Chapter 12
Field Study III: Evidence Gained from Site Studies for the Performance of Ferrate(VI) in Water and Wastewater Treatment

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Abstract The work presented in this chapter was to validate whether ferrate(VI) can be used as an alternative to the existing coagulant (e.g., ferric chloride) for both drinking water and domestic sewage treatment via a 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 the raw water and for the ozonized water, respectively, which is satisfactory to the treated water quality demand for the particle removal. Moreover, ferrate(VI) can remove 10% metformin, benzotriazole and acesulfame from raw water, but $FeCl_3$ with ozonation cannot. When treating domestic sewage at pilot-scale trials, ferrate(VI) demonstrated encouraging performance as well; at a very low dose range, 0.1–0.2 mg $Fe^{(VI)}$/L, ferrate(VI) achieved better performance in comparison with high-dosed ferric sulfate. This will reduce chemical demand and sludge production, and, therefore, it results in a low operating cost and substantial cost saving in treating sewage.

Keywords BOD removal · Coagulation · COD removal · Drinking water treatment · Ferrate(VI) · Micropollutant reduction · Particle removal · Phosphorus removal · Sewage treatment

12.1 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 with 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 2007, 2014; Jiang and Lloyd 2002; Sharma 2002; Sharma et al. 2015). The studies revealed that ferrate(VI) can disinfect microorganisms, partially degrade and/or oxidize organic and inorganic impurities,

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remove suspended/colloidal particulate materials, and reduce phosphate concentrations significantly in sewage treatment. Most recently, researches have reported using ferrate(VI) to treat emerging micropollutants in water purification processes (Lee et al. 2005; Jiang et al. 2005). However, the implementation of ferrate (VI) technology in practice represents a challenge due to the instability of a ferrate (VI) solution and a high production cost of solid ferrate(VI) products. The research has been directed at generation and application of ferrate(VI) in situ (Jiang et al. 2009). Practical advantages of ferrate(VI) over the existing water and wastewater treatment methods can only be demonstrated when water industry is able to implement the technology into full-scale application. To do so, a series of pilot-scale trials using ferrate(VI) for water and wastewater treatment are needed to establish the database of the comparative treatment performance and to assess the operating cost against the existing technologies.

This chapter reviews the field work in drinking water and wastewater treatment carried out by this author's team to identify the optimal operating conditions for using ferrate(VI) as an alternative to currently used chemicals in the treatment of drinking water and sewage.

12.2 Materials and Methods

12.2.1 Pilot-Scale Trials of Using Ferrate(VI) Coagulation before Filtration in Drinking Water Treatment Processes

The pilot plant was designed and set up by Lake Constance Water Supply according to the parameters shown in Table 12.1. The water flew through a microsieve filter (15 μm), and then into the customized ozone mixer followed by seven contact tanks. Next, ferrate(VI) and $FeCl_3$ were pumped into two flowing waters to be treated by peristaltic pumps separately with the required volume dosage. Water/coagulant mixtures were directed into two separate chambers in which suitable flocculation occurred before the flow entered two parallel filter columns with similar flow conditions. The filter columns are made of steel tube

Table 12.1 Design parameters of pilot plant filters

Filter parameter	Unit	Details
Total height	m	3.6
Filter area	m^2	0.283
Average flow rate	L/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 12.2 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

running vertically having the design parameters mentioned in Table 12.1. The operating conditions of filters can be seen in Table 12.2.

Analysis of various water quality parameters and residual ozone concentration followed the standard methods (Eaton et al. 1995). Analysis of micropollutants, metformin, benzotriazole, and acesulfame was carried out using an Agilent 1100 LC system (Agilent, Waldbronn, Germany) equipped with an API 4000 triple quadrupole mass spectrometer with electrospray ionization (Applied Biosystems, Darmstadt, Germany). The column was Ultra Aqueous C18 (250 mm × 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 25 °C. 100 μL of the sample was injected directly without any further sample pretreatment. 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 °C inside the ionization section with nitrogen gas flows of 40 psi for curtain gas and 60 psi 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, from m/z 130 to m/z 60 at a collision energy of 29 V, and from m/z 130 to m/z 85 at a collision energy of 25 V.

12.2.2 Pilot-Scale Trials of 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 including an alkali tank, a chemical transfer pump, an electrochemical reactor, a power supply, a ferrate(VI) product storage tank, a chemical dosing pump, and a control box; and (2) the treatment part including a submerged pump situated in the influent channel, hose, artificial channel where the ferrate(VI) was dosed, and the exit hose that goes back to the main wastewater flow channel.

