257 s ferrate).
Figure 5.6 Effect of dose and pH on max floc index
Table 5.1 $T_{50}$ (s) of flocculation processes by ferrate

<table>
<thead>
<tr>
<th>Fe Dose (µM)</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>411 ± 2</td>
<td>348 ± 2</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>7.5</td>
<td>299 ± 6</td>
<td>456 ± 0</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>10</td>
<td>161 ± 12</td>
<td>196 ± 22</td>
<td>953 ± 1</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>12.5</td>
<td>194 ± 29</td>
<td>694 ± 207</td>
<td>729 ± 40</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>15</td>
<td>X</td>
<td>159 ± 67</td>
<td>512 ± 1</td>
<td>1303 ± 48</td>
<td>X</td>
</tr>
<tr>
<td>50</td>
<td>X</td>
<td>X</td>
<td>486 ± 18</td>
<td>552 ± 18</td>
<td>1584 ± 174</td>
</tr>
<tr>
<td>100</td>
<td>X</td>
<td>X</td>
<td>129 ± 9</td>
<td>348 ± 12</td>
<td>748 ± 21</td>
</tr>
<tr>
<td>200</td>
<td>X</td>
<td>X</td>
<td>261 ± 57</td>
<td>240 ± 12</td>
<td>490 ± 60</td>
</tr>
</tbody>
</table>

Note: X denotes no coagulation

Table 5.2 $T_{50}$ (s) of flocculation processes by ferric chloride

<table>
<thead>
<tr>
<th>Fe Dose (µM)</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>257 ± 12</td>
<td>569 ± 9</td>
<td>394 ± 15</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>7.5</td>
<td>344 ± 2</td>
<td>X</td>
<td>248 ± 36</td>
<td>780 ± 0</td>
<td>X</td>
</tr>
<tr>
<td>10</td>
<td>X</td>
<td>X</td>
<td>287 ± 13</td>
<td>693 ± 74</td>
<td>X</td>
</tr>
<tr>
<td>12.5</td>
<td>X</td>
<td>X</td>
<td>307 ± 12</td>
<td>355 ± 11</td>
<td>X</td>
</tr>
<tr>
<td>15</td>
<td>X</td>
<td>X</td>
<td>268 ± 2</td>
<td>338 ± 9</td>
<td>1212 ± 30</td>
</tr>
<tr>
<td>50</td>
<td>X</td>
<td>X</td>
<td>549 ± 141</td>
<td>276 ± 48</td>
<td>549 ± 153</td>
</tr>
<tr>
<td>100</td>
<td>X</td>
<td>X</td>
<td>318 ± 6</td>
<td>147 ± 45</td>
<td>126 ± 18</td>
</tr>
<tr>
<td>200</td>
<td>X</td>
<td>X</td>
<td>66 ± 5</td>
<td>84 ± 7</td>
<td>90 ± 12</td>
</tr>
</tbody>
</table>

Note: X denotes no coagulation

In general, it is clear from the results shown in Figures 5.7 – 5.16 that those points which have a high FI max also have a high turbidity removal. Turbidity removal percentages at non-flocculation points were 2.2 as the kaolin suspension demonstrated a minor degree of self-precipitation.
Consistent with the floc index values, turbidity removal was high with coagulation corresponding to ‘sweep zone’ and low corresponding to ‘charge zone’ for both coagulants. For ferrate, turbidity removal ranged between 75.6 and 84.4 % at pH 7 and 8, whilst a lower turbidity removal (22.2 – 71.1 %) was found with the poorer coagulation corresponding to the ‘charge zone’ (see Figure 5.13 and Figure 5.15). A similar behaviour was observed with ferric chloride, where the turbidity removal ranged from 72.9 to 92.2 % in the ‘sweep zone’, decreased to 22.2 – 73.3 % in the ‘charge zone’.

The highest turbidity removal was 84.4 % for ferrate and 92.2% for ferric chloride, both corresponding to the optimal coagulation (highest FI max achieved), viz. 200 µM - pH 8 and 200 µM – pH 7, respectively.

It can be seen from Figure 5.12 that pH 6 seems to be the optimal pH for coagulation with ferric chloride as high turbidity removal was achieved over the whole range of Fe dosage tested (5 – 200 µM). The turbidity removal with ferric chloride at low Fe doses (5 – 15 µM) was even higher than that of ferrate at high Fe doses (50 – 200 µM). In contrast, the coagulation with ferrate was considerably poorer at pH 6 except at the Fe dose of 200 µM.

Although the T₅₀ values increased with pH for ferrate in the ‘sweep zone’, suggesting poorer coagulation, the floc index and turbidity removal increased. As a result, the best coagulation performance of ferrate in terms of floc index and turbidity removal was achieved at pH 8 and at high Fe doses (50 -200 µM), fully corresponding to the ‘sweep zone’.

The optimal pH for coagulation with ferrate at low doses seems to be pH 4, where higher floc index and turbidity removal were achieved compared to pH 5. In addition, there was some evidence of superior coagulation effects with ferrate at pH 4 and 5 at low Fe doses (5 – 15 µM) from Figures 5.13 – 5.16 in comparison to ferric chloride. The reason for this might be that stronger restabilisation effects were seen with ferric chloride, causing flocculation to be diminished or extinguished.
Figure 5.7 Variation of FI max and turbidity removal with Fe dose for ferrate at pH 8.0

Figure 5.8 Variation of FI max and turbidity removal with Fe dose for ferric chloride at pH 8.0
Figure 5.9 Variation of FI max and turbidity removal with Fe dose for ferrate at pH 7.0

Figure 5.10 Variation of FI max and turbidity removal with Fe dose for ferric chloride at pH 7.0
Chapter 5: Coagulation of kaolin suspension

Figure 5.11 Variation of FI max and turbidity removal with Fe dose for ferrate at pH 6.0

Figure 5.12 Variation of FI max and turbidity removal with Fe dose for ferric chloride at pH 6.0
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Figure 5.13 Variation of FI max and turbidity removal with Fe dose for ferrate at pH 5.0

Figure 5.14 Variation of FI max and turbidity removal with Fe dose for ferric chloride at pH 5.0
Figure 5.15 Variation of FI max and turbidity removal with Fe dose for ferrate at pH 4.0

Figure 5.16 Variation of FI max and turbidity removal with Fe dose for ferric chloride at pH 4.0
5.3 Coagulation of 50 mg/l kaolin suspension with sodium sulphite

The data in Table 5.1 showed a general trend whereby $T_{50}$ values increased with coagulation pH and decreased with Fe dose. However it is well-established that the degradation rate of ferrate in water is inversely proportional to pH and directly proportional to Fe dose. The similarity of the change of $T_{50}$ and the inversion of degradation rate of ferrate in aqueous solution with pH and Fe dose is illustrated in Figure 5.17, where k values (degradation rate of 250 µM ferrate in water, s$^{-1}$) were those reported by Li et al. (2005). It is therefore evident that the degree of coagulation of kaolin with ferrate for ‘sweep zone’ conditions correlates well with the degradation rate of ferrate in water.

![Figure 5.17 Variation of 1/k and $T_{50}$ with pH](image)

Tests involving the addition of sodium sulphite were carried out to ascertain whether the inferior coagulation performance of ferrate compared to ferric chloride, corresponding to the ‘sweep’ zone, was because of the slow formation of ferric species from the ferrate decomposition in water. The results for pH 8, 7 and 6 are shown in Figures 5.18 – 5.20,
where the figures denoted by (a) repeated the results of coagulation tests by ferrate without sodium sulphite, and the figures denoted by (b) present the new results with sodium sulphite added under identical conditions.

**Figure 5.18 Flocculation of 50 mg/l kaolin by ferrate with sodium sulphite at pH 8**

It is evident from Figures 5.18 – 5.20 that there were marked increases in the slope and steady maximum floc index for all of the flocculation curves with sodium sulphite compared to those without. In other words, significant improvements in coagulation performance in terms of FI max and T50 were observed when sodium sulphite had been used as a reducing agent for the coagulation by ferrate. These coagulation performances of ferrate (with sodium sulphite) are very much comparable to those of ferric chloride (shown in Figures 5.1 -5.3).
Chapter 5: Coagulation of kaolin suspension

It therefore seems highly reasonable to assume that the slow decomposition of ferrate in water at high pH (6 - 8) is the cause of the inferior performance by ferrate in comparison to ferric chloride. It is reasonably expected that, in real waters, which contain reducing substances (e.g. NOM), the coagulation performance of ferrate should be much better than the kaolin results without sodium sulphite.

Figure 5.19 Flocculation by ferrate with sodium sulphite at pH 7
Chapter 5: Coagulation of kaolin suspension

5.4 Dose-stoichiometry test

This test was carried out at pH 4, where it is believed that coagulation by charge interaction is dominant, with model water containing 100 mg/l kaolin in an attempt to observe a dose-stoichiometric effect, that is to say the optimum dose is double when the colloid concentration is doubled. The results together with those corresponding to the ‘charged zone’ for 50 mg/l suspension are presented in Figure 5.21 and Figure 5.22 in terms of FI max.

It is normally expected that the optimum dose is doubled because the negative charge of the system increases proportionally with the colloid concentration. However, for both kaolin concentrations, the optimum doses lay between a narrow range of 5 - 10 μM, and
2.5 – 7.5 μM for ferrate and ferric chloride respectively. It is difficult to detect the optimum points without supporting zeta potential information under these conditions.

**Figure 5.21** FI max of coagulation with ferrate at pH 4

**Figure 5.22** FI max of coagulation with ferric chloride at pH 4
Nevertheless, there was some evidence of charge stoichiometry that the effective coagulation with 50 mg/l kaolin suspension occurred over a narrower range of Fe dose than with 100 mg/l kaolin suspension (see Figure 5.21 and Figure 5.22). This means the suspension with the lower kaolin concentration needed less counter-ions than the higher concentration to neutralize its charge, resulting in overdose effects that suppressed the coagulation at higher Fe doses.

### 5.5 Floc Strength Test

Figure 5.23 presents the results of the floc strength tests with ferrate and ferric chloride under identical conditions corresponding to a high degree of coagulation (i.e. 200 μM at pH 7). From this Figure, it can be seen that by rapidly increasing the stirring rate from 50rpm (50 s⁻¹) to the higher rate of 400rpm (600 s⁻¹), there was an immediate and rapid decrease in FI, corresponding to a rapid breakage of flocs. The duration of high rate stirring was 120 s from the 400th second to the 520th second. When the stirring speed was subsequently reduced back to 50rpm (50s⁻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 (FI₁), broken (FI₂) and reformed (FI₃) 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 (2004) as:

\[
\text{Strength factor} = \frac{\text{FI}_2}{\text{FI}_1} \cdot 100
\]

\[
\text{Recovery factor} = \left[\frac{\text{FI}_3 - \text{FI}_2}{\text{FI}_1 - \text{FI}_2}\right] \cdot 100
\]

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 5.23 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.

**Figure 5.23 Result of the floc strength test at pH 7 and dose 200 μM**
5.6 Coagulation of kaolin suspension in phosphate buffer

In some studies concerning the oxidation performance of ferrate the complicating influence of coagulation effects are minimized by the use of a phosphate buffer at high pH (pH 9). It is assumed that Fe(III) forms soluble complexes with phosphate, and this phenomena was investigated briefly in this study and the results (presented in section 4.3.2) confirmed that phosphate buffer can prevent the precipitation of reduced iron species for a Fe dose up to 100 µM at pH 6 – 9.

Therefore, it is expected that no significant coagulation occurs with Fe coagulants in phosphate buffer environment at the pH range of 6 to 9. To verify this hypothesis, coagulation tests were carried out with both ferrate and ferric chloride in phosphate buffer environment. The results are summarised in Figures 5.24 – 5.26.

The results showed that the effectiveness of the phosphate in preventing coagulation effects at all pH values, with the exception of pH 4 where some solid phase precipitation is evident. A very similar behaviour was observed with the use of ferric chloride (see Figure 5.26). The flocculation at pH 4 was more substantial than that formed in boric acid buffer at the same pH in terms of FI max for both coagulants.

![Graph showing flocculation time vs floc index for different pH values](image)

**Figure 5.24 Coagulation of 50 mg/l kaolin with 200 µM ferrate in phosphate buffer**
Chapter 5: Coagulation of kaolin suspension

Figure 5.25 Coagulation of 50 mg/l kaolin with 200 µM ferric chloride in phosphate buffer

Figure 5.26 Coagulation of 50 mg/l kaolin with ferrate and ferric chloride at pH 4 in phosphate buffer
5.7 Chapter summary

- In general, for the kaolin suspension (assumed to be an inert colloid system) ferrate demonstrated broadly similar coagulation characteristics to ferric chloride with regard to the influence of pH and Fe dose.

