Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2016.1203825

57 (2016) 26369–26375
November

Taylor & Francis
Taylor & Francis Group

Drinking water treatment by ferrate(VI) and toxicity assessment of the treated water

Jia-Qian Jiang[a,*], Hari B.P. Durai[a], Michael Petri[b], Tamara Grummt[c], Rudi Winzenbacher[d]

[a]*School of Engineering and Built Environment, Glasgow Caledonian University, Glasgow G4 0BA, Scotland, UK, email: jiaqian.jiang@gcu.ac.uk (J.-Q. Jiang)*
[b]*Qualitätssicherung und Forschungslabor, Zweckverband Bodensee-Wasserversorgung, Süssenmühle 1, 78354 Sipplingen, Germany*
[c]*Fachgebiets II 3.6 Toxikologie des Trink- und Badebeckenwassers, Umweltbundesamt, Heinrich-Heine-Strasse 12, 08645 Bad Elster, Germany*
[d]*Betriebs- und Forschungslabor, Zweckverband Landeswasserversorgung, Am Spitzigen Berg 1, 89129 Langenau, Germany*

Received 27 December 2015; Accepted 15 June 2016

ABSTRACT

The work presented in this paper identified whether ferrate(VI) can be used as an alternative to the existing $FeCl_3$ in drinking water treatment plant at Lake Constance Water Supply of Germany. The performance of ferrate(VI) was tested in a pilot plant, which includes micro-screening, pre-ozonation, coagulation, and rapid filtration processes. With a ferrate (VI) dose of 0.1 mg/L and without pH neutralization, the average particle removal percentage (in terms of particle counting) after filtration was 93% for raw water and 97% for ozonized water, which is satisfied to the treated water quality demand for particle removal. In comparison with using ozonation and $FeCl_3$ coagulation, ferrate(VI) can remove 10% metformin, benzotiozole, and acesulfam from raw water but $FeCl_3$ with ozonation cannot. Moreover, ferrate(VI) treated water did not generate bromate but ozonated water did (~11 μg/L). Finally, ferrate(VI) can effectively replace both ferric chloride and hydrogen peroxide in terms of achieving the required treatment performance and minimizing residual ozone, and no interaction between genotoxic effects and ferrate(VI) treatment was observed. This adds promising benefit of using ferrate(VI) for the given water quality and operating conditions in drinking water treatment.

Keywords: Coagulation; Drinking water treatment; Ferrate(VI); Genotoxicity test; Micro-pollutant reduction; Ozonation; Particle removal

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 (2.2 V) is greater than that of ozone (2.0 V) 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

*Corresponding author.

Presented at CEST2015—14th International Conference on Environmental Science and Technology, Rhodes, Greece, 3–5 September 2015

has been addressed [1–5]. The studies revealed that ferrate(VI) can disinfect micro-organisms, partially degrade and/or oxidize organic and inorganic impurities, and remove suspended/colloidal particulate materials in a single dosing and mixing unit process. Most recently, researches have reported using ferrate (VI) to treat emerging micro-pollutants in water purification processes [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* [8,9]. Practical advantages of ferrate(VI) over existing water and wastewater treatment methods can only be demonstrated 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 wastewater treatment are needed to establish the database of the comparative treatment performance and to assess the operating cost against the existing technologies.

On the other hand, N-Nitroso-dimethyl-amine (NDMA) is highly toxic and NDMA's contamination of drinking water is of particular concern due to the minute concentrations at which it is harmful. The US Environmental Protection Agency has determined that the maximum admissible concentration of NDMA in drinking water is 7 ng/L [10]. Moreover, ozonation has been widely used for pre-oxidation and disinfecting drinking water and NDMA is to be formed in ozonation if a given precursor is present in raw water [11]. NDMA does not readily biodegrade, adsorb, or volatilize and thus is difficult to be removed from drinking water. Suggested technologies which could be used to treat NDMA-containing water [12] include high levels of UV irradiation in a wavelength of the 200–260-nm range which breaks the N–N bond and reverse osmosis which is able to remove approximately 50% of NDMA. However, it is worth testing alternative technologies for the removal of NDMA from drinking water.