Ferrate(VI) 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. The absorbance was converted to the concentration using an absorption coefficient of 1100 1/(M cm). The ferrate(VI) dosing flow rate was determined based on the desired dose and the measured ferrate(VI) concentration. The samples after ferrate (VI) dosing and mixing were collected and analyzed for the concentrations of suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), total phosphorus (P), pH, and residual Fe.

12.3 Results and Discussion

12.3.1 Pilot-Scale Drinking Water Treatment Performance

The tested lake water was of better quality, so the required coagulant dose was low (0.1 mg Fe/L). For the given operating conditions (Table 12.2), particle removal percentage after filtration was 93% for raw water and 97% for the ozonized water (Fig. 12.1). As can be seen in Fig. 12.1, there were larger numbers of 1 μm particles

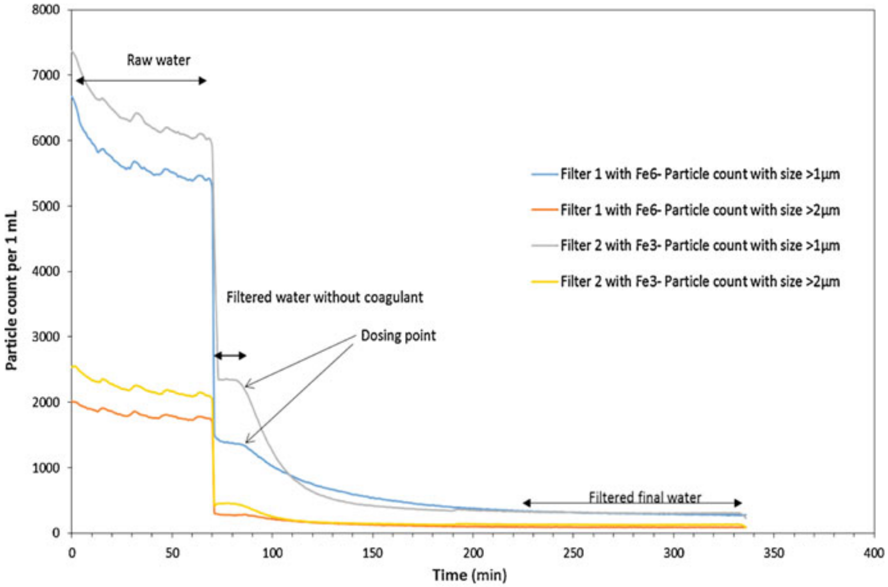

Fig. 12.1 Particle removal by coagulation at 0.1 mg Fe/L and pilot plant filtration from raw water (Filter 1—ferrate, Filter 2—$FeCl_3$). (Reproduced from Jiang et al. 2018)

Table 12.3 Comparative performance of ferrate(VI) and $FeCl_3$

	Unit	Raw water		Ozone water	
		Ferrate(VI)	$FeCl_3$	Ferrate(VI)	$FeCl_3$
Fe dosage	Mg/L	0.1			
Turbidity	%	~80	~80	~90	~90
UV-254	No change				
DOC	No change				
Residual Fe	μg/L	~16	~9	~15	~12
Particle removal	%	~93	~94	~98	~98
Bromate formation	μg/L	0	0	~11	~11
Benzotriazole removal	%	10	0	10	0
Acesulfame removal	%	10	0	10	0
Metformin removal	%	10	0	10	0
X-ray contrast medium removal	%	100	100	100	100

than those 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 the coagulants, such differences were not shown.

The field trials were carried out at the pilot plant where the operating conditions followed the main plants. 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 (4 mg O_3/L) running at the main plant. Table 12.3 shows the comparative performance of ferrate(VI) and $FeCl_3$ at 0.1 mg/L dosage in pilot-scale experiments. Both performed similarly in the removal of particles, UV absorbers, and dissolved organic carbon (DOC) under the given conditions. However, ferrate (VI) can achieve 10% reduction of metformin, benzotriazole, and acesulfame, but $FeCl_3$ with ozonation cannot remove any of these compounds. Moreover, the ferrate (VI)-treated water did not generate bromate, but the ozonated water did although the resulting bromate concentration was 11 μg/L.

12.3.2 *Crude Sewage Treatment Performance in the Pilot Plant*

During the pilot-plant study, properties of the crude sewage were tested. Concentrations of the target quality parameters varied from 242 to 730 mg/L for the SS, 523 to 1125 mg/L for the COD, 235 to 441 mg/L for the BOD, and 11.3 to 18.5 mg/L for the phosphate as total P.

The comparative performance of ferrate(VI) and ferric sulfate can be seen in Table 12.4. With a low dose (0.03 mg Fe/L), ferrate(VI) can achieve similar or better performance than a high dose of ferric sulfate (37 mg Fe/L).