- Floc formation with ferrate was relatively rapid and substantial at neutral pH and moderate Fe concentrations, corresponding to ‘sweep coagulation’, while at low pH (4 and 5) there was some evidence of charge destabilization and charge stoichiometry.

- There was no significant difference in the strength of the flocs formed by each coagulant under optimal conditions.

- The principal differences between ferrate and ferric chloride as coagulants were 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 and sometimes less extensive than with ferric chloride.

- It was discovered that the reason for the difference in the magnitude and rate of floc growth was mainly the slow formation of Fe(III) species at neutral to high pH owing the low degradation rate of ferrate in aqueous solution at these pH.

- There was no coagulation with both coagulants at pH 5 to 8 in phosphate buffer, showing that phosphate buffer can prevent the precipitation from Fe(III) for pH 5 - 8.
CHAPTER 6: RESULTS - COAGULATION OF HUMIC ACID COLLOIDAL SYSTEMS

6.1 Introduction

This chapter reports the results of the investigation of comparative oxidation and coagulation effects of ferrate in the treatment of HA using the PDA apparatus and SEC techniques as described in chapter 3. This chapter also compares the performance of ferrate with ferric chloride. Accordingly, this chapter is structured to illustrate the interaction between ferrate and HA in comparison to ferric chloride as a reference Fe coagulant under the same conditions.

6.2 Coagulation test with model water containing humic acid

6.2.1 Coagulation of HA model water

The interaction between ferrate and HA was investigated extensively in comparison with ferric chloride as a reference ferric coagulant. Using the coagulation test method (see section 3.5), the coagulation behaviour of HA in model water (20 mg/l and 10 mg/l HA) at a given pH in the range of 4 – 7 was conducted in order to determine the optimum dose as Fe of both ferrate and ferric chloride. The coagulation performances of both coagulants with 20 mg/l HA are shown in Figures 6.1 – 6.8, where the x-axes denote the elapsed time from the start of the test (floculation time) and the y-axes present the floc index of the process. The small numbers at the tips of the downward arrows are the T50 values of the corresponding curves expressed in seconds. The results in terms of the maximum floc index and DOC removal by ferrate and ferric chloride are presented in Figures 6.9 – 6.16, where x-axes denote Fe dose, 1st and 2nd y-axes present floc index max and DOC removal respectively. Based on these results, the optimal Fe dose and the corresponding dose stoichiometry were calculated and shown in Tables 6.1 and 6.2.
Chapter 6: Coagulation of humic acid colloidal systems

Figure 6.1 Coagulation of 20 mg/l HA in model water with ferrate at pH 4

Figure 6.2 Coagulation of 20 mg/l HA in model water with ferric chloride at pH 4
Figure 6.3 Coagulation of 20 mg/l HA in model water with ferrate at pH 5

Figure 6.4 Coagulation of 20 mg/l HA in model water with ferric chloride at pH 5
Chapter 6: Coagulation of humic acid colloidal systems

Figure 6.5 Coagulation of 20 mg/l HA in model water with ferrate at pH 6

Figure 6.6 Coagulation of 20 mg/l HA in model water with ferric chloride at pH 6
Chapter 6: Coagulation of humic acid colloidal systems

Figure 6.7 Coagulation of 20 mg/l HA in model water with ferrate at pH 7

Figure 6.8 Coagulation of 20 mg/l HA in model water with ferric chloride at pH 7
Figure 6.9 Coagulation results of model water containing (a) 20 mg/l HA, and (b) 10 mg/l HA with ferrate at pH 4
Figure 6.10 Coagulation results of model water containing (a) 20 mg/l HA, and (b) 10 mg/l HA with ferric chloride at pH 4
Figure 6.11 Coagulation results of model water containing (a) 20 mg/l HA, and (b) 10 mg/l HA with ferrate at pH 5
Figure 6.12 Coagulation results of model water containing (a) 20 mg/l HA, and (b) 10 mg/l HA with ferric chloride at pH 5
Figure 6.13 Coagulation results of model water containing (a) 20 mg/l HA, and (b) 10 mg/l HA with ferrate at pH 6
Figure 6.14 Coagulation results of model water containing (a) 20 mg/l HA, and (b) 10 mg/l HA with ferric chloride at pH 6
Figure 6.15 Coagulation results of model water containing (a) 20 mg/l HA, and (b) 10 mg/l HA with ferrate at pH 7
Figure 6.16 Coagulation results of model water containing (a) 20 mg/l HA, and (b) 10 mg/l HA with ferric chloride at pH 7
Table 6.1 Optimal Fe dose (mgFe/mgHA)

<table>
<thead>
<tr>
<th>pH</th>
<th>Ferrate</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 mg HA/l</td>
<td>0.56</td>
<td>0.42</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>10 mg HA/l</td>
<td>0.21</td>
<td>0.35</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Table 6.2 Optimal dose stoichiometry (mgFe/mgC removed)

<table>
<thead>
<tr>
<th>pH</th>
<th>Ferrate</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 mg HA/l</td>
<td>2.8</td>
<td>2.2</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>10 mg HA/l</td>
<td>1.1</td>
<td>1.9</td>
<td>6.6</td>
</tr>
</tbody>
</table>

The results presented in Figures 6.1 – 6.8 show that as long as significant coagulation occurred the floc index rises rapidly with flocculation time until it reached a maximum value (FI max) and subsequently leveled off or decreased slightly. The reason for the decrease of FI values is that the large flocs could not be maintained in suspension at a low mixing rate leading consequently to intermittent settling and re-dispersion. Figures 6.1 – 6.8 also reveal that for both coagulants the coagulation performance in terms of floc growth increased with Fe dose to an optimal dose and then decreased beyond this optimal point. Significant coagulation did not occur at low or very high doses. The comparative FI results for ferrate were substantially different to those for ferric chloride. In the majority of cases the FI max values for ferrate were
greater than those for ferric chloride. In other words, greater coagulation performance in terms of floc growth was evident for ferrate. It further appears, at low pH, that the optimal doses in terms of FI max were much greater than those in terms of T50, for example for ferrate at pH 4 (see Figure 6.1) T50 was 1110 s at 200 µM (optimal dose for FI max), but the optimal T50 was 145s corresponding to the Fe dose of 50 µM. This is because the magnitude of the floc is proportional to the Fe doses, however, at low pH charge restabilisation occurs at higher Fe dose, leading to slower floc formation.

The two principal conclusions that may be drawn from Figures 6.9 – 6.16 are firstly that while the value of the FI is not an absolute quantity, it is a relative measure of the size and density of coagulant flocs, where the results show a much greater degree of coagulation/flocculation for ferrate at Fe doses greater than (up to double) the optimal Fe dose in comparison to ferric chloride. Secondly, it is evident that in contrast to the observed behaviour in terms of maximum floc growth, the resulting HA removal (as % DOC removal) with ferrate was found to be slightly inferior to that with ferric chloride. For ferrate the HA removal kept increasing with Fe doses despite the FI decreasing beyond the optimal Fe dose (most clearly shown in Figure 6.13). It is surmised that the difference in the coagulation behaviour of ferrate and ferric chloride is attributed to the oxidation effects of ferrate.

It appears further that the maximum DOC removal was evident at the doses corresponding to the maximum floc growth (FI max) rather than the optimal doses in terms of T50. The optimal Fe dose and the corresponding values of FI max and DOC removal for 20 mg/l HA model water are presented comparatively in Table 6.3 and Table 6.4.

It is worth noting that at the Fe doses beyond the optimal points (e.g. at 100 µM ferric chloride, pH 5: Figure 6.12a), where no significant floc growth was observed, the DOC removal was still high (sometimes highest). Similarly, at pH 7, although flocculation did not occur at Fe dose of 400 µM for ferrate, and 200 µM for ferric chloride, the DOC removal was still very high (see Figure 6.15). This is because the ion-humic complex aggregates were removable by the 0.45 µm filter membrane thus the HA (DOC) was effectively removed by this filtration process, although the aggregates were not sufficiently large to be detectable by the PDA. This phenomenon
had been recognised in some previous studies (Narkis and Rebhun, 1975, Chadik and Amy, 1983). It was reported that the coagulation of HS resulted in a colloidal sol which could not be removed by sedimentation due to its very slow settling velocity, but was effectively removed by centrifugation or membrane filtration.

### Table 6.3 Coagulation of 20 mg/l HA with ferrate

<table>
<thead>
<tr>
<th>pH</th>
<th>Optimal Fe dose (µM)</th>
<th>FI max</th>
<th>DOC removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>200</td>
<td>0.45</td>
<td>86.1</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>0.53</td>
<td>84.3</td>
</tr>
<tr>
<td>6</td>
<td>225</td>
<td>1.50</td>
<td>79.8</td>
</tr>
</tbody>
</table>

### Table 6.4 Coagulation of 20 mg/l HA with ferric chloride

<table>
<thead>
<tr>
<th>pH</th>
<th>Optimal Fe dose (µM)</th>
<th>FI max</th>
<th>DOC removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>62.5</td>
<td>0.35</td>
<td>88.6</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>0.52</td>
<td>89.2</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>0.56</td>
<td>91.9</td>
</tr>
</tbody>
</table>

At pH 4 and 5, the interaction between hydrolysed Fe species and HA is nevertheless predominantly charge neutralization which is characterised with an optimal Fe dose, and a well-defined Fe/HA mass stoichiometry. These phenomena can be seen in Figure 6.12a and Figure 6.12b in terms of FI response (maximum floc index), where a clear optimal Fe dose of 0.28 mgFe/mgHA was derived for ferric chloride with both HA concentrations of 20 mg/l and 10 mg/l (shown in Table 6.1). This corresponds to a dose stoichiometry at pH 5 of 1.4 mgFe/mgC removed (see Table 6.2). Similarly, as can be seen in Table 6.1, the dose stoichiometry at pH 4 for ferric chloride with 20 mg/l and 10 mg/l HA model water were slightly different, viz. 0.9 and 0.7 mgFe/mgC removed, respectively. Furthermore, the optimal Fe dose for ferric chloride decreased from 0.28 to 0.18 mgFe/mgHA when the pH decreased from 5 to 4. The reason for this is that the charge of HA model water is believed to become less negative as pH
decreases, as reported by Duan and Gregory (2003), thus it requires a lower dose of coagulants to achieve maximum FI.

In contrast to ferric chloride, a dose stoichiometry is not clear for ferrate (see Table 6.1 and Table 6.2). Even conversely, the optimal Fe dose increased from 0.42 mgFe/mgHA to 0.56 mgFe/mgHA as the pH changed from 5 to 4. This phenomenon indicates that the charge of the HA suspension might not be less negative as pH decreases from 5 to 4 in the case of ferrate, possibly as a consequence of ferrate oxidation effects; this is discussed in chapter 7.

Comparing Figure 6.9a and Figure 6.10a shows that coagulation performance of 20 mg/l HA at pH 4 with ferrate over the studied Fe dose range was superior in terms of floc growth (viz. 0.45 for ferrate; 0.38 for ferric chloride), but inferior in regard to HA removal (87.7 % for ferrate; 88.6 % for ferric chloride) in comparison with ferric chloride. The coagulation range for ferrate was much broader than for ferric chloride, viz. 75 – 200 µM compared to 75 – 125 µM.

The results given in Figure 6.11 and Figure 6.12 show that the comparative FI values for ferrate were substantially different to those for ferric chloride at pH 5. For both HA concentrations the optimal dose of ferrate, corresponding to a 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 (i.e. for the charge restabilisation region). In general, the degree of coagulation/floculation for ferrate was much greater than for ferric chloride. In contrast, the resulting DOC removal with ferrate was found to be slightly inferior to that with ferric chloride. While the absolute removal of organic carbon was high in both cases (viz. 85 % for ferrate; 90% for ferric chloride) the ferrate performance was consistently less than ferric chloride over the complete range of Fe doses studied.

Figure 6.13a exhibits a sharp increase in FI max values for ferrate, whereas the FI max with ferric chloride enhanced slightly (as shown in Figure 6.14a). The effective coagulation range also increased with pH, from 75 – 200 µM Fe (pH 4 and 5) to 225 – 350 µM (pH 6) for ferrate, and 37.5 – 125 µM to 150 – 400 µM for ferric chloride. The movement in effective range indicates that the coagulation mechanism of HA by Fe coagulants at pH 6 was different to that at pH 4 and 5.
Comparing the results for ferric chloride at pH 5 (Figure 6.12) and pH 7 (Figure 6.16) it can be seen that a much greater Fe dose (> 300 µM) was required to achieve the maximum floc growth at pH 7 than at pH 5 (50 µM), and the narrow Fe dose range for coagulation at pH 5 was not evident at pH 7. Comparison of the coagulation of 10 mg/l HA by ferrate with ferric chloride at pH 7 (see Figure 6.15b and 6.16b), 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 other pH values (4, 5 and 6). An explanation for this may be that the oxidation effects of ferrate on the organic macro-molecules at pH 7 were greater than at lower pH values, leading to a much greater Fe dose to achieved equivalent coagulation.

