

Practical application of ferrate(VI) for water and wastewater treatment – Site study's approach

Jia-Qian Jiang^{a,b,*}, Cécile Stanford^c, Michael Petri^d

^a School of Engineering and Built Environment, Glasgow Caledonian University, Glasgow G4 0BA, Scotland, United Kingdom

^b Faculty of Engineering and Physical Science, University of Surrey, Guildford GU2 7XH, United Kingdom

^c Process Capacity, Integrated Planning, Southern Water Service, Falmer, East Sussex BN1 9PY, United Kingdom

^d Qualitätsversicherung und Forschungslabor, Zweckverband Bodensee-Wasserversorgung, Suessenmuehle 1, 78354 Sipplingen, Germany

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ABSTRACT

This paper presents the work aiming to validate the practical feasibility of ferrate(VI) used as an alternative to the existing coagulant (e.g., ferric chloride/sulphate) for both drinking water and domestic sewage treatment via series of pilot plant trials. For drinking water treatment, a ferrate(VI) dose of 0.1 mg/L can achieve 93% and 97% particle removal (in terms of particle counting) after the filtration for raw water and for the ozonized water, respectively, which is satisfied to the treated water quality requirement for the particles' removal. Moreover, ferrate(VI) can remove 10% metformin, benzotriazole and acesulfam from raw water but FeCl₃ with ozonation can't. When treating domestic sewage at pilot scale trials, ferrate(VI) demonstrated encouraging performance as well, at a very lower dose range, 0.1–0.2 mg Fe/L, ferrate(VI) achieved better performance in comparison with high dosed ferric sulphate. This will reduce chemical demand and sludge production and therefore results in a low operating cost and generates substantial cost saving in treating sewage.

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Introduction

Ferrate(VI) is a very strong oxidant, under acidic conditions, the redox potential of ferrate(VI) ions is 2.2 V, which is well compatible to that of ozone (2.0 V) (Jiang and Lloyd, 2002). Exploration of the use of ferrate(VI) for water and wastewater treatment has been addressed (Jiang et al., 2001; Jiang, 2014; Sharma et al., 2015). The studies revealed that ferrate(VI) can kill a large amount of microorganisms, partially degrade and/or oxidise organic and inorganic impurities, remove suspended/colloidal particulate materials and reduce phosphate concentrations significantly in sewage treatment. Most recently, researches have been reported using ferrate(VI) to treat emerging micro pollutants in water purification processes and the performance of ferrate(VI) was encouraging (e.g., Lee et al., 2005; Jiang et al., 2005; Sharma et al., 2008). However, these research findings have not yet led to the

full-scale implementation of the ferrate(VI) in water industry owing to the difficulties associated with the relatively high cost of the ferrate(VI) products which water industries could not afford, the instability of the reagent depending on its method of preparation, and the lack of evidence of significant advantages of ferrate(VI) over the existing water and wastewater treatment methods, which can only be demonstrated when the water industry implements the technology into full scale application. In doing so, a series of pilot scale trials using ferrate(VI) for water and waste water treatment are needed to establish the database of the comparative treatment performance and to assess the operating cost against the existing conventional technologies and this is the aim of this research.

This paper reports the field researches carried out in collaboration with water companies to identify the optimal operating conditions of using ferrate(VI) to replace existing chemicals in the treatment of drinking water and domestic sewage. The field study was conducted when the ferrate(VI) was both generated and applied at the operational site thereby resolving (i) the problem of ferrate(VI) instability and (ii) the cost for the transportation and storage of the ferrate(VI) product.

* Corresponding author at: School of Engineering and Built Environment, Glasgow Caledonian University, Glasgow G4 0BA, Scotland, United Kingdom (J.-Q. Jiang).

E-mail address: jiaqian.jiang@gcu.ac.uk (J.-Q. Jiang).

Materials and methods

Pilot-scale trials using ferrate(VI) coagulation before filtration in drinking water treatment

Pilot plant was designed and set up by Lake Constance Water Supply with designed parameters shown in Table 1. Water flows through a micro sieve filter (15 μm), then into the customized ozone mixer followed by seven contact tanks. Next, ferrate(VI) and FeCl_3 were pumped into two flowing water streams in parallel by peristaltic pumps with the required volume dosage. Water/coagulant mixtures were directed into two separated chambers where suitable flocculation occurred before the flow entered two parallel filter columns with similar flow conditions. Filter columns are made of steel tube running vertical with design parameters mentioned in Table 1. The operating conditions of filters can be seen in Table 2.

