

COMPARATIVE PERFORMANCE OF POTASSIUM FERRATE(VI) IN DRINKING WATER AND SEWAGE TREATMENT

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EXTENDED ABSTRACT

The use of potassium ferrate(VI) as an alternative water treatment chemical for both drinking water and sewage treatment has been studied and is reported in this paper. The performance of potassium ferrate(VI) was evaluated in comparison with sodium hypochlorite (NaOCl) and NaOCl plus ferric sulphate (FS) and aluminium sulphate (AS). The effects of the dosages of ferrate(VI), NaOCl and FS/AS and sample pH values on the treatment performance were investigated.

The study demonstrates that in drinking water treatment, ferrate(VI) can remove 10-20% more UV_{254} abs. and DOC than FS for the same dose compared in natural pH range (6 and 8). The THMFP was reduced to less than $100 \mu\text{g l}^{-1}$ by ferrate(VI) at a low dose. In addition to this, ferrate(VI) can achieve disinfection targets (> 6 Log inactivation of *E. coli*) at a very low dose (6 mg l^{-1} as Fe) and over wide working pH in comparison with chlorination (10 mg l^{-1} as Cl_2) plus coagulation (FS, 4 mg l^{-1} as Fe). In sewage treatment, ferrate(VI) can reduce 30% more COD, and kill 3 Log more bacteria compared to AS and FS at a similar or even smaller dose.

Key words: Potassium ferrate, coagulation, disinfection, water treatment, sewage treatment

1. INTRODUCTION

Coagulation and oxidation/disinfection are two important unit processes for water and wastewater treatment. Coagulation destabilizes colloidal particles and transfers small particles into large aggregates and adsorbs dissolved organic materials onto the aggregates, which can then be removed by sedimentation and filtration. Disinfection is designed to kill the harmful organisms (e.g. bacteria and viruses) and oxidation is used to degrade various contaminants. A wide range of coagulants and oxidants/disinfectants can be used for water and wastewater treatment. The most common coagulants used include ferric sulphate, aluminium sulphate, and ferric chloride, and the oxidants/disinfectants used are chlorine, sodium hypochlorite, chlorine dioxide, and ozone. A more efficient water treatment chemical reagent should ideally be able to inactivate microorganisms, partially degrade and oxidise the organic and inorganic impurities, and remove colloidal/suspended particulate materials and heavy metals.

Potassium ferrate(VI) (K_2FeO_4) possesses all above multifunctions. Under the acidic conditions, the oxidation-reduction potential of the ferrate(VI) ions (2.2 V) is greater than ozone (2.0 V), which is the strongest oxidant among all the oxidants/disinfectants practically used in water and wastewater treatment. As well as the high oxidation

capacity, the ferrate(VI) also possesses the coagulation function, since it is reduced to form ferric ions or ferric hydroxide in the oxidation of other contaminants. Such unique properties make the ferrate(VI) to be a dual function chemical reagent and could combine the pre-disinfection/oxidation with coagulation into one unit and therefore to reduce the capital cost in the building of mixing chambers of water treatment plants.

Using potassium ferrate(VI) as a chemical reagent for water and wastewater treatment has been well reviewed by the authors [1]. Previous work has been focused on the use of ferrate(VI) to oxidise various synthetic organic matter (e.g., benzene) [2], and inorganic contaminants (e.g., cyanide and hydrogen sulphide) [3]. There are limited studies to address the use of ferrate(VI) as a coagulant for removing colour [4, 5] and as a disinfectant for killing bacteria [6, 7] in drinking water treatment and few work has been reported to address the use of ferrate to treat sewage. This study thus assess the treatment performance of ferrate(VI) comparing with that of conventional disinfectants and coagulants for drinking water and sewage treatment.