### 6.2.2 Floc strength

The strength of ferrate-humic and ferric-humic flocs was assessed by observing their breakage and reformation via the FI response to a sudden increase in mean velocity gradient using the Gator jar. The tests were carried out at optimal doses of pH 6 because substantial flocs had been achieved with medium Fe doses under these conditions; that is, 225 µM Fe with ferrate and 300 µM Fe with ferric chloride. In these tests the coagulation process was carried out as previously until the steady maximum FI was reached, and then a higher mixing rate (300 rpm, 600 s⁻¹) was applied for 2 min. Subsequently, the mixing rate was reduced back to the normal mixing condition (50 rpm) to provide an opportunity for the flocs to recover from the breakage.

Figure 6.17 summarises the results from the floc strength test in which the variations of floc index by coagulation of ferrate and ferric chloride are plotted against the flocculation time. Based on these results, the strength factor and recovery factor of ferrate-humic and ferric-humic floc were calculated (shown in Table 6.5).
Table 6.5 Strength and recovery factors of ferrate-humic and ferric-humic flocs

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>FI₁</th>
<th>FI₂</th>
<th>FI₃</th>
<th>Strength factor¹</th>
<th>Recovery factor²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrate</td>
<td>1.8</td>
<td>0.32</td>
<td>0.6</td>
<td>18%</td>
<td>19%</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>0.59</td>
<td>0.14</td>
<td>0.18</td>
<td>24%</td>
<td>9%</td>
</tr>
</tbody>
</table>

¹ : FI₂/FI₁ ; ² : FI₃-FI₂/FI₁-FI₂

It can be seen in Figure 6.17 that both ferrate and ferric chloride flocs exhibited similar responses to the sudden application of a greater shear stress: the FI diminished sharply due to the impact of shear stress and a minor degree of recovery when the shear stress was reduced. It is worth noting that the recovery of the flocs had not been seen in the case of kaolin flocs. However, the recovery factor of ferrate-humic flocs was significantly greater than that of ferric-humic flocs. The difference in recovery factors of the two coagulants indicates that there might be a difference in the nature of the two flocs. Although the strength factor of ferric-humic floc was slightly higher than that of ferrate-humic floc, this may not be an accurate representation of the true strengths of the flocs. This is because both flocs reduced to a similar FI level during
breakage, but the absolute value of ferrate floc was much higher, leading to a smaller relative ratio.

### 6.3 Test with upland coloured water

Tests were carried out using samples of raw water supplied from an upland reservoir and the water quality at the time of sampling had a DOC of 11mgC/l and a UV$\text{254}$ absorbance of 50.8 m$^{-1}$, giving a SUVA of 4.6 l/mg.m. Because of the limited amount of the raw water sample, the tests were conducted at pH 5 only, which is widely chosen practically for the removal HS by coagulation.

Figure 6.18 and Figure 6.19 present the PDA outputs for the coagulation of raw water with ferrate and ferric chloride respectively, in which the variation of floc index is plotted against flocculation time. The resulting HA removal (% DOC removal) is shown in conjunction with the corresponding FI max values in Figure 6.20 and Figure 6.21.

Comparing Figure 6.18 and Figure 6.19 shows that both chemicals had a similar coagulation range, however the flocculation by ferric chloride declined substantially at Fe doses greater than 350 µM due, it is assumed, to restabilisation effects, whilst a similar decline in flocculation for ferrate was not significant. The results of the tests shown in Figure 6.20 and 6.21 indicate 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. 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 as observed in the previous tests with humic acid. One reason for the slightly inferior results with ferrate is that there may be a greater quantity of smaller molecular weight organic compounds present in the treated water compared to the conventional ferric salt due to the oxidation effects of ferrate.
Chapter 6: Coagulation of humic acid colloidal systems

Figure 6.18 Coagulation of raw water with ferrate at pH 5

![Graph showing coagulation of raw water with ferrate at pH 5]

Figure 6.19 Coagulation of raw water with ferric chloride at pH 5

![Graph showing coagulation of raw water with ferric chloride at pH 5]
Figure 6.20 Coagulation performance of ferrate with raw water at pH 5

Figure 6.21 Coagulation performance of ferric chloride with raw water at pH 5
6.4 Oxidation of humic acid

The previous investigation of the effects of 5 mM phosphate buffer on ferrate (see section 4.3.2) confirmed that the phosphate buffer can prevent coagulation – precipitation of amorphous Fe(OH)₃ at Fe doses up to 100 µM over the pH range from 6 to 9. Further study of the influence of phosphate buffer on the coagulation of kaolin suspension with ferrate and ferric chloride (see section 5.6) confirmed the effectiveness of 5 mM phosphate buffer in preventing coagulation over the pH range from 5 to 9. It was therefore decided to use 5 mM phosphate buffer to perform an oxidation reaction between ferrate and HA where no coagulation was expected, in order to study the direct effects of any oxidation on the nature of the HA.

The oxidation tests using 20 mg/l HA model water were carried out following the coagulation procedure described in section 3.5.3 in which 2 litres of water sample (also buffered with 1 mM bicarbonate) were brought into contact with ferrate in the Gator jar under a sequence of mixing conditions for 30 min. The floc index was observed by the PDA to verify if there was any significant coagulation. The results as DOC removal are summarised in Table 6.6.

Similar tests were conducted using upland coloured water and the results are presented in Table 6.7.

Table 6.6 DOC removal from model water by oxidation with ferrate

<table>
<thead>
<tr>
<th>Fe dose</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 µM</td>
<td>61.0% *</td>
<td>19.3% **</td>
<td>14.4%</td>
<td>1.0%</td>
</tr>
<tr>
<td>200 µM</td>
<td>65.8% *</td>
<td>18.1% **</td>
<td>14.9%</td>
<td>3.0%</td>
</tr>
<tr>
<td>300 µM</td>
<td>66.0% *</td>
<td>30.7% **</td>
<td>25.2%</td>
<td>6.5%</td>
</tr>
</tbody>
</table>

*: significant coagulation was detected at these points.

**: minor coagulation was expected but not observed.
Chapter 6: Coagulation of humic acid colloidal systems

Table 6.7  DOC removal from upland coloured water by oxidation with ferrate

<table>
<thead>
<tr>
<th>Fe dose</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
<th>pH 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 µM</td>
<td>*</td>
<td>31.6%**</td>
<td>20.8%</td>
<td>12.1%</td>
<td>9.9%</td>
</tr>
<tr>
<td>200 µM</td>
<td>*</td>
<td>35.5%**</td>
<td>22.9%</td>
<td>13.3%</td>
<td>11.4%</td>
</tr>
<tr>
<td>300 µM</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

*: significant coagulation was detected at these points – no subsequent analysis of water quality.
**: minor coagulation was expected but not observed.

The results given in Table 6.6 and Table 6.7 show the interaction between ferrate and HS in both model water and raw water involved direct oxidation as expected, except at pH 4 where the presence of coagulation effects confused the results. Flocculation was found with raw water at the Fe dose of 300 µM which was not evident with model water. This may be because that raw water contained some turbidity and these particles acted as nuclei that boosted the flocculation process. Thus the raw water was more likely to be coagulated than model water. It is well accepted that the removal of organics by ferrate oxidation is proportional to the Fe dose, which explains the increases of DOC removal with Fe dose in the range of 100 µM to 300 µM, as observed with both model water and raw water.

It is noticeable that the effectiveness of organics mineralization by direct oxidation with ferrate (measured as DOC removal) decreased with increasing pH. This phenomenon was found with both model and raw water. An explanation for this is that the oxidation effects of ferrate on the organics are greater at lower pH as the oxidation potential of ferrate decreases with pH.

It is clear that the effectiveness of organic removal by oxidation with ferrate was very much inferior to that by coagulation with ferric chloride, and by oxidation/coagulation with ferrate at the same Fe dose and pH. The results at pH 5 and at the Fe dose of 100 µM showed that organics removal by the combined effect of coagulation and oxidation (Figure 6.11a) was substantially greater than that by solely oxidation (Table 6.6), with the extent of DOC removal of 83.4% compared to 19.3%, respectively.
6.5 Fractionation

This test was conducted to investigate the change in organics fractions of HA after oxidation by ferrate. The conditions chosen for this test were pH 7 and Fe doses of 200 and 300 µM where no measurable coagulation was found in the previous experiments. It was supposed that under these conditions the interaction between HA and ferrate was exclusively oxidation. Thus, the change in organic fractions of the treated HA could be attributed to direct effects of oxidation.

The organics fractions of 20 mg/l HA model water before and after treatment with ferrate and ferric chloride were detected following the procedure described in section 3.3.7. The volume of each fraction eluted was collected and measured. DOC and iron measurements were subsequently carried out. The absolute carbon content of each fraction was calculated and changed to a relative mass ratio (%). The results given in Table 6.8 are the average of 4 sample runs for untreated HA model water and of 2 runs for treated HA water.

The Fe content of eluted hydrophobic fractions is believed to be organic-bound Fe because the unbound Fe molecules were not captured by the XAD-8 resin, thus they went directly through the column with the hydrophilic fractions. Therefore, the Fe/C ratio can represent the degree of bonding between Fe and the organics. These ratios are shown in Table 6.9. It should be noted that the Fe content of hydrophilic fraction included the unbound inorganic Fe, so the latter is also included in the corresponding Fe/C ratio.
Table 6.8 Fractionation result of 20 mg/l HA sample (%)

<table>
<thead>
<tr>
<th>Organic fraction</th>
<th>Untreated HA</th>
<th>FeCl₃ (200 µM)</th>
<th>Ferrate (200 µM)</th>
<th>Ferrate (300 µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic-base</td>
<td>0.8 ± 1</td>
<td>2.0 ± 1</td>
<td>0.4 ± 1</td>
<td>3.8 ± 1</td>
</tr>
<tr>
<td>Hydrophobic-acid</td>
<td>84.6 ± 5</td>
<td>89.3 ± 8</td>
<td>72.8 ± 13</td>
<td>27.2 ± 11</td>
</tr>
<tr>
<td>Hydrophobic-neutral</td>
<td>3.1 ± 5</td>
<td>0.3 ± 3</td>
<td>4.9 ± 8</td>
<td>19.0 ± 5</td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>11.5 ± 5</td>
<td>8.4 ± 5</td>
<td>21.9 ±11</td>
<td>50.0 ± 8</td>
</tr>
</tbody>
</table>

Table 6.9 Fe/C ratio of organic fractions

<table>
<thead>
<tr>
<th>Organic Fraction</th>
<th>FeCl₃ (200 µM)</th>
<th>Ferrate (200 µM)</th>
<th>Ferrate (300 µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic-base</td>
<td>0.22 ± 0.1</td>
<td>0.27 ± 0.1</td>
<td>1.83 ± 1</td>
</tr>
<tr>
<td>Hydrophobic-acid</td>
<td>0.45 ± .5</td>
<td>3.67 ± 0.6</td>
<td>13.40 ± 3</td>
</tr>
<tr>
<td>Hydrophobic-neutral</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Hydrophilic*</td>
<td>12.45 ± 1</td>
<td>3.32 ± 0.2</td>
<td>3.03 ± 2</td>
</tr>
</tbody>
</table>

* included unbound Fe

The results in Table 6.8 show that the original HA model water contained mainly a hydrophobic acid fraction equivalent to approximately 85%. The second major fraction was hydrophilic (11.5 %) and the two other fractions made up approximately 4 %. The interaction between ferric chloride and HA under these no-flocculation conditions caused no significant change in the organic fractions of HA, whereas considerable transformation of the hydrophobic acid fraction into hydrophilic was observed with ferrate. It seems that the extent of this transformation increases with ferrate doses as the higher ferrate concentration caused greater oxidation effects.
Figure 6.22 illustrates clearly the changes in organic fractions of HA due to the oxidation effects by ferrate.

The results provide evidence that the humic macro-molecular structures are cleaved into smaller entities (see evidence in the next section), more hydrophilic electronegative fractions by the oxidation effect of ferrate, 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, the assumed increase in electronegativity with ferrate causes the equivalent Fe dose for maximum FI, corresponding to charge neutralization, to increase. Similarly, the Fe dose range for effective coagulation increases substantially with ferrate dose beyond the charge neutralization dose, since greater ferrate doses cause greater electronegativity, and this avoids charge restabilisation. However, at relatively much greater 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.