Various water quality parameters and residual ozone concentration were analysed according to the standard methods (APHA, AWWA, 1995). Analysis of micro pollutants, metformin benzotriazole and acesulfam, was carried out using an Agilent 1100 LC system (Agilent, Waldbronn, Germany) equipped with a API 4000 triple quadrupole mass spectrometer with electrospray ionization (Applied Biosystems, Darmstadt, Germany). The column was an Ultra Aqueous C18 (250 mm \times 4.6 mm) from Restek (Bad Homburg, Germany). Water (eluent A) and acetonitrile/water (95/5 Vol%/Vol%, eluent B) with 0.1 Vol% formic acid were used as mobile phase with a flow rate of 0.75 mL/min. The column was brought to a constant temperature to 25 $^\circ\text{C}$. 100 μL of the sample were injected directly without any further sample pre-treatment. The eluent program started with 5% eluent B, increased linearly within 6 min to 80% eluent B and increased linearly from 6 to 12 min to 95% eluent B. After the analytic run the eluent was set back to 5% eluent B from 12 to 18 min. The LC-column was coupled to the mass spectrometer directly into the ion source which was heated to 650 $^\circ\text{C}$ inside the ionization section with nitrogen gas flows of 2.758×10^5 Pa for curtain gas and 4.137×10^5 Pa for the ion source gases 1 and 2, respectively. The ion spray voltage was set to 5.5 kV. The mass spectrometer was operated in the positive mode. The detection of metformin was performed with three multiple reaction monitoring transitions: from m/z 130 to m/z 71 at a collision

energy of 19 V, was from m/z 130 to m/z 60 at a collision energy of 29 V and was from m/z 130 to m/z 85 at a collision energy of 25 V.

Pilot-scale trials dosing ferrate(VI) into crude sewage for wastewater treatment

A pilot-scale reactor system consists of two major components: (1) the ferrate(VI) production component and (2) the sewage treatment component, that includes a portion of the crude sewage pumped from the inlet channel and returning further into the same channel after being dosed in-line with ferrate(VI).

Ferrate(VI) was produced by batches, production time was 30 min per each preparation. The resulting ferrate(VI) was measured using an established spectroscopy method where the absorbance of the ferrate(VI) solution was measured at 505 nm and the absorbance was converted to the concentration using an absorption coefficient of 1100 ($1/\text{M} \cdot \text{cm}$). The ferrate(VI) dosing flow rate was determined based on the desired dose and ferrate(VI) concentration measured. Samples after ferrate(VI) dosing and mixing were collected and analysed for the concentrations of suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total phosphorus (TP), pH and residual Fe.

Results and discussion

Pilot-scale drinking water treatment

The tested lake water had good quality and then the required coagulant dose was low (0.1 mg/L as Fe). For the given operating conditions (Table 2), particle removal percentage after filtration was 93% for raw water and 97% for ozonized water (Fig. 1). As can be seen in Fig. 1, there were larger numbers of 1 μm particles than that of 2 μm . For both raw water and ozonated water, two filters had different performance; Filter 1 achieved slightly better performance than Filter 2. However, after dosing coagulants, such differences were extinct.

The field trials were carried out at the pilot plant where the operations were kept for the same conditions as that of the main plant. And therefore, the ferrate(VI) dose used was very low, 0.1 mg Fe/L, in order to equally compare with the performance of ferric chloride (0.1 mg Fe/L) and ozonation (1.2 mg O_3/L) running at the main plant. Table 3 shows the comparative performance of ferrate(VI) and FeCl_3 at 0.1 mg/L dosage in pilot scale experiments. Both performed to similar levels in the removal of particles, UV_{254} -abs and dissolved organic carbon (DOC) for the given conditions. However, ferrate(VI) can achieve 10% reduction of metformin, benzotriazole and acesulfam but FeCl_3 with ozonation can't remove any of these compounds. Moreover, ferrate(VI) treated water did not generate bromate but ozonated water generated bromate concentration of 2.5 $\mu\text{g}/\text{L}$.

The outstanding performance of ferrate(VI) in drinking water treatment has been reported previously at doses greater than 1 mg/L as Fe, which showed ferrate(VI) performed better than other coagulants for reducing the turbidity, UV_{254} -abs, DOC and total coliform (Jiang et al., 2001; Graham et al., 2010). However, in this study when the ferrate(VI) dose was 0.1 mg/L as Fe, the ferrate(VI) did not outperform to ferric chloride in terms of their overall performance. Nevertheless, the additional benefits of using ferrate(VI) are obvious as observed from this study; with the removal of micropollutants and without generating bromate, this could attract interesting from water industries to apply the ferrate(VI) into practice.