Table 12.4 Comparative performance[a] of crude sewage treatment with ferric sulfate and ferrate (VI)

Chemical and dose	Average percentage removal for the given doses of given chemical (%)			
	SS	P	COD	BOD
Ferrate(VI) (0.03 mg Fe/L)	79	56	50	30
Ferric sulfate (37 mg Fe/L)	78	59	54	43

aCrude sewage properties: [SS] = 730 mg/L; [P] = 18.5 mg/L; [COD] = 1125 mg/L; [BOD] = 388 mg/L

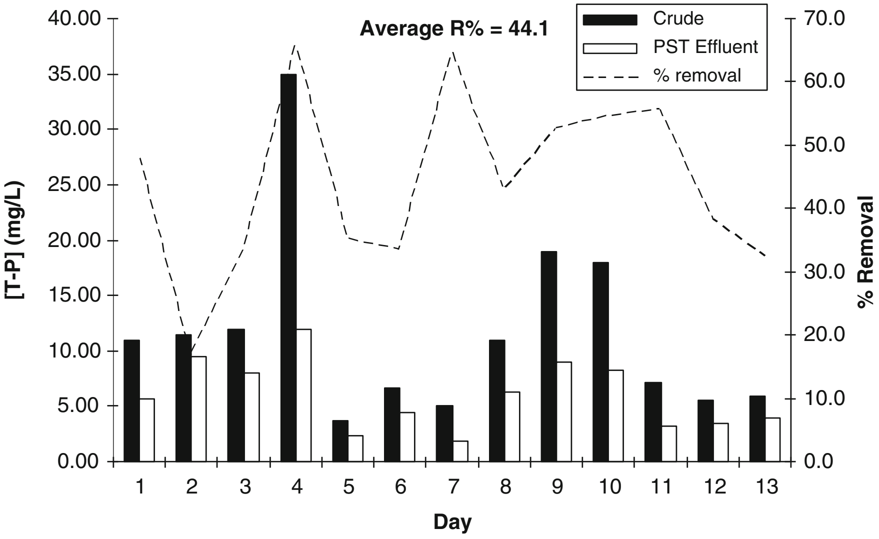

Fig. 12.2 Total phosphorus concentration in crude sewage and the effluent after pre-sedimentation tank (PST) and percentage removals of P. (Reproduced from Jiang et al. 2018)

Figs. 12.2, 12.3, 12.4 and 12.5 show concentrations of P, 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 dose (0.16 mg $Fe^{(VI)}$/L), ferrate (VI) achieved, in average removals, 64% of SS, 44% of phosphate, 46% of COD, and 40% of BOD when the pH was above 9. The comparative performance of ferrate (VI) and ferric sulfate shows that the ferrate(VI) dose of 0.16 mg $Fe^{(VI)}$/L can achieve similar results to those of ferric sulfate at a relatively high dose (25 mg $Fe^{(III)}$/L). Much smaller dose demand of ferrate(VI) can significantly reduce the chemical requirement and sludge production, so it could result in cutting the operating cost in the treatment of sewage.

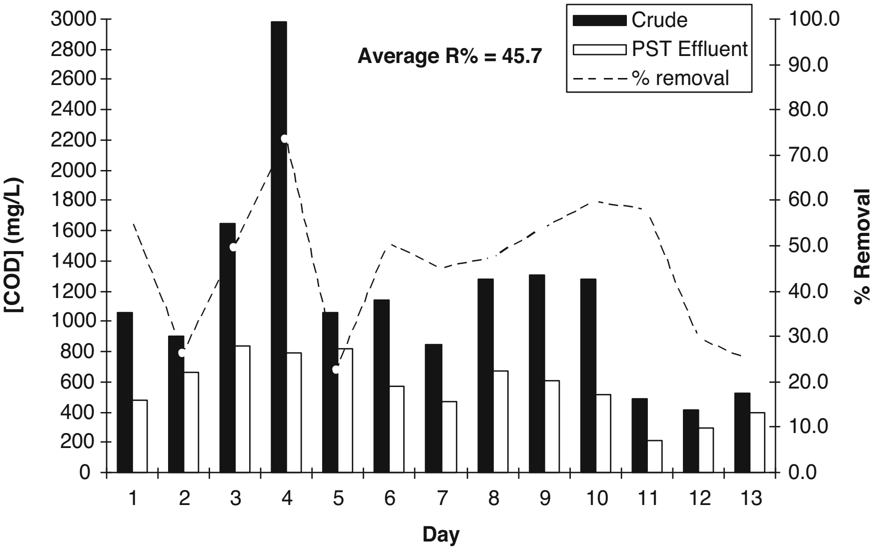

Fig. 12.3 COD concentration in crude sewage and the effluent after pre-sedimentation tank (PST) and percentage removals of COD. (Reproduced from Jiang et al. 2018)