![Figure 6.22 Comparative change in organic fractions of HA model water](image)

**Figure 6.22 Comparative change in organic fractions of HA model water**

(\% C mass)

It is evident from Table 6.9 that the Fe/C ratio (organically bound Fe) of treated HA water (hydrophobic fraction) by ferric chloride was considerably inferior to the case
with ferrate; the greater Fe/C ratio was associated with the hydrophobic-acid fraction. This means that, in the case of using ferrate there may be more Fe molecules bound to the organics. A principal conclusion that may be drawn from Table 6.9 is that the interaction between ferrate and HA brought about a substantial extent of Fe-organics bonding.

The observed change of the hydrophobic-acid fraction into more hydrophilic fractions by the oxidation effects of ferrate and the higher extent of Fe-organics bonding was believed to be associated with the cleaving of the macro-molecular HA into smaller structures, thus giving more available places for the Fe to form bound-complexes with the remaining organics; as a result, the ratio between Fe and organics increased substantially. To confirm this assumption tests were undertaken to show changes in the molecular weight distribution of the organics in the reaction with ferrate.

6.6 Change in molecular weight distribution of HA

Previous experimental results in this study indicated that ferrate might cleave the macro-molecules of HA into smaller structures owing to its oxidation effects that were found with ferrate. Thus it was necessary to study the change in size related parameters of the treated HA. Molecular weight was chosen as a representative size parameter of the organics because of the availability and reliability of the analytical technique of size exclusion chromatography (SEC). The primary objective of this experiment was therefore to ascertain whether ferrate changes the molecular weight distribution of HA.

6.6.1 The interference of the presence of residual iron

The scanning results (see Figure 4.5) confirmed that hydrolysed Fe has a UV light absorbance between 190 and 400 nm and their spectra are analogous to that of HA (see Figure 4.3 and Figure 4.4). The results of residual iron analysis of treated HA by ferrate and ferric chloride showed that iron was present in the treated solution at a level sufficient to interfere with the UV$_{254}$ absorbance which is widely used as a measure of humic substances concentration. Thus it is problematic that the residual iron in the test solution also contributes to the UV absorbance at the wavelength of 230 nm at which the concentration of HA is detected in the SEC analysis. It was
reasonably expected that the presence of Fe in treated solution might add some peaks to the chromatogram of HA molecular weight distribution, leading to uncertain conclusions.

Figure 6.23 shows the molecular weight distribution of Fe(III) species in the filtrate (through 0.45 µm pore size membrane) of 200 µM ferric chloride solution at different pH values. It can be seen from the Figure 6.23 that Fe(III) hydrolysis species at pH 4 and 5 have two peaks at 450 and 20,000 daltons. However, at pH 6 and 7 the absorbance was as low as the baseline variation. This might be due to the low concentration of Fe(III) species in the filtrate as Fe(III) precipitated at pH 6 and 7 as amorphous Fe(OH)$_3$ and was filtered out in this test.

Similarly, the MW distribution of reduced ferrate (filtered through 0.45 µm membrane) from self-decomposition in phosphate buffer at pH from 4 to 7 is shown in Figure 6.24 as a reference for the MW distribution of dissolved Fe(III) species in phosphate buffer. The presence of the phosphate buffer prevented significant coagulation and unacceptable loss of HA from the solution (< 30%). The results shown in Figure 6.24 confirmed that the molecular weight of the residual iron species in phosphate buffer also distributed in the same range as HA, viz. 500 - 2000 daltons.
It is therefore concluded that the molecular distribution of treated HA by Fe coagulants is very likely to be obscured to some extent by the presence of residual iron.

Figure 6.24 MW distribution of reduced ferrate (200 µM) in phosphate buffer

6.6.2 Change in molecular weight distribution of HA by the oxidation effects of ferrate

Figure 6.25 summarises some of the SEC analysis results in which the MW distribution of oxidized HA is plotted with x-axis presenting molecular weight (dalton) and y-axis expressing the corresponding UV absorbance at 230 nm (UV\textsubscript{230}). The samples used in this test were taken from the oxidation test (see section 6.4), involving a 20 mg/l HA solution oxidized by 200 µM ferrate in phosphate buffer at different pH values. The line denoted untreated HA (blue line) presents the MW distribution of a 20 mg/l HA solution (pH 6.3) which is used as the standard MW distribution of untreated HA in this study.
It can be seen from the Figure 6.25 that the UV absorbance of treated HA was complicated due to the presence of residual Fe. It should be noted that when the phosphate buffer was used, no coagulation was seen (except pH 4), leaving all the residual Fe dissolved in the solution. Thus these reduced Fe(III) species contributed to the UV absorbance in the outputs of SEC analysis.

The MW distribution curve of oxidized HA at pH 7 is very much similar to that of reduced Fe in phosphate buffer at the same pH (shown in Figure 6.24). It is somewhat difficult to examine the change in MW distribution of treated HA owing to this complication. However, by assuming the band between 2,000 and 20,000 daltons, which is not seen with untreated HA, was caused by residual Fe, it might be concluded that the main peak at around 1,400 daltons was attributed to the remaining oxidized HA. Thus the shift of MW distribution of oxidized HA toward smaller weight was evident compared to the original HA.
Chapter 6: Coagulation of humic acid colloidal systems

The MW distribution curves of oxidized HA at pH 5 and 6 had an extra peak at around 20,000 daltons compared to the untreated HA. These peaks coincided with that of reduced ferrate at the same pH (see Figure 6.24). However, the height of the peaks of treated HA was higher than that of reduced ferrate, suggesting that these peaks were not only attributed to the residual Fe but also the pre-flocculated aggregates of Fe-bound organics. These aggregates were not sufficiently large to be detected by the PDA or captured by the 0.45 µm membrane filter.

Focusing on the bands at lower weight shown in Figure 6.26, there was a trend that the center of the bands shifted from right to left as the pH decreased from 6 to 4. An explanation for this decrease in MW might be that the organic marco-molecular structures were cleaved into smaller molecules. The greater extent of molecular cleaving at lower pH might be because of stronger oxidation potential of ferrate as it decreases with pH. With regard to the higher UV absorbance (AU) of the treated HA, this may be the consequence of the residual oxidized HA bonding with the Fe, thereby contributing to the light absorbance. A similar behaviour was seen with oxidized HA at pH 7 although the pattern of the reduced ferrate at this condition was different from that of reduced ferrate at pH 5 and 6 (see Figure 6.25).

![Figure 6.26 A closer look at lower MW band of oxidized HA](image_url)
At pH 4 the MW distribution (see Figure 6.25) is represented by treated HA because there was no residual Fe in the treated solution. This is because effective coagulation was evident in the oxidation test at pH 4, and no residual Fe was detected. The interaction between ferrate and HA at this pH is the combination of oxidation and coagulation. Figure 6.27 gives a closer detail of the MW distribution of treated HA at pH 4 in comparison to untreated HA. The original HA has a shoulder at 600 daltons and a broad band between 700 and 10,000 daltons while for the treated HA sample the shoulder almost disappeared and the main band narrowed to between 700 and 4,000 daltons. This phenomenon indicated that the low MW fraction (around 600 dalton) was completely degraded and the higher MW fraction (4,000 – 10,000 daltons) was cleaved into small molecules (700 – 4,000 daltons) by ferrate.

Figure 6.27 A closer look at MW distribution of HA treated by ferrate at pH 4
6.6.3 Change in MW distribution of treated HA under no coagulation conditions

Although the SEC analysis of oxidized HA by ferrate shows evidence of some reduction in MW of oxidized HA with ferrate in phosphate buffer, a strong conclusion cannot be drawn because the UV absorbance was complicated as a result of the presence of residual Fe. Furthermore, the form of the residual Fe species in phosphate buffer is still unknown. Thus it was necessary to look at other conditions that gave little or no coagulation and where the form of residual Fe is predictable.

Figure 6.28 presents the SEC analysis results of samples which were taken from treated HA (20 mg/l) solutions with 200 µM ferrate/ ferric chloride at pH 7 whereby no coagulation was detected by the PDA. As can be seen from this Figure, the MW distribution of treated HA samples was overwhelmed by the high peaks around 11,000 daltons. These high peaks, 10 times higher than that of untreated HA, might be the combined absorbance of residual Fe species and pre-flocculated aggregates of Fe-humic complexes. Because of this complication no clear conclusion can be drawn. Thus it was important to separate the organic complexes and the residual Fe species.

Figure 6.28 MW distribution of HA treated by 200 µM ferrate at pH 7
With regard to the need of separation of inorganic Fe and the Fe-organic complexes in the treated samples, the XAD – 8 resin was considered to be able to do the separation as this type of resin is designed to capture macro-molecular organics. The results of fractionation tests (see section 6.5) indicated that the inorganic Fe went through the XAD-8 column and as a result the hydrophobic fractions (eluted from the column) did not contain residual Fe. In the fractionation tests, the samples of treated HA with ferrate (0.2mM, 0.3 mM)/ ferric chloride (0.2 mM) at pH 7 were fractionated to determine the change in organic fractions caused by ferrate/ ferric chloride under conditions giving little visible coagulation. Thus a calculated volume of each hydrophobic fraction was taken and mixed at a certain ratio (with adding DI water if necessary) so that the obtained mixture had the same organic concentration as the treated HA samples. These mixtures were subsequently taken for SEC analysis and the results are illustrated in Figure 6.29.

![MW distribution of hydrophobic fraction of treated HA at pH 7](image)

**Figure 6.29 MW distribution of hydrophobic fraction of treated HA at pH 7**

It can be seen from Figure 6.29 that the peaks at around 20,000 daltons were greatly decreased by the removal of the residual Fe. The MW distribution of treated organics with ferric chloride had an almost identical shape to the untreated organics, indicating that ferric chloride did not cause any change in MW of the organics under no-
coagulation conditions. In contrast, the main band (3,000 – 7,000 daltons) of treated organics with ferrate clearly shifted towards the small molecular weight fractions. In addition, the small peak at 400 daltons disappeared, implying that the small HA molecules were completely oxidized by ferrate. It is therefore evident that the hydrophobic fraction (90 %) of HA was cleaved into smaller structures by the oxidation effects of ferrate.

6.6.4 Molecular distribution of HA treated by coagulation with ferrate and ferric chloride

Attempts were made to investigate the change in molecular distribution of treated HA by the overall effects of ferrate/ ferric chloride. However, treated HA (20 mg/l) solutions at pH 4 and 5 had relatively high concentrations of residual Fe. Although the residual iron concentration at pH 6 was very low (approximately zero) the SEC chromatograms of treated HA (20 mg/l) at this pH could not be used because the concentration of residual organics was below the detection limit owing to high organic removal efficiency.

It was therefore decided to carry out a coagulation test with model water containing double the HA concentration, 40 mg/l HA, under the same conditions and manner as all other coagulation tests. The treated HA solutions with 200 µM Fe doses at pH 5, whose quality is summarised in Table 6.10, were selected from these tests. The treated solutions were subsequently taken to SEC analysis after settlement and filtration, and the results are shown in Figure 6.30.

Table 6.10 Quality of treated HA (40 mg/l) at pH 5

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Fe Dose (µM)</th>
<th>FI max</th>
<th>Residual DOC (mg/l)</th>
<th>Residual Iron (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrate</td>
<td>200</td>
<td>0.72</td>
<td>1.26</td>
<td>&lt; 0.03</td>
</tr>
<tr>
<td>Ferric chloride</td>
<td>200</td>
<td>0.68</td>
<td>0.83</td>
<td>&lt;0.03</td>
</tr>
</tbody>
</table>
Figure 6.30 Molecular weight distribution of HA (40 mg/l) treated by coagulation

As can be seen in the Figure 6.30, the remaining HA molecules, which had been treated by coagulation with ferric chloride, were distributed between 500 and 2,000 daltons. This indicates, as observed previously by others, that larger macromolecules are more readily removed by coagulation. This is because the larger colloidal particles tend to aggregate more easily than the smaller colloids. A similar behaviour was found with the remaining HA from the overall effects by ferrate (oxidation and coagulation). Comparing the UV absorbance of the residual HA suggests that the HA concentration after treatment by ferrate was higher than by ferric chloride, which is consistent with the DOC removal results.
6.7 Potential measurement

The surface charge of colloids plays a key role in water treatment processes involved in the removal of particles as it is commonly related to the stability of the colloids. Zeta potential, a surface charge indicator, is widely used to monitor the charge neutralization process when performing coagulation experiments. Although it is important to observe the change in charge of the colloids (zeta potential), potential measurement was not carried out for every coagulation test in this study due to limitation with the availability lack of charge measuring equipment. However, the results of coagulation tests showed that the Fe dose range for coagulation with ferrate broadens substantially with dose, possibly because charge restabilisation effects at higher Fe doses are avoided by greater HA electronegativity arising from ferrate oxidation. Therefore, an attempt was made to show this hypothesis by measuring the Zeta potential of the HA colloidal system after adding 100 and 200 µM ferrate. The Zeta potential of 20 mg/l HA was -9.24 mV and this is plotted as the blue line in Figure 6.31. The test was carried out at pH 5 using the same procedure as the coagulation test, with sample measurement carried out 3 min after the coagulant had been added to the test solution. A sample volume of 10 ml was taken to measure zeta potential. The results are summarized in Figure 6.31. Full details are given in section 3.7.4.