With regards to the superior oxidation performance of ferrate(VI), it has been suggested that this could be attributed to the high

Table 1
Design parameters of pilot plant filters.

Filter parameter	Unit	Details
Total height	m	3.6
Filter area	m^2	0.283
Average flow rate	1/h	~ 1700
Average flow velocity	m/h	~ 6
Running time	h	40–100
Filter media		40 cm EVERZIT N (0.8–1.6 mm); 60 cm Sand (0.4–0.7 mm); ~ 18 cm Supporting material

Table 2
Pilot plant operating conditions (Fe dose = 0.1 mg/L).

Parameters	Details
Initial/final flow rate (L/h)	1500/1000
Running time (h)	5–7
Online measurement instrument	Particle counter; flow rate, pH and conductivity
Final water sampling time	After 4 h of dosing coagulant
Ozone dosing (mg/L)	~ 1.2 (dose); ~ 0.7 (at ozone mixer outlet)
Residual ozone concentration before sand filters (mg/L)	0.05–0.08

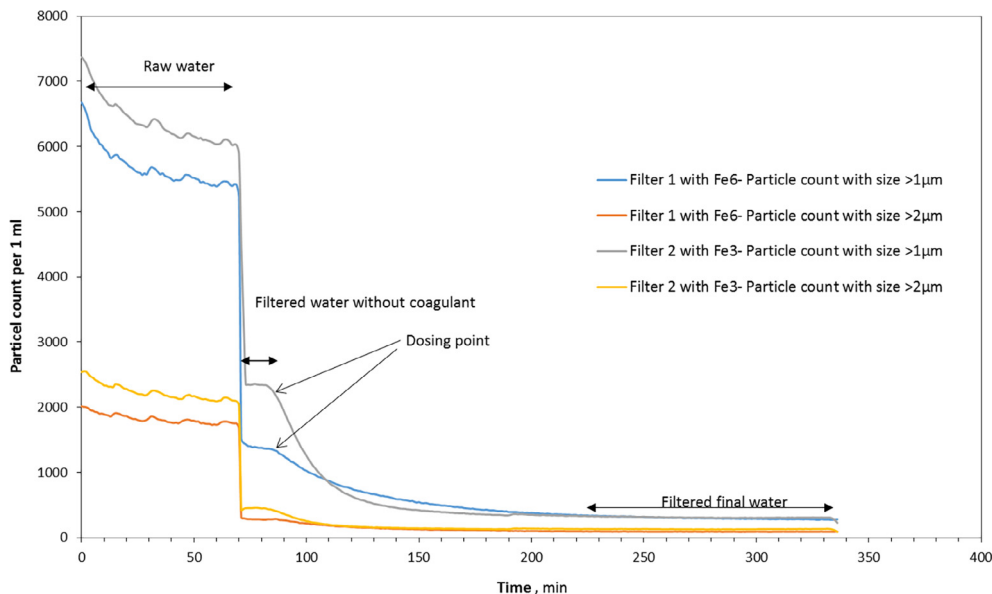
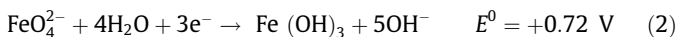
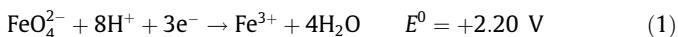


Fig. 1. Particle removal by coagulation at 0.1 mg/L as Fe and pilot plant filtration from raw water (Filter 1 – Ferrate(VI), Filter 2 – FeCl₃).

Table 3
Comparative performance of ferrate(VI) and FeCl₃.

	Unit	Raw water		Ozone water	
		Ferrate(VI)	FeCl ₃	Ferrate(VI)	FeCl ₃
Fe dosage	mg/L	0.1			
Turbidity removal	%	~80	~80	~90	~90
UV-254		No change			
DOC	mg/L	No change			
Residual Fe	µg/L	~16	~9	~15	~12
Particle removal	%	~93	~94	~98	~98
Bromate formation	µg/L	0	0	~2.5	~2.5
Benzotriazole removal	%	10	0	10	0
Acesulfam removal	%	10	0	10	0
Metformin removal	%	10	0	10	0

redox potential and multiple functions of the chemical. Under acidic conditions (see Eq. (1)), the redox potential of ferrate(VI) is the strongest ($E^0 = +2.20$ V) among all oxidants/disinfectants used for water and wastewater treatment. Even under neutral conditions (Eq. (2)), the redox potential of ferrate(VI) ($E^0 = +0.72$ V) is still greater than that of permanganate (MnO_4^-) which is a strong oxidant.