The work presented in this paper was a study following up the previous work [13] on the use of *in situ*-generated ferrate(VI) for both drinking water and wastewater treatment at pilot and full scale. The specific objective of this research was 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. Additionally, the presence of both metformin and N, N-dimethyl-sulfamide (DMS), has been detected at Lake Constance, has the potential to produce NDMA when the lake water is chlorinated and/or ozonated [14,15], and then, experiments were carried out to examine the effect of using ferrate(VI) on the formation of NDMA in drinking water treatment. Finally, genotoxicity tests were carried out to examine whether a ferrate(VI) treatment would result in any potential toxicity in the treated water.

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-dimethylsulfamide (DMS, Chemos GmbH) were used to spike them into raw water to test the formation of NDMA after ferrate(VI) treatment. For the micro-pollutant 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 of analytical grade were obtained from Signal–Aldrich (Steinheim, Germany). Ferrate production procedures have been described elsewhere [8]. Ferrate(VI) is unstable under neutral and acidic pH. However, in this study, it was generated at high alkali conditions and used immediately after generation and then there were no ferrate stability problems.

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 and Photo 1. Water flows through a micro-sieve filter (15 μm), which filters all kinds of large particles (including algae), and then flows into the customized ozone mixer followed by seven contact tanks.

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	h^{-1}	~1,700
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); and ~18-cm supporting material

Photo 1. Pilot-scale filters.

And then, ferrate and $FeCl_3$ were pumped into two flowing waters 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.

2.3. Water quality analysis

Analysis of various water quality parameters and residual ozone concentration followed the standard methods [16]. 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 × 3-mL dichloromethane, 3 × 3-mL methanol, and 3 × 3-mL ultra-pure 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 × 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.

The analysis of micro-pollutants, Metformin benzotiozole 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 × 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 phases with a flow rate of 0.75 mL/min. The column was brought to a constant temperature: 25˚C. Hundred microliters 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˚C inside

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

Parameters	Details
Initial/final flow rate (L/h)	1,500/1,000
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

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.

2.4. Genotoxicity assessment

In the present study, two genotoxicity tests were combined, namely the *Salmonella typhimurium* reverse mutation assay (Ames test) and the Micronucleus test (MN). The two test systems belong to the basic set of tools for genotoxicity testing and they are sufficient for achieving a satisfactory result for possible genotoxic effects [17].

The Ames test was carried out as a plate incorporation assay following the DIN 38415-4. To measure the micronuclei, the *in vitro* MicroFlow® (Litron Laboratories, Rochester USA) was used. Based on the knowledge that most of the human genotoxic carcinogens require metabolic activation, the test was performed with metabolic competent: Hep G2 and HepaRG™ cells. The samples were tested before and after concentration (1:1,000) using C_{18} Polar Plus® column and Oasis HLB.

3. Results and discussion

3.1. Removal of small particle (<2 μm)

Lake Constance's water has better quality and 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.

3.2. NDMA formation after ferrate(VI) treatment

When metformin was used as precursor, no more than 2 ng/L of NDMA formation was observed after dosing 0.1-mg/L ferrate(VI) in the water treatment (Fig. 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,