![Figure 6.31 Change in HA Zeta Potential by addition of coagulants at pH 5](image)

Figure 6.31 Change in HA Zeta Potential by addition of coagulants at pH 5
As can be seen in Figure 6.31, the results of the charge measurement demonstrated a significant difference in behavior between ferrate and ferric chloride. However, the charge measurement results could not explain the coagulation behaviour of HA at pH 5 with these two coagulants. For example, a considerable charge reversal was seen at the Fe dose 100 µM with ferric chloride; however this was not entirely consistent with the highest FI achieved under these conditions (see Figure 6.12a). Furthermore, with ferrate, coagulation was not detected at the Fe dose of 50 µM (see Figure 6.11a), whereas the charge of the colloids was completely neutralized. Nevertheless, it is clear that the zeta potential of the HA solution decreased (less negative) by the addition of the coagulants. When the coagulant dosage was increased to a higher value (100 and 200 µM), charge reversal was evident with ferric chloride, however, this phenomenon was not clear with ferrate. The results indicated that besides adding positive ions to the solution, ferrate also alters the charge of the HA by oxidation effects, tending to make the charge more negative. As a result, the charge neutralization effectiveness of ferrate was inferior to that of ferric chloride, leading to a broadening of the coagulation range for ferrate corresponding to the ‘charge neutralisation’ zone.

6.8 Chapter summary

- The interaction between HA and ferrate was extensively investigated in comparison to ferric chloride in this study. The results showed that ferrate achieved comparable or better floc formation to ferric chloride over a much broader Fe dose range. However, the degree of organics removal (DOC) was lower than ferric chloride. The results obtained from model waters containing HA were consistent with those for samples of a natural upland coloured water.

- The organics removal by ferrate via oxidation alone was much lower than by the overall effects of oxidation and coagulation. 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 a greater amount of Fe species to achieve their removal. It was also observed that ferrate altered the charge of...
HA, most likely increasing its electronegativity, while overall the apparent change of the charge was less negative due to neutralization by counter-ions.

- HA floc formed by ferrate appeared to have a higher recovery factor (after shear disruption) than floc formed by ferric chloride.
CHAPTER 7: GENERAL DISCUSSION

The overall aim of this study was to evaluate ferrate as a coagulant in water and wastewater treatment processes, as it had not been investigated thoroughly in the previous work. In general, all the original objectives have been successfully achieved. Ferrate was prepared in the laboratory with a modified solvent washing process to obtain high purity ferrate samples (up to 98%). The effect of phosphate buffer on the coagulation performance of ferrate was carefully examined and the results were subsequently applied in order to bring about solely oxidation reactions between ferrate and humic acid. The coagulation performance of ferrate with model waters (containing kaolin or humic acid) and real waters was fully investigated. Organic removal by oxidation and overall effects (oxidation and coagulation) were assessed separately. The impact of ferrate oxidation on the nature of residual organics such as molecular size distribution and organic fractions was observed.

7.1 Ferrate preparation

It was evident from the literature review that the preparation of aqueous ferrate (either sodium or potassium ferrate) by the wet oxidation method is relatively straightforward, and the preparation of aqueous potassium ferrate following the method described by Panagoulopoulos (2004) was employed. A volume of 120 ml of ferrate solution was achieved after about 4 hours. The highest concentration of ferrate solutions achieved was 0.037 M, which decreased by 56.6% after 1 week while refrigerated at 4°C. This solution was strongly alkaline (pH =13), which particularly limits its application in research because it greatly increases the pH value of the test solution. As a result, the adjustment of the pH of test solutions becomes difficult and may be unacceptable.

Following exactly the protocol described by Li et al. (2005), it was found that precipitating the ferrate out of solution was much more complicated compared to the making of ferrate solution. Further steps were carried out to purify, and precipitate the ferrate and dry the ferrate product. The first experiment failed because of using inappropriately-sized P-0 filters as their capacity was not mentioned in the reference.
paper. When using an inadequate capacity filter, the filtration rate was slow and consequently a large amount of Fe(VI) was reduced during the prolonged filtration process. It could be seen in the experiment that the slurry changed from dark purple to yellowish brown. The subsequent experiments (using 600 ml capacity P-0 filter) yielded about 8 – 10 g of ferrate per batch with a purity of between 85 – 90%.

It was observed that at the later stage (after 20 minutes) of the chlorine absorption process, the solution in the absorber became more concentrated, leading to a higher pressure head. As a result, the chlorine generated in the flask tended to flow up through the funnel above and escape to the open air. This loss of chlorine gas apparently reduced the concentration of potassium hypochlorite which was visible as the yellow color of the solution was lighter. Panagoulopoulos (2004) reported that the concentration of the ferrate solution (product yield) was proportionally dependent on the strength of the hypochlorite solution (represented by Cl/Fe molar ratio) used to oxidize ferric salts. He found that the yield of ferrate increased when the Cl/Fe molar ratios increased from 6/1 to 10/1. Therefore, it is essential to improve the strength of the hypochlorite solution in order to have a higher ferrate yield. Thus, it was important to prevent the loss of chlorine during the absorption process. A closed, cylindrical dropping funnel with slightly compressed air applied was used instead of an open funnel to stop the chlorine leaking and to maintain a regular bubbling process. Accordingly, the yield of ferrate increased up to 10-12 g per batch.

After many experiments were carried out under careful observation, it was visible that the colour of the solid ferrate obtained from the final filtration step (using P-3 fritted glass filter) changed from dark purple to yellowish brown when it was washed with methanol. This phenomenon suggested that there was an interaction between methanol and ‘wet’ ferrate, in other words, ferrate reacted with methanol in the presence of water to a certain extent. Wood (1958) also signaled a similar phenomenon as a precaution to the protocol of Thompson et al. (1951). He reported that the ferrate is destroyed when being washing with ethanol if it is not dried sufficiently. The reason is that aqueous ferrate readily reacts with ethanol. The reaction between aqueous ferrate and ethanol may explain the low
purity (80-90%) of ferrate prepared by Williams and Riley (1974). This implies that the prerequisite washing process (four times x 25 ml n-hexane plus four times x 10 ml n-pentane) does not dry the ferrate sufficiently to be further washed with methanol. Therefore, extra care was taken with the washing process. Finally, it was found that double the number of washings by n-hexane and n-pentane improved the purity of the ferrate. Using the modified drying process (shown in Table 4.2), the highest purity of 97 ± 0.5 % was achieved. It should be noted that omitting of methanol washing step is not a wise action as the product is still wet with the washing solvents. Freeze drying was also tried in this work, but it did not help to improve the purity of the product. The purity of the ferrate obtained by freeze drying was 85-90%.

7.2 Analysis of ferrate in aqueous solution

The concentration of potassium ferrate in aqueous solutions was determined by UV-visible absorbance using a Shimadzu spectrophotometer. Both direct and indirect analysis methods were used to determine the concentration of ferrate samples. The results showed that the method developed by Lee et al. (2005b) was reliable. The absorption coefficient obtained based on Lee’s method was 1,146.7 M⁻¹.cm⁻¹ which is almost the same as the commonly used value of 1,150 M⁻¹ cm⁻¹ (Bielski and Thomas, 1987, Jiang and Lloyd, 2002).

7.3 Effect of phosphate buffer on ferrate coagulation

The effect of phosphate buffer on the precipitation of by-products from the decomposition of ferrate was investigated and the results are reported in section 4.3.2.

According to the preliminary test results (see Table 4.4), no precipitation of ferrate was found in phosphate buffer at pH 9.3 over the range of Fe/P molar ratio between 0.02 and 0.04. Further test results (see Table 4.5) show that the precipitation of 100µM reduced Fe(III) in 5mM phosphate buffer (molar Fe/P = 0.02) were virtually zero at pH 9.3. This means that all the reduced Fe(III) existed in soluble forms under these conditions. This finding verified the general use of phosphate buffer to prevent the precipitation of ferrate.
at pH 9.3 by previous researchers (Sharma and Bielski, 1991a, Huang et al., 2001, Gunten et al., 2005). Superficially, this appears to be inconsistent with the extensive use of ferric salts for removing phosphate in wastewater. However, there is a substantial difference in the molar ratios of metal to phosphate between the two cases. Gillberg et al. (1996) found that the quantity of orthophosphate precipitated was directly proportional to the Al/P molar ratio. At pH 8.5, the percentage of orthophosphate precipitated decreased from around 50% for Al/P = 2 to nearly zero for Al/P = 0.5. This suggests that a similar behavior can be expected for Fe. It is possible that the precipitate would be negligible for lower Fe/P, e.g. 0.02 in this study.

In the tests presented in chapter 4, the quantity of Fe-P precipitates was also negligible at pH 6.0, 7.0 and 8.0, but substantial at pH 5.0 and 4.0. This indicated that Fe(III) precipitated in the phosphate buffer, and was completely removed by filtration (0.45μm pore size) at pH 4 and 5, but remained soluble in the solution at higher pH (6.0 -9.3). This is consistent with the concentration of residual Fe in the filtrates (shown in Table 4.6). These precipitates can be FePO$_4$.2H$_2$O as it is known that the well-defined reaction with simple orthophosphate solutions can result in final products such as FePO$_4$.2H$_2$O in accordance to the stoichiometry of the reaction; and these compounds are stable solid phases when precipitated in a low pH range (Leckie and Stumm, 1970). According to the stoichiometry of the reaction, the concentration of FePO$_4$ generated was 100 μM or 10$^{-4}$M. It can be seen from the theoretical solubility diagram of FePO$_4$ (shown on Figure 7.1) prepared by Leckie and Stumm (1970), 10$^{-4}$ M FePO$_4$ does not exceed the solubility limit at pH > 7.0. This is possibly the reason for the fact that no precipitate was found at pH 9.3 and 8.0. However the results were not entirely correlated with this diagram over the pH range of 2.5 to 7.0. Gillberg et al. (1996) reported a similar behavior for the interaction between ferric salts and phosphate. They demonstrated that the precipitation of orthophosphate by ferric sulphate and ferric chloride (at molar ratio Fe/P = 1:1) consistently decreased with pH over the pH range of 4.0 – 8.5, although the solubility of FePO$_4$ is believed to be a minimum at pH 5.3 (Leckie and Stumm, 1970, Metcalf and Eddy, 1991). Leckie and Stumm (1970) also recognised that the calculation of residual phosphorous in equilibrium with FePO$_4$ is not simple because of the reaction of Fe(III)
ions with OH\textsuperscript{-}, depending on pH. Moreover, it is believed that Fe(III) forms soluble complexes with phosphate (Bielski, 1991). The SEC analysis results (see Figure 4.6) revealed the molecular weight of soluble complexes of Fe(III) and phosphate ranged from $10^3$ to $10^4$ dalton at pH 7, 8 and 9, increased to $10^4 - 3 \times 10^4$ at pH 5, and disappeared at pH 4. The SEC analysis results are consistent with that of the precipitation test. They indicate that the complexes (or chelates) of F(III) and phosphate may be some kind of polymers, rather than simple compounds such as $FeHPO_4^+$, $FeH_2PO_4^{+2}$ and $Fe(HP_2O_7)^{3-}$, as summarized by Leckie and Stumm (1970).

Figure 7.1 Solubility diagrams for solid phosphate phases
(taken from (Leckie and Stumm, 1970))
As expected, no coagulation of kaolin suspension in excess phosphate was observed over a pH range from 5 to 8 with Fe dose up to 200 µM (Fe/P = 0.04) for both ferrate and ferric chloride (see section 5.6). At pH 4, the coagulation was not suppressed, but improved substantially in terms of floc formation. Waite and Gray (1984) also reported a similar effect where ferrate was found to be more efficient in removing the turbidity of bentonite-added lake water buffered by phosphate in comparison with carbonate buffer and distilled water. However, it was not clear whether the experiments were carried out at the same pH, so caution is required in interpreting these results.