2. EXPERIMENTAL METHODS

The preparation of potassium ferrate(VI) was following an established procedure [8]. The concentrations of the ferrate(VI) were measured using both chromate titration and spectroscopy methods [1]. For the spectroscopy method, the given amount of ferrate(VI) was diluted into a given volume of 8 M KOH solution and the absorbance at its characteristic wavelength of 504 nm was measured (Helios a Spectrophotometer). The absorbance at 504nm of ferrate(VI) solution was then be converted to the ferrate(VI) concentration using a determined coefficient, ϵ , which is defined as the ratio of the ferrate(VI) absorbance at 504nm (cm^{-1}) to the ferrate concentration (M). The value of ϵ was obtained through a characterization procedure; where the absorbance at 504nm was measured against individual ferrate concentration determined by the chromate titration method [9], and a calibration line was thus plotted, its slope is ϵ , which was $1150 \text{ cm}^{-1}\text{M}^{-1}$ for this study.

Standard jar tests were conducted to evaluate and compare the treatment effectiveness of ferrate(VI) with that of traditional coagulants and disinfectants, which includes a rapid mixing at a speed of 400 rpm for 1 min and then allowed to flocculate at a speed of 35 rpm for 20 min. After slow mixing finished, the samples were allowed to settle for a period of 60 min. Then, a supernatant was withdrawn for the measurement of various quality parameters and the procedures of which followed the Standard Methods [10]. All experiments were duplicated and the results presented were mean values with the deviation of less than 5%.

For drinking water treatment, the jar-test experiments were conducted at two pH values (6 and 8). The model waters were prepared by mixing 0.1 N NaHCO_3 solution with given amount of either humic or fulvic acid and 1mL pure culture of *E. coli*. The number concentration of *E.coli* of model water was 3.2×10^8 per 100 mL. Humic acid solution was prepared at a concentration of 20 mg l^{-1} , which gives UV_{254} abs of 49.54 m^{-1} and DOC of 9.54 mg l^{-1} as C. The corresponding specific UV_{254} absorbance (SUVA) was $5.20 \text{ m}^{-1} (\text{mg C})^{-1}$ l. The fulvic acid solution was prepared at a concentration of 25 mg l^{-1} , giving UV_{254} abs of 36 m^{-1} and DOC 12.4 mg l^{-1} as C, and the corresponding SUVA value was $2.9 \text{ m}^{-1} (\text{mg C})^{-1}$ l. The chemicals evaluated were ferrate(VI) and ferric sulphate (FS) at the dose range between 0 and 20 mg l^{-1} as Fe, and sodium hypochlorite (with strength of 1% as Cl_2) at doses between 0 and 10 mg l^{-1} as Cl_2 . The performance evaluated was based on the removal/inactivation of both humic/fulvic acid and *E.coli*. The water quality parameters before and after treatment were measured, including UV-abs at 254 nm, Vis-abs at 400

nm, dissolved organic carbon (DOC), trihalomethane formation potential (THMFP, 7 days), *E.coli.* number and residual Fe concentrations.

For sewage treatment experiments, the ferrate(VI) was evaluated compared with FS and aluminium sulphate (AS). For the coagulation with ferrate(VI), pH was adjusted to either 5 or 7, and in the case of AS and FS, pH was not adjusted – the final pH varied from 6.75 to 7.48 depending on the coagulant doses. The coagulant doses of three chemicals ranged from 0.07 to 0.56 mM as either Al or Fe. At the end of sedimentation, 100 ml of supernatants was withdrawn and measured for the suspended solids (SS), colour ($Vis_{400-abs}$), and total and faecal coliforms, which were calculated based on the parameters of the blank samples (no coagulant addition, only pH adjustment). The pH was adjusted with the addition of either sulphuric acid or sodium hydroxide. Wastewater samples were collected from a Sewage Treatment Works of Thames Water. All sewage samples were obtained from the plant influent prior to the primary grit chamber. Samples were collected in high density polyethylene (HDPE) jerricans, which were washed and rinsed with tap water before use. There is a variation in the values of the parameters as a result of either the time of sampling or the change in sewage flow rate and qualities, as shown in Table 1.