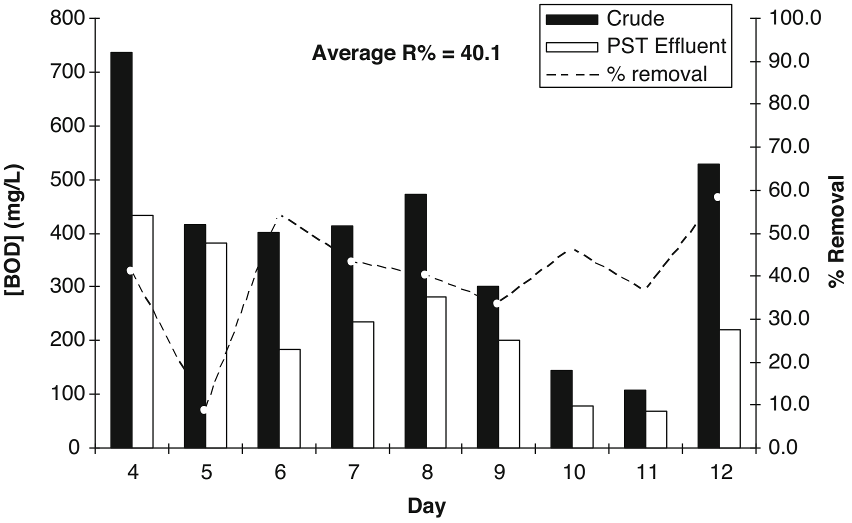

Fig. 12.4 BOD concentration in crude sewage and the effluent after pre-sedimentation tank (PST) and percentage removals of BOD. (Reproduced from Jiang et al. 2018)

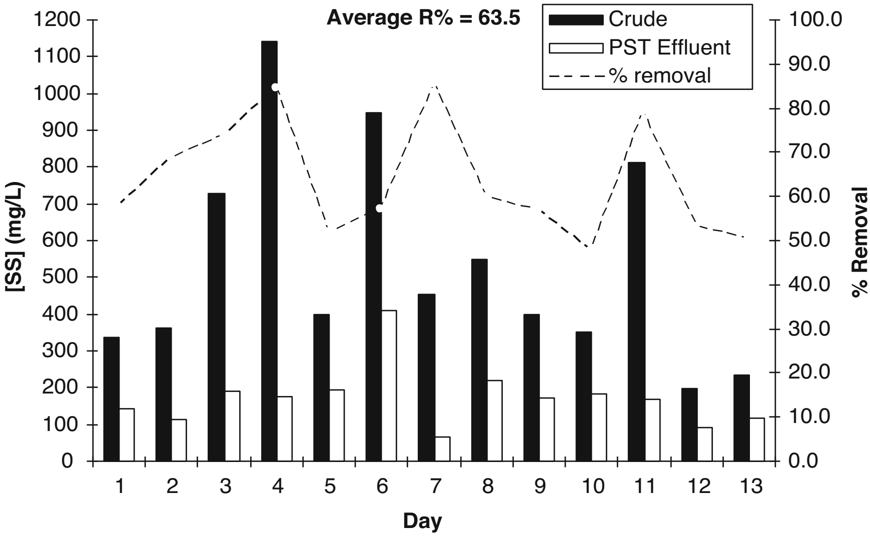

Fig. 12.5 Suspended solids concentration in crude sewage and the effluent after pre-sedimentation tank (PST) and percentage removals of SS. (Reproduced from Jiang et al. 2018)

12.4 Conclusions

Pilot-scale field tests with low ferrate(VI) doses for drinking water treatment achieved average particle removal percentage of 93% for the raw water and 97% for the ozonized water in terms of particle counting data. No pH neutralization was required after dosing ferrate(VI). In comparison with using ozonation and $FeCl_3$ coagulation, ferrate(VI) has the additional benefits: it can remove 10% metformin, benzotriazole, and acesulfame, whereas $FeCl_3$ with ozonation cannot. Additionally, the ferrate(VI)-treated water did not generate bromate, while the ozonated water did.

As for the sewage treatment, pilot-scale tests demonstrated that with very low dose range, 0.1–0.2 mg $Fe^{(VI)}$/L, ferrate(VI) achieved removal targets of phosphorus, COD, BOD, and suspended solids from the crude sewage, while the dose demand of ferric sulfate (25 mg Fe/L) was much higher than that of ferrate(VI); these will reduce the chemical demand and sludge production and therefore generate substantial cost saving in treating sewage. Depending on individual circumstances, the ferrate(VI) technology could be implemented in wastewater treatment practice.

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