Phosphate buffer (5mM) was also found to be effective in suppressing the coagulation of 20 mg/l HA water over the pH range 5-7 by ferrate with Fe dose up to 300 µM (Fe/P = 0.06) (see section 6.4). Similar results were obtained with a natural upland coloured water, except the significant coagulation at Fe dose of 300 µM. This might be because the natural water contained some suspended solid, making it easier to coagulate.

To sum up, it was found in this study that a large excess of phosphate can effectively prevent Fe(III) from precipitation over the pH range from 6.0 to 9.3, and thus it can suppress the coagulation of kaolin suspensions and humic acid colloidal systems by ferrate and ferric chloride under particular conditions. However, the precise nature of the interaction between Fe(III) and orthophosphate in large excess of phosphate is still unclear and was not explored within the scope of this study. This would be an interesting topic for future work.

## 7.4 Coagulation of kaolin suspension

As mentioned previously, the aim of this experiment was to investigate the coagulation performance of ferrate with a colloid system in comparison to ferric chloride as a traditional coagulant, where oxidation effects on the colloid could be excluded. Thus, kaolin colloidal suspension was used in all the experiments, prepared by adding kaolin to DI water. The experiments were designed to acquire the data which sufficiently describe the coagulation performance of the two Fe chemicals and reasonably identify the mechanism of the flocculation process. Comparative experiments were conducted using
the apparatus combining a PDA and a gator jar (see section 3.5.3.). The coagulation of kaolin suspension for a given pH in the range of 4 to 8 was carried out for both ferrate and ferric chloride at two ranges of Fe doses. The flocculation process was dynamically observed by the PDA and recorded to a computer via a data logger. To provide a quantitative basis for comparison, two values have been extracted from each PDA response; these are the FI max and T50. In addition to this qualitative assessment, turbidity removal (%TR) was used as a quantitative parameter to evaluate the process.

In previous studies, ferrate was found to be a promising coagulant (Waite, 1979), or even much better coagulant compared to traditional coagulants such as FeSO4.7H2O and Fe(NO3)3 (Waite and Gray, 1984), FeCl3 and Al2(SO4)3 (Deluca et al., 1992). However, Solo and Waite (1988) reported that ferric chloride was as efficient as ferrate in terms of turbidity removal. Similarly, Farooq and Bari (1986) reported that at pH values between 7.6 and 7.8, turbidity removal was not achieved with ferrate dose up to 50 mg/l (254 µM) after 90 min of settling in the treatment of secondary effluent. On the contrary, the turbidity of the treated samples increased with the increasing Fe doses because of the resulting flocs did not settle well. Ma and Liu claimed that pre-oxidation with ferrate significantly enhanced the coagulation of algae in cultured and lake waters by alum (Ma and Liu, 2002a), as well as the coagulation of surface waters (Ma and Liu, 2002b). They noted that the effect of ferrate increased with increasing organic contents in the waters. It implied that the interaction between ferrate and the organics either improved the flocculation process to some extent or gave a better floc which consequently increased the turbidity removal. Wang (2003) and Panagoulopoulos (2004) broadly observed the turbidity removal of ferrate from model waters and surface waters. However, the mechanism of ferrate coagulation was not given.

In undertaking the coagulation experiments in this study using the PDA instrument, it was evident that floc index and flocculation time were well related, whereby the higher the floc index, the shorter the T50. Furthermore, it is clear from the results (see Figures 5.7 – 5.16) that those conditions which gave a high FI max also corresponded with a high turbidity removal, whereas the turbidity removal was negligible when no flocculation was
observed. A better flocculation was characterized by a larger FI index and a smaller T<sub>50</sub>, leading a higher turbidity removal. This confirmed that the PDA is a useful instrument for studying the flocculation process.

For this type of colloidal system, ferrate demonstrated, in principle, very similar coagulation characteristics to ferric chloride with regard to the influence of pH and Fe dose. For both chemicals, coagulation occurred in two clearly distinguished zones (see Figure 5.60). Floc formation was relatively rapid and substantial at pH values in the range of 6-8 and higher Fe concentrations. This is consistent with the so-called ‘sweep flocculation’ mechanism whereby kaolin particles are incorporated within amorphous ferric hydroxide precipitates. While at lower pH values (4 and 5) only lower Fe doses (5 - 15 µM) brought about significant flocculation, corresponding to ‘charge neutralisation’ coagulation. At lower pH values, 4 and 5, and [Fe]>15µM, no floc formation was evident with both chemicals. This is in agreement with previous studies (Amirtharajah and O'Melia, 1990), which suggested that under these conditions the coagulant exists primarily as charged iron hydrolysis species (e.g. $Fe(OH)^{2+}$, $Fe(OH)^{+}$) that re-stabilize the kaolin suspension. However, at lower doses (5, 10 and 15 µM), the balance of charges is such that some degree of destabilization occurs, leading to coagulation.

Clear re-stabilization due to an overdose effect was evident (see Figure 5.4b) as no floc formation was found at doses higher than 5 µM of ferric chloride. This is consistent with the dose dependence in the coagulation of ferric chloride which is illustrated in Figure 2.8. In good agreement with the floc index values, turbidity removal values demonstrated good coagulation occurred in the ‘sweep coagulation’ zone and poorer coagulation occurred in the ‘charge neutralisation’ zone for both coagulants.

The similarity in coagulation behavior of ferrate and ferric chloride was also confirmed by the results of the floc strength test (see section 5.5). The results indicated similar floc strengths for the two coagulants, but with ferrate flocs being slightly weaker than those from ferric chloride. 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 (Duan and Gregory, 2003). The generally similar response suggested that the flocs could have similar physical structures arising from the aggregation of the insoluble Fe hydrolysis products and kaolin particles. The zero recovery factors may be a consequence of the use of organic-free model water. Thus, together with the similarity in dose and pH mechanism, this verified that the coagulation mechanism of ferrate is similar to that of ferric chloride, a hydrolyzing coagulant.

Although generally there was a similar coagulation behavior, some significant differences between ferrate and ferric chloride in terms of the coagulation performances with the kaolin suspension were found in this study. The principal differences were that, in general, the coagulation performance of ferrate was inferior to ferric chloride in terms of the magnitude of floc formation (FI values), the rate of floc growth (T₅₀), and consequent turbidity removal. In the ‘sweep coagulation’ region (high pH – high Fe doses), the floc index of ferrate was always less than that of ferric chloride; a similar behavior was observed with turbidity removal. Moreover, the values of T₅₀ of ferrate were greater than that of ferric chloride, suggesting that ferrate exhibited a slower flocculation than ferric chloride. However, in the ‘charge neutralisation’ zone (pH: 4 – 5, Fe doses: 5-15 µM), there was some evidence of a superior coagulation effect with ferrate. This could be attributed to a stronger overdose effect of ferric chloride as it was seen at lower doses than in the case of ferrate (see Figure 5.15 and Figure 5.16). Figure 5.13 It is apparent that the comparative turbidity removals of ferrate and ferric salt obtained here are in exceptionally good agreement with the results of the coagulation of model water (low range: low organic content) by Panagoulopoulos (2004), where the turbidity removal by ferrate was inferior to that by ferric sulphate over the pH range of 4.5 – 7.5 and Fe dose range of 0.05 – 0.3 mM except at pH 4.5 and Fe dose of 0.09 mM (low pH – low Fe dose: charge zone).

Another major difference in the coagulation behavior between ferrate and ferric chloride is that increasing pH tends to retard the flocculation of ferrate, leading to a substantial drop in floc index and turbidity removal (see section 5.3). It can be seen from observing
the $T_{50}$ values that they increased with pH from 6 to 8 in the case of ferrate and with the decrease of Fe dose. The results of a jar test coagulation study of river water (low organic content), shown in Figure 7.2 and Figure 7.3, by Panagoulopoulos (2004) also indicated a similar behavior for ferrate. It can be seen from Figure 7.3 and Figure 7.3 that the coagulation performance by ferrate decreased markedly when the pH increased from 7 to 8. At pH 8, detectable flocculation with ferrate did not occur during approximately 20 min at low dosages (< 0.1 mmol/l). This compares well with the results presented here, where flocculation did not occur within 20 min of slow mixing at pH 8 and a Fe dose of less than 0.1 mM (see Figure 5.1).

It is assumed that the retardation of ferrate flocculation is caused by the slower self-decomposition rate of ferrate in water at lower ferrate doses and higher pH. In other words, it is possible that the delayed generation of Fe(III) from ferrate at higher pH retarded the flocculation process of ferrate. At pH 5, the ferrate self-decomposition rate in water is believed that is very rapid (i.e. chemical reduction in seconds), while at pH 7 the rate has been determined and a half-life of approximately 3 min has been reported (Li et al., 2005). Thus, this could give an explanation for the fact that the coagulation performance by ferrate was quite comparable to that of ferric chloride at low pH (4 and 5), but inferior at higher pH (6, 7 and 8).

This hypothesis was further strengthened by the results of the coagulation test involving the addition of sodium sulphite (section 5.3). By adding this reducing agent ($Na_2S_2O_3$) to the model waters, the flocculation by ferrate was enhanced dramatically. As a result, the values of Floc index and $T_{50}$ were comparative to that of ferric chloride. Qu et al. (Qu et al., 2003) reported a similar behaviour in their study of FA reduction using two dosing approaches in their experiments on FA reduction by oxidation/coagulation with ferrate. In approach 1 ferrate was added directly into turbid, neutral water (pH=7) during the rapid mixing, while in approach 2 the turbid water was slightly pre-acidified to pH 4 before adding ferrate in order to enhance the decomposition rate of ferrate and the solution was re-adjusted to neutral pH to start the coagulation. The results showed that the turbidity removal was very low for approach 1, whereas for approach 2, the turbidity removal was
very high. This indicated that, although the two flocculation processes occurred at pH 7, the coagulation performance of ferrate in approach 1 was inferior because its decomposition rate at pH 7 is much slower than that at pH 4 in approach 2. Therefore, it is concluded that the coagulation performance of ferrate is strongly influenced by the degradation rate of ferrate, and thus the formation rate of reduced Fe$^{3+}$ from Fe$^{6+}$.

Figure 7.2 Turbidity removal from river water at pH 7 by aluminum sulphate (AS), ferric sulphate (FS), and ferrate (FR)

(reproduced from (Panagoulopoulos, 2004))
7.5 Coagulation and Oxidation of humic substances by ferrate

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. The coagulation behavior of HA in model water (20 mg/l and 10 mg/l HA) by ferrate and ferric chloride at a given pH in the range of 4 – 7 was observed by using the PDA connected to the Gator Jar (see section 3.7). Besides the measurements of DOC and UV$_{254}$ absorbance as the parameters expressing the organic content of the treated solution, the floc formation and its time dependence were recorded by the PDA data logger. A summary of the salient results are shown in Figure 7.4 to Figure 7.7.
Figure 7.4 Coagulation of model water containing 20 mg/l HA with ferrate

Figure 7.5 Coagulation of model water containing 20 mg/l HA with ferric chloride
Figure 7.6 DOC removal from model water containing 20 mg/l HA with ferrate

Figure 7.7 DOC removal from model water containing 20 mg/l HA with ferric chloride
Chapter 7: General discussion

It was evident from these experiments that at pH 4 and 5, the interaction between hydrolysed Fe species and HA is predominantly charge neutralization which is characterised in terms of an optimal Fe dose, and a well-defined Fe/HA mass stoichiometry. A clear optimal Fe dose of 0.28 mgFe/mgHA was derived for ferric chloride with both HA concentrations of 20 mg/l and 10 mg/l (shown in Table 6.1). This corresponds to a dose stoichiometry at pH 5 of 1.4 mgFe/mgC removed. For upland water samples (Figure 6.20 and Figure 6.21), the optimal dose stoichiometry at pH 5 was slightly greater at approximately 1.7 mgFe/mgC 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 optimal Fe dose at pH 4 for ferric chloride with 20 mg/l and 10 mg/l HA model water were slightly different, viz. 0.18 and 0.14 mgFe/mgHA (see Table 6.1), respectively. Thus, the optimal Fe dose for ferric chloride decreased from 0.28 to 0.18 mgFe/mgHA when the pH decreased from 5 to 4. The reason for this is that the charge of the HA is believed to be less negative as pH decreases, as reported by Duan and Gregory (2003), and thus lower doses of coagulants are required to achieve charge neutralization and coagulation.

In contrast to ferric chloride, a dose stoichiometry is not clear for ferrate in low pH conditions (see Table 6.1 and Table 6.2). Furthermore, the optimal Fe dose increased from 0.42 mgFe/mgHA to 0.56 mgFe/mgHA when the pH changed from 5 to 4. This phenomenon indicates that the charge of the HA suspension might not be less negative, but more negative when the pH decreases from 5 to 4 in the case of ferrate, possibly as a consequence of ferrate oxidation effects; this is discussed later.

