PILOT SCALE DRINKING WATER TREATMENT BY FERRATE(VI)

JIANG J.Q.[1], DURAI H.B.P.[1], PETRI M.[2] and WINZENBACHERB R.[3]

[1] School of Engineering and Built Environment, Glasgow Caledonian University,
Glasgow G4 0BA, Scotland, United Kingdom
[2] Zweckverband Bodensee-Wasserversorgung, Süßenmühle 1, 78354 Sipplingen, Germany
[3] Zweckverband Landeswasserversorgung, Am Spitzigen Berg 1, 89129 Langenau, Germany
E-mail: jiaqian.jiang@gcu.ac.uk

ABSTRACT

The work presented in this paper was to identify whether ferrate(VI) can be used as replacement to the existing FeCl3 in drinking water treatment at Zweckverband Bodensee-Wasserversorgung (Lake Constance Water Supply) of Germany. The performance of ferrate(VI) was tested by pilot scale experiments; filtrates with a dose of 0.1 mg/L ferrate(VI) had the average particle removal percentage of 93% for the raw water and 97% for the ozonized water. No pH neutralization was required.. In comparison with using ozonation and FeCl3, ferrate(VI) produced much less N-Nitroso-dimethyl-amine (NDMA), a toxic oxidation products after ozonation.

Keywords: Coagulation; drinking water treatment; ferrate(VI); oxidation; particle removal, micro pollutant reduction

1. Introduction

Ferrate (VI) ion has the formula FeO_4^{2-}, and is a very strong oxidant. Under acidic conditions, the redox potential of ferrate (VI) ions is greater than ozone and is the strongest of all the oxidants/disinfectants practically used for water and wastewater treatment (1). The exploration of the use of ferrate(VI) for water and wastewater treatment has been addressed (e.g., 1-5). The studies revealed that ferrate(VI) can disinfect microorganisms, partially degrade and/or oxidise organic and inorganic impurities, and remove suspended/colloidal particulate materials in a single dosing and mixing unit process. Most recently, researches have been reported using ferrate(VI) to treat emerging micro pollutants in water purification processes (e.g., 6,7). However, challenges have existed for the implementation of ferrate(VI) technology in practice due to the instability of a ferrate(VI) solution or high production cost of solid ferrate(VI) products. Research has been directed at the generation and application of ferrate(VI) in situ (e.g., 8, 9). Practical advantages of ferrate(VI) over existing water and wastewater treatment methods should only be shown when water industry could implement 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 technologies. The work presented in this paper was a study following-up the previous work on the use of in-situ generated ferrate(VI) for both drinking water and waste water treatment at pilot- and full-scale. The specific objectives of this paper were to identify the optimal operating conditions of using ferrate(VI) to replace the existing chemicals in drinking water treatment at Lake Constance Water Supply of Germany.

2. Materials and methods

2.1. Materials

Ferric chloride was obtained from the large scale plant in Lake Constance water Supply. Commercially available Metformin (1, 1-Dimethylbiguanide hydrochloride) (Sigma Aldrich) and N,N-dimethyl-sulfamide (DMS, Chemos Gmbh) was used to spiking them into raw water for the test of the formation of N-Nitroso-dimethyl-amine (NDMA) after ferrate(VI) treatment. For the micro pollutants analysis, analytical standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany) or Sigma-Aldrich (Steinheim, Germany). Ultra-pure water, methanol and acetonitrile

with LC-MS grade were purchased from Carl Roth (Karlsruhe, Germany). Ammonium acetate, ammonium carbonate and acetic acid were analytical grade and obtained from Signal-Adrich (Steinheim, Germany). Ferrate production procedures have been described elsewhere (8).

2.2. Pilot scale filtration trials after ferrate(VI) coagulation

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 (15μm), which filters all kinds of unwanted biological particles, and was then flows in to the customized ozone mixer followed by seven contact tanks. And then, ferrate and FeCl3 were pumped into two flowing water separately 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.