Table 1 Characteristics of industrial wastewater (Jan-Mar 2003)

Parameter	Range
pH	7.25-7.88
Turbidity (NTU)	29.4-73.3
Total suspended solids ($mg\ l^{-1}$)	97 – 303
$UV_{254-abs}$ (cm^{-1})	0.168 – 0.316
Colour as $Vis-abs$ at 400nm (cm^{-1})	0.011 – 0.041
Total COD ($mg\ l^{-1}$)	353 – 527
Soluble COD ($mg\ l^{-1}$)	154 – 194
Total Coliform (per 100 ml)	4×10^8 – 2.2×10^9
Faecal Coliform (per 100 ml)	3.3×10^8 - 2×10^9

3. RESULTS AND DISCUSSION

3.1. Comparative performance of drinking water treatment

For treating FA containing model water, the superior performance of ferrate(VI) was observed when coagulation pH was 6 and 8. At pH 6, the ferrate can achieve 10-15% more $UV_{254-abs}$ removal than FS in the dose range between 8 and 14 $mg\ l^{-1}$ as Fe, and 10 % more DOC removal than FS in the dose range between 2 and 12 $mg\ l^{-1}$ as Fe. At pH 8, ferrate(VI) can remove 20% more $UV_{254-abs}$ and 10-20 % more DOC than FS over wide dose ranges (4 – 18 $mg\ l^{-1}$ as Fe). The superior performance of ferrate(VI) at pH 6 and 8 for removing FA is encouraging since pH in natural surface waters are normally in this range, and it is not necessary to lower the coagulation pH in order to achieve the maximum natural organic matter removal. Fig. 1 shows that the SUVA values in the treated water with ferrate(VI) were much lower than that with FS for the same dose compared, indicating that ferrate(VI) can degrade the FA first and the degraded organic matter could be easily removed by coagulation; the evidence of this is that the remaining DOC in the coagulated water with ferrate was lower than that with FS (Fig. 2). This should give extra advantages in using ferrate(VI) to remove FA. The superior performance of ferrate(VI) has also been demonstrated when treating humic acid containing water.

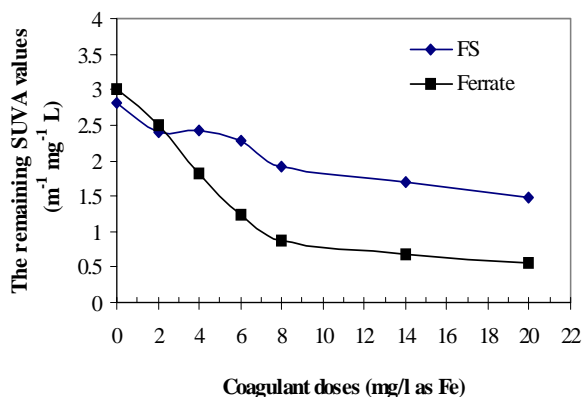


Fig. 1. The remaining SUVA values in the treated effluents with ferrate(VI) and FS at pH 8, FA model water

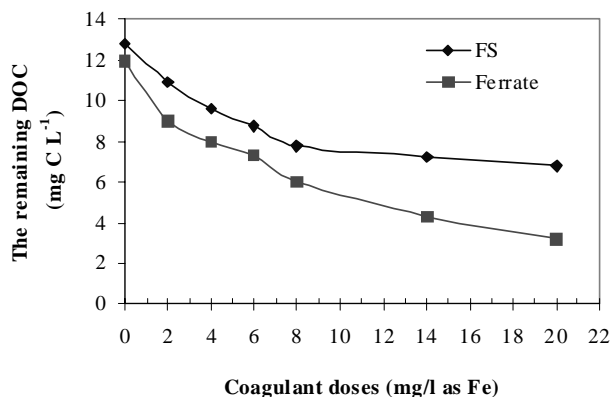


Fig. 2. The remaining DOC in the treated effluents with ferrate(VI) and FS at pH 8, FA model water