At pH 6 the results showed a sharp increase in FI max values for ferrate, whereas the FI max with ferric chloride enhanced slightly (compare Figure 7.4 and Figure 7.5). The effective coagulation range also increased with pH for both chemicals. The movement in effective range indicates that the coagulation mechanism of HA by Fe coagulants at pH 6 was different to that at pH 4 and 5. It is believed that at pH 6 coagulation of HA occurs by a combination of ‘sweep flocculation’ via ferric hydroxide precipitation and charge interaction between the HA molecules and soluble cationic species.
At pH 7, the coagulation of NOM by iron salts is well known to be less effective than at lower pH (pH 4 and 5), since the principal mechanism is believed to be adsorption of HS on to iron hydroxide precipitates rather than charge neutralization and precipitation of ion-humate complexes (Duan et al. 2002); thus coagulation requires a much greater Fe concentration in order to precipitate sufficient quantities of Fe(OH)$_3$. The results of coagulation at pH 7 were as expected (see Figure 7.4 and Figure 7.5). It can be seen that a much greater Fe dose was required to achieve the maximum floc growth at pH 7 than at pH 4 and 5 for both coagulants, and the narrow Fe dose range for coagulation at pH 4 and 5 was not evident at pH 7.

In general, a greater coagulation performance in terms of floc growth was evident for ferrate compared to ferric chloride in the pH range of 4 - 6. While the performance at the optimal Fe doses at pH 4 and 5 was similar, the results show a much greater degree of coagulation/flocculation for ferrate at Fe doses greater than (up to double) the optimal Fe dose in comparison to ferric chloride. In the majority of cases the FI max values for ferrate were greater than that for ferric chloride. However, in contrast to the observed behaviour in terms of maximum floc growth, the resulting HA removal (as % DOC removal) with ferrate was found to be slightly inferior to that with ferric chloride ( Figure 7.7 and Figure 7.7). While the absolute removal of organic carbon was high in both cases, the ferrate performance was consistently less than ferric chloride over the complete range pH (4 -7) and Fe doses studied. This behavior was observed with both the HA model solutions and the upland coloured water (Figure 6.20 and Figure 6.21). Eikebrokk (1999) also reported a high removal (~80 %) of DOC by ferric chloride sulphate at pH 5 for a low alkalinity, high humic raw water. It is noted that with ferrate at pH 6 and the HA removal increased with Fe dose despite the FI decreasing beyond the optimal Fe dose (most clearly shown in Figure 6.13).

It is surmised that the difference in the coagulation behaviour of ferrate and ferric chloride is attributed to the oxidation effects of ferrate. In previous studies of the oxidation effects of ozone on humic substances, Graham (1999) summarized 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 (e.g. 10% at 1mgO₃/mgC); a slight decrease in the high apparent molecular fractions; a significant increase of the carboxylic functions; and the formation of ozonation by products. Ferrate is believed to cause similar effects, given that its nominal oxidation strength ($E^0 = 2.20$ V (Jiang and Lloyd, 2002)), is equivalent to ozone ($E^0 = 2.07$ V). Thus experiments on the direct oxidation of ferrate on humic substances 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 (see Table 6.6) 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, the extent of direct oxidation was substantial with a DOC reduction of approximately 20%. A similar, but greater, effect was observed with samples of the upland coloured water (~35%, Table 6.7). 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 mineralization, it was expected that ferrate would modify the size and the nature of the humic substances. Therefore, the fractionation test was conducted to investigate the change in organic fractions of humic substances by oxidation with ferrate. The HA model water samples were treated with ferrate/ ferric chloride under conditions which it was assumed that no coagulation would occur (pH 7, Fe dose < 300 μM). The original and treated samples were fractionated by using XAD resin (section 3.3.7). The results (shown in Table 6.8) provide strong evidence that the humic macro-molecular 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 coagulation behavior and organic removal. Thus, it speculated that the increase in electronegativity with ferrate causes the equivalent Fe dose for maximum FI, corresponding to charge neutralization (at pH 4 and 5), to increase. Similarly, the Fe dose
range for effective coagulation increases substantially with ferrate dose beyond the charge neutralization dose, because greater ferrate doses cause greater electronegativity, and thus, charge restabilisation is avoided. 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 7.4, Fe dose > 200 μM, pH 5). The greater electronegativity of the HA can interact with more Fe(III) species, thus the HA treated with ferrate was expected to have a greater Fe/C ratio than that with ferric chloride, resulting in more voluminous floc when precipitated. The results shown in Table 6.9 support this assumption. This could explain the superior floc formation and higher floc strength recovery factor with ferrate observed in all the laboratory tests. 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 was well as humic substances, the enmeshment of turbidity by more voluminous flocs may be a considerable advantage in their removal. This expectation is supported by the data (shown in Figure 7.8) obtained by Wang (2003) where turbidity removal by ferrate was superior at Fe doses > 6 mg/l despite the DOC removal was inferior in comparison with ferric sulphate.
An attempt was made to obtain supporting information from colloid charge measurement and Figure 6.31 shows the Zeta potential of colloids formed 3 min after coagulant addition. The results, although preliminary in nature, indicate significant differences in behavior 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 (to 200 mg/l as Fe), thus there is no charge reversal as the increasing Fe dose is matched by increasing HA electronegativity from ferrate oxidation.

The results of the tests carried out with upland coloured water show 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.

In contrast to the greater floc formation (most clearly at pH 6), the degree of organics removal (DOC) with ferrate was clearly inferior to ferric chloride in the laboratory tests. This is in line with the results of Wang’s experiments on the coagulation/oxidation of HA model water (shown in Figure 2.4) where the COD removal by ferrate was inferior to that
of ferric sulphate. Similarly, the results of Panagoulopoulos (2004) show that ferric sulphate, overall, performed better than ferrate on treating HA model waters in terms of UV$_{254}$ absorbance removal.

Initially, it appears from the results that the extent of the reduced effectiveness in HA removal by ferrate increased with pH. With closer examination, this also involved an increase in Fe dose, since Fe concentration had to be increased substantially with pH to obtain effective coagulation. This phenomenon was observed by Jiang and Wang (2003) as they found that the DOC removal percentage decreased with ferrate dose from 80% ([Fe] = 6 mg/l) to 50% ([Fe] = 10 mg/l). It suggested that at higher Fe doses, in practice, there may be a greater quantity of smaller molecular weight, hydrophilic organic compounds present in the final water due to the oxidation effect of ferrate which was found to increase with Fe dose (see Table 6.8). More hydrophilic fractions of HA were obtained when treated with 0.3 mM ferrate than with 0.2 mM, viz. 37.9% and 20.1, respectively. Furthermore, the results of the direct oxidation test (shown in Table 6.6 and Table 6.7) suggest that the extent of HS removal by oxidation with ferrate also increased with Fe doses (i.e. ferrate to HS mass ratio) when pH was kept constant. This is consistent with the conclusion of Qu et al. (2003) in their research on the reduction of fulvic acid in drinking water with ferrate that FA removal increased with the $K_2$FeO$_4$ : FA mass ratio when pH and reaction time were kept constant. Jiang and Wang (2003) also discovered that ferrate effectively reduced THMFP at [Fe] = 1mg/l (80%), however, the THMFP increased considerably with increasing ferrate dose ([Fe] $\geq$ 2mg/l). They argued that the HS molecules might be degraded to form a number of smaller molecular fractions of organic compounds by the stronger oxidation effect of ferrate at higher doses. These smaller molecules might be difficult to remove via coagulation. This is also the possible reason to the decrease in DOC removal at Fe doses > 6 mg/l. Consistently, previous studies (Sinsabaugh, 1986, Jiang et al., 1994) have indicated that NOM with smaller molecular fractions are more difficult to remove by coagulation. A similar behaviour was reported by O’Melia et al. (1999) for the pre-oxidation of water containing moderate/high TOC concentration where ozonation was known to have 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.

Some evidence of general reduction in molecular weight was indicated from the size exclusion chromatography analysis, although in most of cases the results were tentative owing to the inevitable inherent interference of residual inorganic Fe(III) species in the UV detection of the SEC separated molecular fractions. Thus, only the hydrophobic fractions of the treated HA were able to be completely separated from the residual Fe, consequently, their SEC analysis results (illustrated in Figure 6.29) were reasonably reliable. These chromatograms show a clear shift of the main peak of HA treated with ferrate towards smaller molecular weight compared to the original HA, whereas the HA treated with ferric chloride was unchanged. This supports the idea that the HS is cleaved into smaller structures, which are more difficult to remove by coagulation, by the oxidation effect of ferrate, leading to an overall inferior HA (DOC) removal by ferrate compared to ferric chloride.

In a previous investigation using model waters containing humic and fulvic acids, Jiang and Wang (2003) 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. In contrast, the results obtained in this study display significant differences to the study by Jiang and Wang. It is evident that the nature of 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, the coagulant dose, and the mass ratio between metal ion and humic substances are all believed 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 pre-oxidation and charge interaction/ sorption between humic substances and cationic Fe hydrolysis species and amorphous Fe(OH)$_3$. Overall, taking together the results of previous work (Wang, 2003, Jiang and Wang, 2003,
Panagoulopoulos, 2004) and this study, it may be concluded that the influence of ferrate oxidation is positive when the organic matter is relative easy to oxidize (e.g. wastewater COD, fulvic acid), and negative when it is more recalcitrant (e.g. humic acids). However, given the complexity of the inter-related processes of ferrate oxidation, Fe(VI) chemical reduction, Fe(III) formation and precipitation, and HS charge neutralization/adsorption, this conclusion may be an over-simplification and further investigation is required to consider this in detail.
8.1 Conclusions

8.1.1 Preparation of and characterisation of ferrate

The method described by Li et al. (2005) for preparing solid phase potassium ferrate did not give a product with a purity as high as reported (99%). Doubling the number of washing cycles with each solvent prior to washing with methanol was needed to prevent the degradation of the newly prepared ferrate, caused by the reaction between wet ferrate and methanol. The highest purity of sample obtained by this method was 97 ± 5%. The absorption coefficient of ferrate in aqueous solution at 510 nm was determined to be 1,146.7 M$^{-1}$.cm$^{-1}$ with $R^2 = 0.9999$. The indirect ABTS method (2005b) for ferrate determination was found to be reliable and gave similar results to the direct spectrophotometric method.

8.1.2 Effect of phosphate buffer on ferrate coagulation

This study has evaluated and confirmed that phosphate buffer can effectively prevent reduced iron species, mainly Fe(III), from precipitating over the pH range of 6.0 to 9.3, and thus it can suppress the coagulation of kaolin suspensions and humic acid solutions by ferrate and ferric chloride over the pH range 5.0 – 9.3. A similar behaviour is also observed with a natural upland coloured water. It is important that the reaction is maintained with a large excess of phosphate which is indicated by the Fe/P molar ratio. Thus the suppression of coagulation is successful at Fe/P molar ratios up to 0.06 for model water containing humic acids, and up to 0.04 for the natural water.

There was one exception that phosphate cannot prevent the precipitation of Fe(III) at pH 4 under the same Fe/P ratios. In contrast to the expected suppression of the coagulation by Fe(III), the coagulation of kaolin suspension by both ferrate and ferric chloride in terms of floc formation improved substantially in the presence of phosphate.

However, the precise nature of the interaction between Fe(III) and orthophosphate in a large excess of phosphate is still unclear and has not been explored within the scope of
this study. It was found that the molecular weight (MW) of Fe complexes in phosphate buffer mainly ranged from 1,000 to 10,000 daltons, which is similar to that of humic acid (HA). Thus, the use of phosphate buffer in oxidation reactions of ferrate with HA can interfere in the measurement (by UV absorbance detection) of MW distributions of treated HA, associated with residual Fe, either free ions or complexes, in the solution.

### 8.1.3 Coagulation of kaolin suspension

In general, ferrate demonstrated very similar coagulation characteristics to ferric chloride with regard to the influence of pH and Fe dose. Floc formation with ferrate was relatively rapid and substantial at neutral pH and moderate Fe concentrations, corresponding to ‘sweep coagulation’, while at low pH (4 and 5) there was some evidence of charge destabilization and charge stoichiometry. There was no significant difference in the strength of the flocs formed by each coagulant under optimal conditions. It can be concluded from these results that both chemicals exhibited the ‘classical’ behaviour of a hydrolyzing metal coagulant.

In this study, ferrate did not appear to be a superior coagulant in comparison with ferric chloride in treating a kaolin suspension, serving as a representative ‘inert’ (organic-free) colloid suspension. In contrast, its performance as a coagulant was inferior to ferric chloride in terms of floc formation and turbidity removal, and the extent of inferior performance of ferrate increased with pH. This was ascribed to the relatively slow formation of Fe(III) species at neutral to high pH, owing to the low degradation rate of ferrate in aqueous solution under these conditions. In real waters, with the presence of sufficient background reactive species, this difference in performance is not likely to be significant.