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	l/hr	~1700
Average flow velocity	m/h	~6
Running time	hr	40-100
Filter media		40 cm EVERZIT N (0.8-1.6mm); 60 cm Sand (0.4-0.7mm); ~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 hrs 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

2.3. Water quality analysis

Analysis of various water quality parameters followed the standard methods (10). The formation of NDMA was measured by the gas chromatograph (GC) - mass spectrometer (MS) method with a solid phase extraction (SPE) before the measurement. Clarus 500 GC (Perkin-Elmer, Germany) coupled to a Perkin-Elmer Clarus MS single quadrupole mass spectrometer (MS) was used. Coconut charcoal SPE cartridges (Resprep EPA-Method 521, Restek, Germany) were conditioned by rinsing with 3 x 3mL dichloromethane, 3 x 3 mL methanol and 3 x 3 mL ultrapure water. The sample volume was drawn under vacuum through the SPE-cartridges (flow rate 5-10 ml/min). After loading, the cartridges were dried under gentle stream of air. The analytes were eluted with 4 x 2 mL dichloromethane into a 10 mL glass tube. Small amounts of water present were removed with 2 g sodium sulfate. The dried extracts were concentrated under a stream of nitrogen at 30°C to 1 mL and then transferred to 2 mL GC vials. The extracts were stored at -18°C until instrumental analysis.

3.   Results and discussion

3.1. Removal of small particle (<2 μm)

Lake Constance water has better 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 the ozonized water (Figure 1). As can be seen in Figure 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 Filter2. However, after dosing coagulants, such differences were extinct.

3.2. NDMA formation after water treatment

The presence of NDMA in drinking water has serious adverse health effect. Both metformin and DMS presented in Lake Constance have potential to produce NDMA as byproducts when they react with oxidants (e.g., ozone). Experiments were thus carried out to examine the effect of using ferrate(VI) on the formation of NDMA.

When metformin was used as precursor no more than 2 ng/L of NDMA formation was observed after 0.1 mg/L ferrate(VI) treatment (Figure 2, Left). Initial metformin concentration did not result in great difference in the formation of NDMA. The reason for this is due to less reactivity between ferrate(VI) and metformin.

When DMS was used as precursor, NDMA formation was affected by the concentration of spiked DMS and ferrate(VI) dose; high concentrated DMS (100 μg/L) resulted in high NDMA formation at high doses of ferrate(VI) (4-5 mg/L). On the other hand, relatively low concentration of DMS (10 μg/L) did not cause significant NDMA formation especially when ferrate(VI) dose was <5 mg/L (Figure 2, Right).
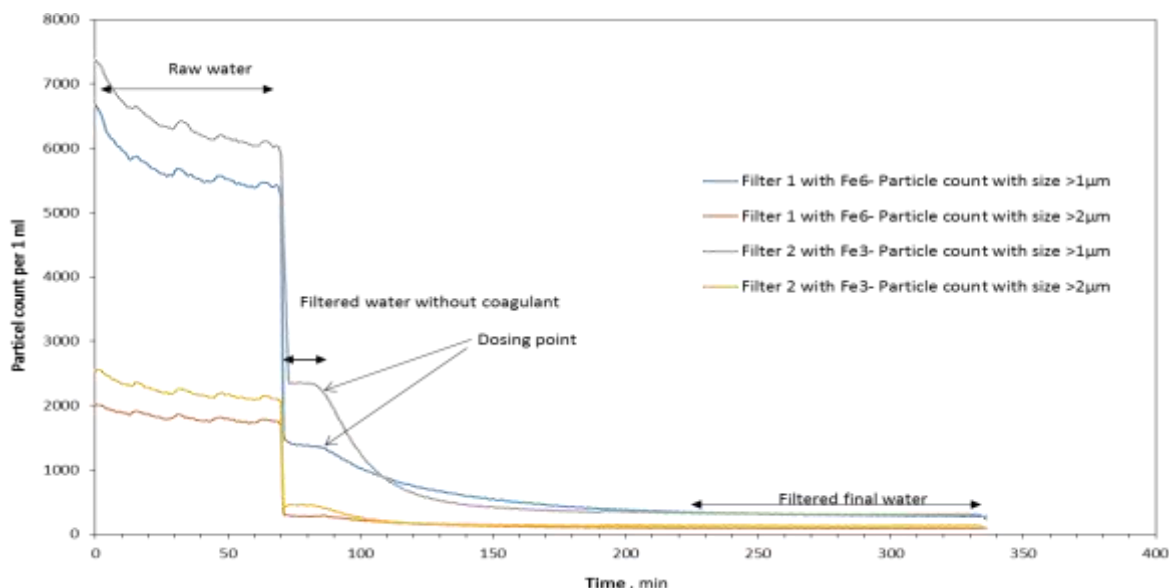