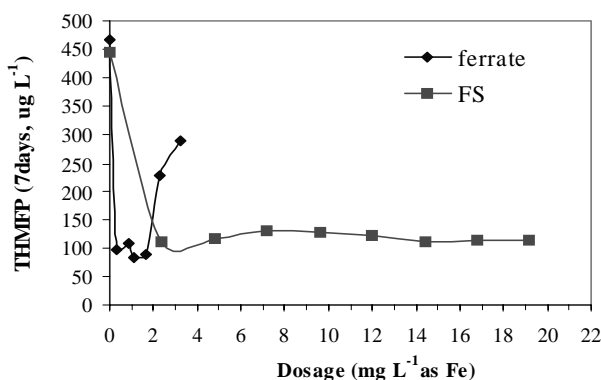


Fig. 3. THMFP (7days) removal with ferrate(VI) and FS, HA model water

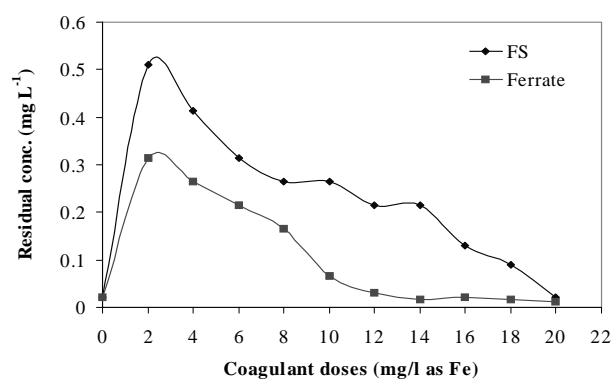


Fig. 4. Residual concentrations of Fe in the treated effluent with ferrate(VI) and FS at pH 6, FA model water

The addition of excess coagulant for improving the removal of disinfection by-products (DBP) precursors through coagulation has been defined as 'enhanced coagulation'. One reason for the introduction of this treatment technique requirement is that an increase in organic precursor removal will reduce the overall public health risks and meet the current DBP standards. This study has investigated the reduction of trihalomethane formation potential (THMFP) with ferrate(VI) and ferric sulphate in a full-scale water treatment works. The results demonstrated the superior performance of ferrate(VI) in reducing the THMFP to meet the drinking water standard (THMFP < 100 µg l⁻¹) at low doses (< 2 mg l⁻¹ as Fe, see Fig. 3), and this could lead to the extension of the definition of 'enhanced coagulation' by using alternative chemicals such as ferrate(VI) for improving the removal of natural organic matter (NOM) or DBP precursors. For the same study trials, the residual concentrations of iron in the coagulated waters with either ferrate(VI) or FS are displayed in Fig. 4 which shows that ferrate(VI) can achieve overall lower Fe residual concentrations in the treated waters, indicating its better coagulation performance. This is

also the case when treating HA acid model water with ferrate(VI) and FS and for different coagulation pHs.

Fig. 5 shows the comparative disinfection performance of ferrate(VI) and sodium hypochlorite with FS for pH 8 and for a given contact time (30 min) and various doses. It can be seen that under studying conditions, 4 mg l⁻¹ FS (as Fe) with 10 mg l⁻¹ Cl₂, or, 8 mg l⁻¹ FS (as Fe) with 8 mg l⁻¹ Cl₂, were required to achieve 100% inactivation of *E.coli*, whilst a small ferrate(VI) dose of 6 mg l⁻¹ as Fe was needed to achieve the same target. The results has demonstrated that in order to achieve 100% inactivation, the relative lower doses of ferrate(VI) was required in comparison with FS plus Cl₂.