### 8.1.4 Coagulation of humic acids

The results of this study have shown that ferrate achieved comparable, or better, floc formation to ferric chloride over a broader Fe dose range at pH values of 4.0 to 7.0. This is ascribed to the greater extent of Fe binding to humic acid molecules. However, associated with this was a lower degree of organics removal (as DOC) than ferric
chloride, where the difference in performance was minor at low pH (4 – 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 coagulant to achieve their removal.

The SEC analysis results verified that there was a shift of the HA molecular weight distribution towards smaller molecular weights when HA was treated with ferrate, whereas no change was observed with ferric chloride. This physical change, together with the greater electronegativity (and charge density) and polarity of oxidized HA molecules, makes them more difficult to coagulate.

8.2 Future work

Some aspects arising from this study would be worth investigating in the future and were not included in the experimental programme owing to the lack of time. These are as follows:

- Phosphate buffer was shown to be effective in preventing the coagulation of kaolin suspension and humic acids by ferrate and ferric chloride. However, the precise nature of the interaction between Fe(III) and orthophosphate in a large excess of phosphate is still unclear. Thus, it would be valuable to examine the kinetics and mechanisms of this interaction to fill this gap in understanding of the phenomena.

- It was found in this study that ferrate oxidation caused significant changes in the nature of the humic acids, and an adverse effect on their subsequent coagulation in terms of DOC reduction, caused by the ferrate cleaving the humic acid molecules into smaller, more electronegative more hydrophilic fractions, which are more difficult to remove by coagulation. However, some previous studies of the treatability of organic waters by ferrate have reported an opposite effect. From this it is concluded that the effect of ferrate on the removal of natural organic
matter by overall oxidation/coagulation depends on many factors, such as the interaction between ferrate and humic substances over various pH – Fe doses, the characteristic of the organic matter, Fe/HS mass ratio, etc. This is very complex in view of the inter-related processes of ferrate oxidation, Fe(VI) chemical reduction, Fe(III) formation and precipitation, and HS charge neutralisation/adsorption. Thus, further investigation is required to consider these complexities in detail.

- Ferrate demonstrated, in this study, its ability to cleave humic substances into smaller molecular fractions by its oxidation characteristics. Thus, it is expected that the application of ferrate can provide a variety of water quality benefits generally in drinking water and wastewater treatment. For wastewater, ferrate may be able to pre-oxidise recalcitrant pollutants, making them more favorable to biodegradation, thus enhancing the subsequent removal of the organics by biological processes. Other applications of ferrate in wastewater treatment are potentially the removal of pesticides and pharmaceutical compounds, and the tertiary treatment of dyes/color in textile wastewaters. In drinking water treatment, the pre-oxidation of contaminated raw water sources (containing humic substances, algae, etc…) by ferrate may avoid the formation of harmful by-products which often occur with other oxidants (e.g. bromated formation from ozone and trihalomethanes from chlorine. Another specific area of further research under consideration is the use of ferrate in an emergency context for people who live in frequently flooded areas where drinking water supply facilities become inoperable during flooding. Owing to its multi-functional treatment properties, ferrate is expected to provide the basis for a simple, household scale treatment process that can provide an acceptable quantity and quality of water after a relatively short process time (e.g. 30 min).
LIST OF REFERENCES


AWWA 2000. *Operation control of coagulation and filtration process*, AWWA,Denver, USA.


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APPENDIX : UV\textsubscript{254} ABSORBANCE REMOVAL

Figure 0.1 UV\textsubscript{254} absorbance removal from model water containing 20 mg/l HA with ferrate

Figure 0.2 UV\textsubscript{254} absorbance removal from model water containing 20 mg/l HA with ferric chloride
Figure 0.3 UV$_{254}$ absorbance removal from model water containing 10 mg/l HA with ferrate

Figure 0.4 UV$_{254}$ absorbance removal from model water containing 10 mg/l HA with ferric chloride
APPENDIX: PUBLICATIONS BASED ON THE RESEARCH


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

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
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 UV254 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 UV254 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 UV254 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. ~ 103 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 NaHCO3 (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 estimated to be 95%, and the concentration of ferrate in strong alkaline conditions. The purity of the ferrate, hypochlorite, and solid phase ferrate was precipitated 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 NaHCO3 (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 measurements 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
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 (i.e. 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...
(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 O₃/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>
<thead>
<tr>
<th>Ferrate dose (μM)</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model water (20 mg/L HA)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>19.3</td>
<td>14.4</td>
<td>1.0</td>
</tr>
<tr>
<td>200</td>
<td>18.1</td>
<td>14.9</td>
<td>3.0</td>
</tr>
<tr>
<td>300</td>
<td>30.7</td>
<td>25.2</td>
<td>6.5</td>
</tr>
<tr>
<td>Upland coloured water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>35.5</td>
<td>22.9</td>
<td>13.3</td>
</tr>
</tbody>
</table>
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 macro-molecular 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 µM). 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.

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 µM) was required to achieve the maximum FI at pH 7 than at pH 5 (50 µM), and the

<table>
<thead>
<tr>
<th>Organic fraction</th>
<th>Untreated HA</th>
<th>FeCl₃ (0.2 mM)</th>
<th>Ferrate (0.2 mM)</th>
<th>Ferrate (0.3 mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic base</td>
<td>0.7</td>
<td>2.0</td>
<td>0.4</td>
<td>5.1</td>
</tr>
<tr>
<td>Hydrophobic acid</td>
<td>81.5</td>
<td>89.5</td>
<td>66.9</td>
<td>38.3</td>
</tr>
<tr>
<td>Hydrophobic-neutral</td>
<td>3.0</td>
<td>2.5</td>
<td>4.5</td>
<td>12.1</td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>11.1</td>
<td>8.4</td>
<td>20.1</td>
<td>37.9</td>
</tr>
</tbody>
</table>

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).
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, \( \sim 250 \mu M \), but ferrate achieved a much greater extent of coagulation (FI max) which increased with Fe dose up to 500 \( \mu M \). 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 (i.e. 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 \( \mu M \) 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 (\( \sim 5\% \)), 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


EVALUATING THE COAGULATION PERFORMANCE OF FERRATE – A PRELIMINARY STUDY

Khoi Tran Tien¹, Nigel Graham¹* and Jia-Qian Jiang²

¹Department of Civil and Environmental Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.
²Centre for Environmental Health Engineering, School of Engineering, C5, University of Surrey, Guildford GU2 7XH, U.K.

E-mail: n.graham@imperial.ac.uk; Fax: 44 207 5946124
1. 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. 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 UV254 absorbance and dissolved organic carbon for waters containing humic and fulvic acids in comparison with ferric sulphate. Ma and Liu 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, there appear to be very few studies that have considered this in detail; it is assumed that this is mainly because of the difficulty of separating the oxidation and coagulation effects when ferrate is applied. This paper summarizes some early results from an ongoing laboratory-based project that is investigating the coagulation effect.

2. Materials and Methods

a) 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.. Ferric chloride stock solution (0.01 M) was made by dissolving 2.71 g FeCl₃.6H₂O (from BHD) in 1L deionised water fight before the tests. Kaolin (light) stock suspensions 5 g/l and 10 g/l were prepared by adding kaolin light powder (from Fisher) into 1L deionised distilled water and mixing thoroughly. Bicarbonate buffer solution (0.1 M) was made by dissolved 8.41g NaHCO₃ (from Fisher) in 1L of deionised water. Boric acid/ NaOH pH 9.0 buffer solution was prepared by adding 50 ml 0.1M boric acid/ 0.1M KCl solution, and 20.8 ml 0.1M NaOH then diluting to 100 ml with deionised water.

b) Experimental procedures

i) Coagulation tests

Our studies involve observation of the reactions between ferrate and an aqueous suspension of kaolin powder (50mg/l) at different ferrate doses (5 to 200μM) and pH values (4 to 8), and comparing the observations with the use of ferric chloride under identical conditions. Kaolin is assumed to be inert to the oxidation effects of ferrate, so the observations of particle 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. Ferrate chemical was prepared as potassium ferrate with a purity of 90% by the wet oxidation method in which ferric nitrate was oxidized with potassium hypochlorite, and solid phase ferrate was precipitated in strong alkaline conditions. The purity of the ferrate, and the concentration of ferrate in solution, was determined by a spectrophotometric method.
The coagulation process was followed by use of a photometric dispersion analyzer (PDA 2000), which is an instrument for observing rapidly changing particle suspensions via an optical technique that analyses the light transmitted through a flowing suspension; the instrument gives an output that is a relative measure of the change in particle size and density distributions. 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 1 Principle of photometric dispersion analysis](reproduced from PDA 200 user manual)

**ii) Floc strength tests**

The test samples preparation were similar to that of coagulation test, in other words, the conditions of dose 200 μM and pH 7 were selected as it gave commonly optimum coagulation performance.

Two litres of sample mixtures was added to the reactor, initially stirred at 200 rpm for 60 seconds (G = 350s⁻¹), then maintained at 50 rpm (G = 50s⁻¹) for an appropriate period of time so as to get to maximum flocculation (about 400 seconds). A sudden increased shear rate was applied by increasing the mixing speed to 400 rpm (600s⁻¹) for 120 seconds, then reducing the speed to 50 rpm and keeping at this condition until the test ended. Floc index was observed and recorded continuously during the test so that its strength factor and recovery factor could be determined clearly.

**c) Apparatus**

The experimental apparatus is shown in figure 2.
3. 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 (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 have been extracted from each PDA response; these are the $T_{50}$ and $RMS_{max}$. 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 $T_{50}$ (rapid destabilization and floc growth) and a high $RMS_{max}$ (large, voluminous floc particles).

The results of the tests with the two chemicals show some similarities and significant differences in the coagulation behaviour between ferrate and ferric chloride. In general, substantial floc formation was observed with both chemicals at the highest Fe concentrations (50, 100 and 200μM), 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.
Figure 3. Coagulation of 200μM FeCl₃·6H₂O with 1mM NaHCO₃ buffer solution

Figure 4. Coagulation of 200μM Ferrate with 1mM NaHCO₃ /Boric acid buffer solution
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<sub>50</sub> value was 66s, corresponding to 200μM Fe at pH 6, whilst for ferrate the lowest T<sub>50</sub> value was 258s, corresponding to 200μM Fe at pH 7. However, the F<sub>1max</sub> 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 FeCl₃.

![Diagram](image)

Figure 5 Variation of F<sub>1max</sub> with dose and pH

As it can be seen from figure 5, for both ferrate and ferric chloride, coagulation effects were observed at all doses (5μM to 200μM) 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 at high pH (6 - 8) and high dose (50 to 200μM) region, which is known as sweep floc region, and poor coagulation occurred at low pH (4-5) and low dose (5, 10 and 15μM). 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<sub>50</sub> and lower values of F<sub>1max</sub> observed with the ferrate.

At lower pH values, 4 and 5, and [Fe]>15μM, no floc formation was evident with both chemicals. This is consistent with previous studies which suggest that under these conditions the coagulant exists primarily as charged Fe hydrolysis species 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 10μM Fe dose, the ferrate coagulation performance was superior to the ferric chloride (see figure 6).
Figure 7 presents the results of the dynamic test on the flocs of ferrate and ferric chloride at common optimum condition (200 μM at pH 7). It is apparent that an irreversible breakage (recovery factor = 0) occurred in both cases of ferrate and ferric chloride. This is consistent with the well known effect in practice that flocs formed by hydrolysing coagulants tend to be weak and not fully reversible in the case of sweep coagulation (Duan and Gregory, 2002). The similar response to the dynamic test of the flocs suggested that they could have similar structure as a result of aggregation of ferric hydroxide and kaolin particles.
Figure 7  Result of the floc strength test at pH 7 and dose 200 μM

Figure 8  Coagulation test of ferrate with phosphate buffer
Concluding Remarks

Ferrate demonstrates very similar coagulation characteristics to Ferric chloride (viz. variation with pH and Fe dose). The principal difference between the ferrate and the ferric chloride as a coagulant was that the magnitude of floc formation with ferrate was always inferior to that observed with ferric chloride, and that in most cases the rate of floc growth was slower with ferrate. However, there was some evidence of a superior coagulation effects with ferrate at pH 4 and 5 at low Fe doses (5-15μM).

No significance difference in floc strength between each coagulant was found.

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 (eg. Sharma⁶). Figure 8 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, with the exception of pH 4 where some solid phase precipitation is evident; the precise nature of this precipitate is unclear at present.
References