Figure 1: Particle removal by coagulation at 0.1 mg/L as Fe and pilot plant filtration from raw water (Filter 1-Ferrate, Filter 2- FeCl3)

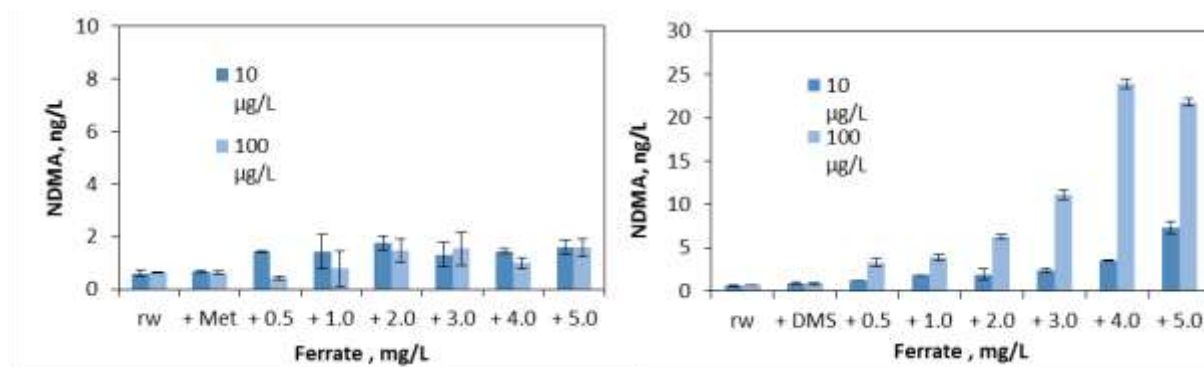**Figure 2:** NDMA formation in Lake Constance water spiked with metformin (Left) and DMS (Right) (10 and 100 μg/L, respectively) and treated with ferrate(VI) (0.1 mg/L dose)

3.3. Comparative performance of FeCl3 and ferrate(VI)

Table 3 shows the comparative performance of ferrate(VI) and FeCl3 at 0.1 mg/L dosage in pilot scale experiments. Both performed similar in the removal of particles, UV-abs and DOC for the given conditions in the pilot plant. However, ferrate(VI) performed better to achieve additional tasks such as replacing H2O2 and removing some micro pollutants. Ferrate(VI) also has the potential to perform as additional disinfectant followed by ozone if necessary.

		Raw water		Ozonated water	
		Ferrate	Fe^{3+}	Ferrate	Fe^{3}
Turbidity	%	~80	~80	~90	~90
UV abs-254	%	0	0	0	0
DOC	%	0	0	0	0
Residual Fe	µg/L	~16	~9	~15	~12
Particle removal	%	~93	~94	~98	~98
Metformin	%	0-10	0	0-10	0
X-ray contrast mediums	%	100	100	100	100

4. Conclusions

Pilot scale filtration experiments with dosing 0.1 mg/L of ferrate(VI) achieved the average particle removal percentage of 93% for the raw water and 97% for the ozonized water. No pH neutralization was required. In comparison with using ozonation and FeCl3 coagulation, ferrate(VI) has the additional benefits; it did not significantly result in the formation of N-Nitroso-dimethyl-amine (NDMA) after the treatment. Moreover, ferrate(VI) can effectively replace both ferric chloride and hydrogen peroxide in terms of achieving the required treatment performance and minimizing residual ozone.

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