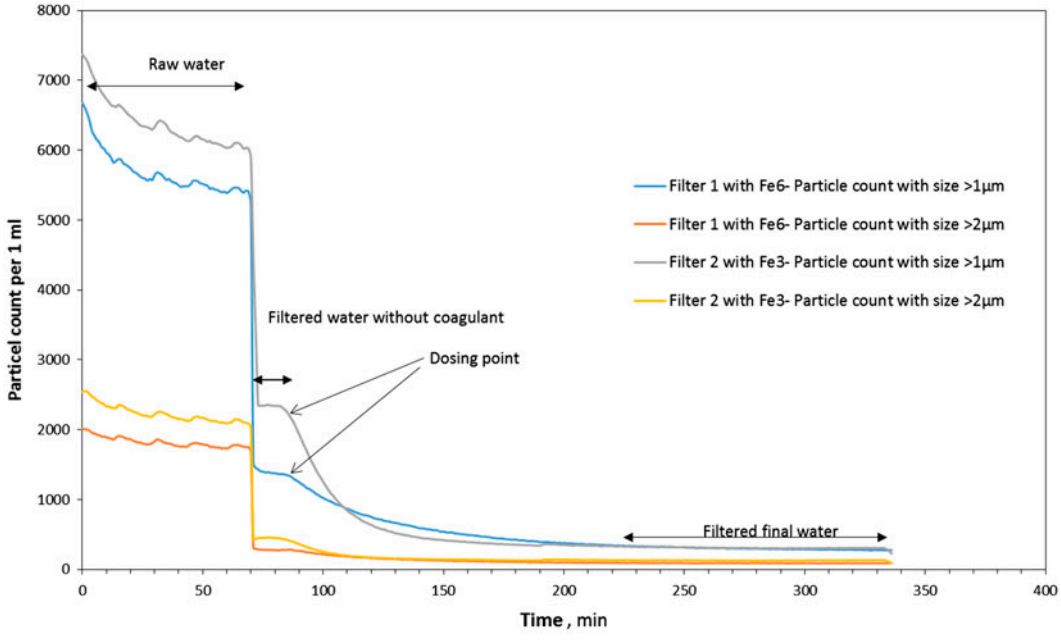

Fig. 1. Particle removal by coagulation at 0.1 mg/L as Fe and pilot plant filtration from raw water (Filter 1-ferrate, Filter 2-$FeCl_3$).

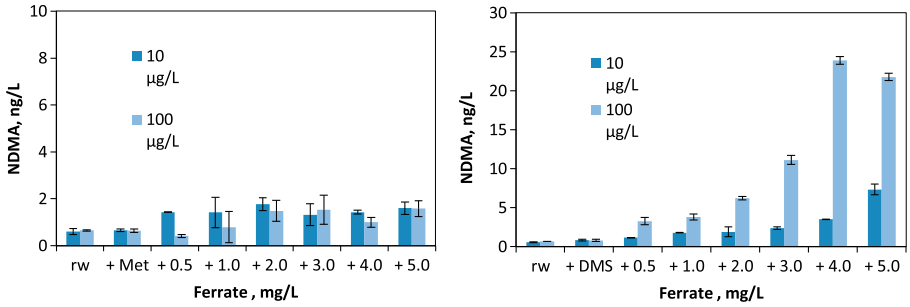

Fig. 2. NDMA formation in Lake Constance; water spiked with metformin (left) and DMS (right) (10 and 100 µg/L, respectively) and treated with ferrate(VI) (0.1-mg/L dose).

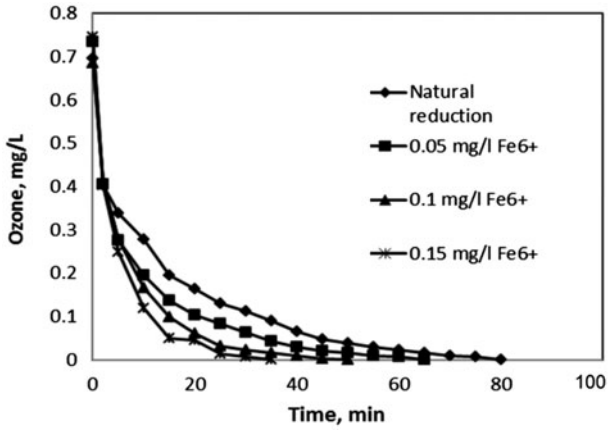

Fig. 3. Ozone reduction by ferrate(VI).

relatively low concentrations of DMS (10 µg/L) did not cause significant NDMA formation, especially when ferrate(VI) dose was <5 mg/L (Fig. 2, right).

Surveys of NDMA formation have been conducted and the work was reviewed [18]. In USA and Japan, raw waters were found to contain NDMA in concentrations of 0–53 ng/L. Chemical disinfection by chlorination, chloramination, chlorine dioxide, and ozone caused an increase in NDMA concentrations. In Japan, ozonation was shown to increase substantially the NDMA concentrations in the two waters. Significantly, more NDMA was found after advanced oxidation processes (H_2O_2/UV) in some waters. Obviously, all oxidation processes will generate NDMA in water treatment; the real production and resulting NDMA concentration mainly depend on the raw water quality characteristics, the type and concentration of disinfectants, and other operating conditions used.