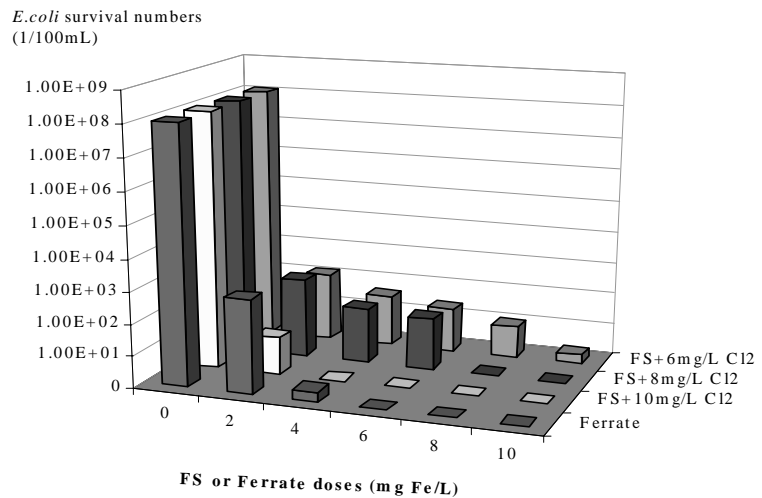


Fig. 5. Comparative disinfection performance with ferrate and Cl₂+FS

3.2. Comparative performance of sewage treatment

In sewage treatment, the superior performance of ferrate(VI) has been demonstrated for the removal of dissolved and total COD (Fig. 6). Removal percentage of total COD with ferrate(VI) was much greater than FS and AS, it was 5-20% more than FS, and 5-28% more than AS for the same doses compared. The overall removal performance of dissolved COD was not as good as that of total COD, but ferrate(VI) still can remove more dissolved COD than AS and FS.

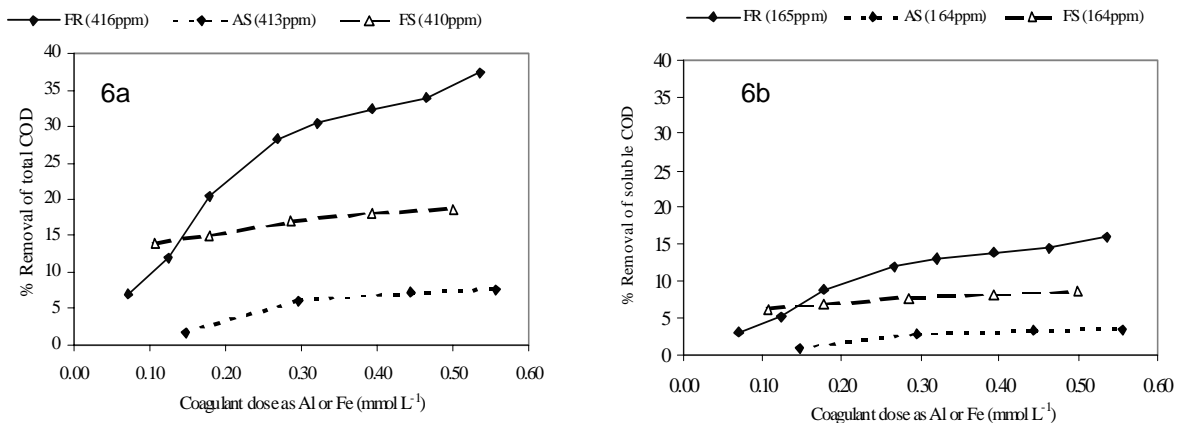


Fig. 6. Comparative performance of COD removal. a) total COD removal, and b) dissolved COD removal. FR = ferrate(VI). Values in the brackets are COD concentrations in raw sewages for the tests.

Possessing of high re-dox potential, ferrate(VI) not only oxidises organic matter present in sewage, but also inactivates bacteria that traditional coagulants lack the power to do.

This study has demonstrated that the disinfection and oxidation capability of ferrate(VI) in treating sewages is very promising. At both pH 5 and 7, ferrate(VI) can achieve more than 4-log₁₀ bacteria inactivation, whilst AS and FS can only achieve approximately 1-Log₁₀ bacteria inactivation (Table 2).