High redox potential alone could not explain the superior performance of the ferrate(VI), there must be other reasons behind such phenomena. First, oxidation by ferrate(VI) could change the property of organic pollutants making them readily removable through coagulation and precipitation. Secondly, the byproducts of the ferrate(VI) oxidation are ferric ion or ferric hydroxide (see Eqs. (1) and (2)) which are basic coagulant resources. Therefore, ferrate(VI) can also perform coagulation after it degrades organic matter and microorganisms.

Crude sewage treatment performance in the pilot plant

During the pilot plant study, properties of the crude sewage were tested. Concentrations of interested quality parameters varied from 242 to 730 mg/L for the suspended solids (SS), 523 to

1125 mg/L for the chemical oxygen demand (COD), 235 to 441 mg/L for the biochemical oxygen demand (BOD), and 11.3 to 18.5 mg/L for the phosphate as total P (TP).

The comparative performance of ferrate(VI) and ferric sulphate can be seen in Table 4. With a low dose (0.03 mg Fe/L), ferrate(VI) can achieve similar or better performance as a high dose of ferric sulphate (37 mg Fe/L).

Figs. 2–5 below show concentrations of TP, COD, BOD and SS from various samples during the given test running period as well as the relevant percentage removals. For the above stated low

Table 4
Comparative performance* of crude sewage treatment with ferric sulphate and ferrate (VI).

Chemical and dose	Average percentage removal at a dose of the chemical (%)			
	SS	TP	COD	BOD
Ferrate(VI) (0.03 mg Fe/L)	79	56	50	30
Ferric sulphate (37 mg Fe/L)	78	59	54	43

* Crude sewage characteristics: [SS] = 730 mg/L; [P] = 18.5 mg/L; [COD] = 1125 mg/L; [BOD] = 388 mg/L.

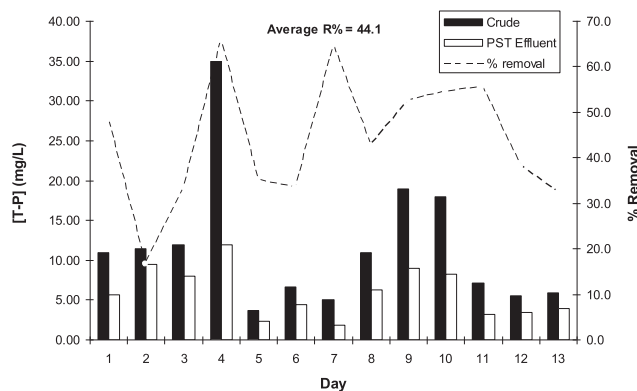


Fig. 2. Total phosphorus (TP) concentration in crude sewage and the effluent after pre-sedimentation tank (PST) and percentage removals of TP.

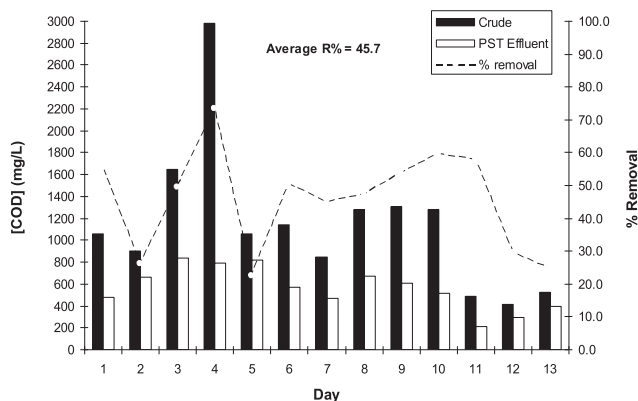


Fig. 3. COD concentration in crude sewage and the effluent after pre-sedimentation tank (PST) and percentage removals of COD.