3.3. Comparative performance of $FeCl_3$ and ferrate(VI)

Table 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 removing particles, UV-abs, and dissolved organic carbon (DOC) for the given conditions in the pilot plant. However, ferrate(VI) can achieve 10% reduction of metformin, benzotiozole, and acesulfam but $FeCl_3$ with ozonation cannot. Moreover, ferrate(VI)-treated water did not

Table 3
Comparative performance of ferrate(VI) and $FeCl_3$

		Raw water		Ozone water	
	Unit	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		No change			
Residual Fe	µg/L	~16	~9	~15	~12
Particle removal	%	~93	~94	~98	~98
Bromate formation	µg/L	0	0	~11	~11
Benzotiozole removal	%	10	0	10	0
Acesulfam removal	%	10	0	10	0
Metformin removal	%	10	0	10	0
X-ray contrast medium removal	%	100	100	100	100

Table 4
Summarized results of the genotoxicity testing

Sample		Genotoxicity			
		Ames test		Micronucleus test/cell line	
		Direct	SPE concentrated	Hep G2	HepaRG™
Ferrate(VI) (0.1 mg/L)-treated raw water	T/420-2	–	–	–	–
Ferrate(VI) (0.1 mg/L)-treated raw water	T/420-3	–	–	–	–
Ferrate(VI) (0.5 mg/L)-treated raw water	T/420-4	–	–	–	–
Ferrate(VI) (0.1 mg/L)-treated ozone water	T/420-5	–	–	–	–
Ferrate(VI) (0.1 mg/L)-treated ozone water	T/420-6	–	–	–	–
Ferrate(VI) (0.5 mg/L)-treated ozone water	T/420-7	–	–	–	–
Raw water	T/420-R	–	–	–	–

generate bromate but ozonated water did, although the resulting bromate concentration was 11 μg/L.

In Lake Constance Water Supply, hydrogen peroxide is used to remove residual ozone in the purified water before supplying to their customer. In this study, ferrate(VI) was dosed to ozonated water to examine if ferrate(VI) can be used to replace H_2O_2 and achieve the same task. Fig. 3 shows that ferrate(VI) has the ability to degrade ozone concentration from 0.7 mg/L (ozone dose at Lake Constance) to less than 0.1 mg/L within 15 min, which satisfies the company's requirement.

This work was carried out at the pilot plant where the operating conditions followed the main plants. And therefore, the ferrate(VI) dose used was very low, 0.1 mg Fe/L, in order to compare the performance of ferric chloride and ozonation. Due to this, the relevant volume dose of ferrate(VI) was very low which did not affect the treated water's pH.

3.4. Genotoxicity of the ferrate(VI)-treated water

The occurrence of genotoxicity in aquatic systems is a serious problem because of the risk to both human and ecosystem health. The systematic use of the basic test strategy can be a useful early warning system in the identification of toxicological hazards due to the implementation of any new treatment techniques, such as ferrate(VI) in this study. Table 4 summarizes the toxicity assessment results. All ferrate(VI)-treated water samples gave negative results in general. The water treatment scheme had no influence on the genotoxic activity. The addition of the metabolic system (Ames, S9-Mix) and the use of metabolic competent cells led to similar negative results, suggesting that ferrate(VI) treatment did not generate toxicity for the study conditions.

4. Conclusions

Pilot-scale filtration experiments with dosing 0.1 mg/L of ferrate(VI) achieved the 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 $FeCl_3$ coagulation, ferrate(VI) has additional benefits; it did not significantly result in the formation of N-Nitrosodimethyl-amine (NDMA) after the treatment and can remove 10% metformin, benzotiozole, and acesulfam but $FeCl_3$ with ozonation cannot. Additionally, ferrate (VI)-treated water did not generate bromate while ozonated water did. Moreover, ferrate(VI) can effectively replace both ferric chloride and hydrogen peroxide in terms of achieving the required treatment performance and minimizing residual ozone. Finally, no interaction between genotoxic effects and ferrate(VI) treatment was observed.

Acknowledgments

We thank Glasgow Caledonian University, Zweckverband Bodensee-Wasserversorgung, and Zweckverband Landeswasserversorgung Water Board of Germany for offering research studentship to H.B.P. Durai. We are also grateful to the staff at the pilot plant and laboratory at Zweckverband BWV. The views of this paper may not necessarily represent those of the two water companies.

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