Table 2. Comparative performance of bacteria inactivation (in Log₁₀ terms)

	AS ¹	FS ¹	FR ²	
Coagulation pH	6.75-7.48	6.75-7.48	5	7
Total Coliform	0.89-1.05	0.89-1	>4	>4
Faecal Coliform	0.96-1	1-1.05	>4	>4

¹ AS and FS dose required was >0.50 mmol l⁻¹ as either Al or Fe(III).

² FR achieved > 4 Log₁₀ bacteria inactivation at doses <0.27 mmol l⁻¹ as Fe(III).

4. CONCLUSIONS

The multi-functions of potassium ferrate(VI) and its superior performance in drinking water and sewage treatment were confirmed in this study. For drinking water treatment, ferrate(VI) can remove 10-20% more UV₂₅₄ abs. and DOC than FS for the same dose compared in natural pH range (6 and 8). In treating a real surface water, the THMFP was reduced to less than 100 µg l⁻¹ by ferrate(VI) at a low dose (< 2mg l⁻¹). In addition to this, ferrate(VI) can achieve the disinfection targets (> 6 Log inactivation of *E. coli*.) at a very low dose (6 mg l⁻¹ as Fe) and over wide working pH in comparison with chlorination (10 mg l⁻¹ as Cl₂) plus coagulation (FS, 4 mg l⁻¹ as Fe). For sewage treatment, ferrate(VI) can reduce 30% more COD and kill 3 Log more bacteria compared to AS and FS at a similar or even smaller dose. The observed ferrate(VI) unique performance might offer significant advantages in practice, since only a single dosing and mixing unit is needed, the capital and running costs are expected to be cheaper, and less management is required, comparing with the conventional two-unit system using disinfectant and coagulant separately.

REFERENCES

- Jiang, J. Q., Lloyd, B. (2002) Progress in the development and use of ferrate (vi) salt as an oxidant and coagulant for water and wastewater treatment. *Water Research*. **36**, 1397-1408.
- Waite, T.D. and Gilbert, M. (1978) oxidative destruction of phenol and other organic water residuals by iron (VI) ferrate. *J. Wat. Pollut. Control Fed.*, **50**, 543-551.
- Sharma, V.K., Rendon, R.A. and Millero, F.J. (1999) Oxidation of sulfur-containing compounds by ferrate(VI) in the aquatic environment. *Abstr. Pap. Am. Chem. S.*, **217**, 110.
- White, D.A. and Franklin, G.S. (1998) A preliminary investigation into the use of sodium ferrate in water treatment. *Environ. Technol.* **19**, 1157-1160.
- Jiang, J.Q. and Wang, S. (2003) Enhanced coagulation with potassium ferrate (VI) for removing humic substances. *Environ. Eng. Sci.* **20**, 627-635.
- Murmann, R.K. and Robinson, P.R. (1974) Experiments utilizing FeO₄²⁻ for purifying water. *Wat. Res.*, **8**, 543-547.
- Jiang, J.Q., Wang, S., and Kim, C.G. (2002) Disinfection performance of potassium ferrate. In: Conference Proceedings, the 3rd IWA World Water Congress, 7-12 April 2002, Melbourne Australia.
- Jiang, J. Q., Lloyd, B. and Grigore, L. (2001) Preparation and evaluation of potassium ferrate as an oxidant and coagulant for potable water treatment. *Environ. Engin. Sci.* **18**, 323-331.
- Vicenteperez, S., Losada, J. and Hernandez, P. (1985) Ferrate(VI)-oxidimetry standardization of reagent with standard iron(II) - titration of aniline. *Anales Quim. B: Inorg. Anal.*, **81**, 93-99.
- AWWA, APHA, WEF (1995). Standard Methods for the examination of water and wastewater. 19th Edition, Washington DC.