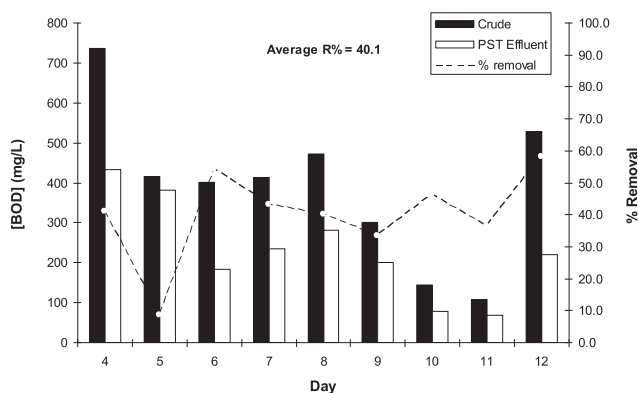


Fig. 4. BOD concentration in crude sewage and the effluent after pre-sedimentation tank (PST) and percentage removals of BOD.

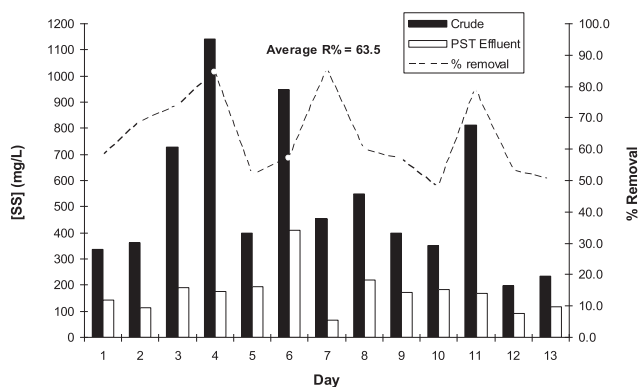


Fig. 5. Suspended solids (SS) concentration in crude sewage and the effluent after pre-sedimentation tank (PST) and percentage removals of SS.

dose (0.03 mg Fe/L), ferrate(VI) can achieve, in average removals, 64% of SS, 44% of TP, 46% of COD, and 40% of BOD when pH was above 9. The comparative performance of ferrate(VI) and ferric sulphate shows that the ferrate(VI) dose of 0.16 mg Fe/L can achieve the similar performance as ferric sulphate could achieve at relatively a high dose (25 mg Fe/L). For the small dose demand, strong precipitation capability of ferrate(VI) solutions is dominant for the removal of TP (Fig. 2) and SS (Fig. 4), and high oxidation capacity of ferrate(VI) was responsible to achieve the industrial acceptable removal efficiency of COD (Fig. 3) and BOD (Fig. 4).

Much smaller dose demand of ferrate(VI) can significantly reduce the chemical requirement and sludge production and therefore provides possibility of cutting off the operating cost in the treatment of sewage.

Concluding remarks

The concept of the water-energy nexus probably refers to two issues, i.e., the relationship between the water used for energy production, and the energy consumed to extract, purify, deliver, heat/cool, treat and dispose of water and wastewater. At this stage, we have not yet gathered comprehensive data of capital and operating cost for full-scale use of ferrate(VI) in water and wastewater treatment, the impact of this work on the energy saving in water treatment is obvious. It is evident that for low chemical dose demand, no coagulant transportation/storage requirement and less sludge production, ferrate(VI) can achieve the same treatment targets in comparison with ferric iron based coagulants.

Pilot-scale field tests with low ferrate(VI) doses for drinking water treatment achieved average particle removal percentage of 93% for raw water and 97% for ozonized water in terms of particle counting data. No pH neutralization was required after dosing ferrate(VI). In comparison with using ozonation and FeCl₃ coagulation, ferrate(VI) brought in additional benefits to remove 10% metformin, benzotriazole and acesulfam. Additionally, ferrate(VI) treated water did not generate bromate whereas ozonated water did.

For the sewage treatment, pilot-scale tests demonstrated that ferrate(VI) can achieve removal targets of TP, COD, BOD and SS from the crude sewage with very low dose range, 0.1–0.2 mg Fe/L, whereas much higher dose of 25 mg Fe/L was required for ferric sulphate. In turn, this will reduce the chemical demand and sludge production, likely to generate substantial cost saving in treating sewage. Depending on individual circumstances, the ferrate(VI) technology could be implemented in wastewater treatment practice.

Although valuable data of ferrate(VI) performance have been collected via the two site studies reported in this paper, several issues have also been raised in order to apply the technology into a full-scale water purification. First the operating cost of the ferrate(VI) production, which needs more trials to run to get the comprehensive figure; secondly, the *in situ* ferrate(VI) production efficiency, which needs improved by the optimisation of the reactor's design and building and then, promoting to a lower and comparable operating cost; finally, full-scale trials are necessary to validate the treatment performance obtained from the pilot-scale studies and to evaluate economic suitability of using ferrate(VI).

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