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

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ABSTRACT

The work presented in this paper was to identify whether ferrate(VI) can be used as an alternative to the existing FeCl₃ 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 required, the average particle removal percentage (in terms of particle counting) after filtration was 93% for the raw water and 97% for the ozonized water, which is satisfied to the treated water quality demand for the particle removal. In comparison with using ozonation and FeCl₃ coagulation, ferrate(VI) can remove 10% metformin, benzotiozole and acesulfam from raw water but FeCl₃ with ozonation can't. Moreover, ferrate(VI) treated water did not generate bromate but ozonated

water did ($\sim 11 \mu\text{g/L}$). 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 were 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 has been addressed [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 [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 waste water 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 (USEPA) has determined that the maximum admissible concentration of NDMA in drinking water is 7 ng L^{-1} [10]. Moreover, ozonation has been widely used for the pre-oxidation and disinfection in drinking water treatment and NDMA is to be formed in ozonation if a given precursor is presenting in raw water [11]. NDMA does not readily biodegrade, adsorb, or volatilize and thus is difficult to be removed from drinking water. Suggested technologies could be used to treat NDMA containing water [12] include high levels of UV irradiation in a wavelength of the 200 to 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 waste water treatment at pilot- and full-scale. The specific objectives of this research 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. Additionally, Lake Constance has

been detected the presence of both metformin and N,N-dimethyl-sulfamide (DMS), which have potential to produce NDMA when the lake water was 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-dimethyl-sulfamide (DMS, Chemos GmbH) was used to spike them into raw water for the test of the formation of 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]. Ferrate(VI) is unstable under neutral and acidic pHs. 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 μ m), which filters all kinds of large particles (including algae), and 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	hr ⁻¹	~1700
Average flow velocity	mhr ⁻¹	~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



Photo 1. Pilot-scale filters

Table 2.

Pilot plant operating conditions (Fe dose = 0.1 mgL⁻¹)

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 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 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.

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 mm x 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°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°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, 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.

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.

The Ames test was carried out as a plate incorporation assay following the DIN 38415-4 [17]. 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

HepaRGTM cells. The samples were tested direct and after concentration (1:1000) by using C₁₈ Polar Plus® column and Oasis HLB.

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 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 Filter2. 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 (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).

Surveys of NDMA formation have been conducted and the work was reviewed [18]. In USA and Japan, the 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 two waters. Significantly, more NDMA was found after advanced oxidation processes (AOP) (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.

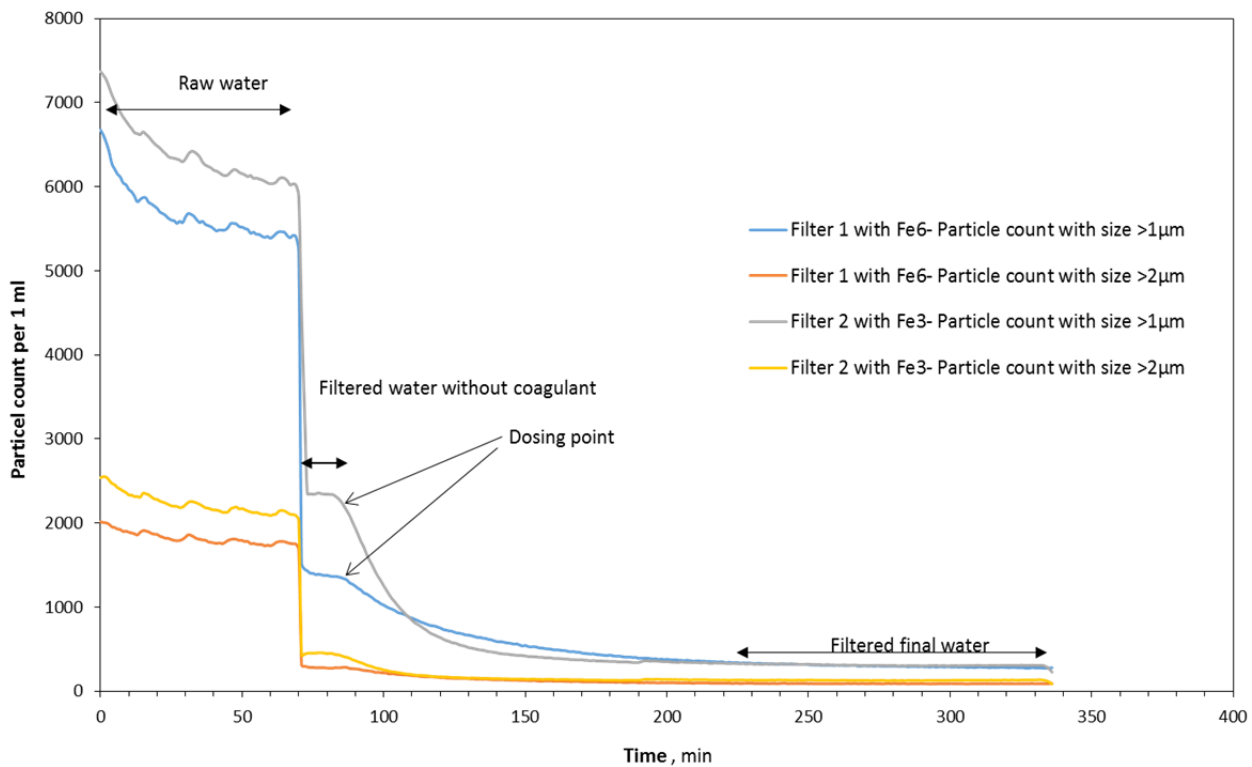


Fig. 1. Particle removal by coagulation at 0.1 mg/L as Fe and pilot plant filtration from raw water (Filter 1-Ferrate, Filter 2- $FeCl_3$)

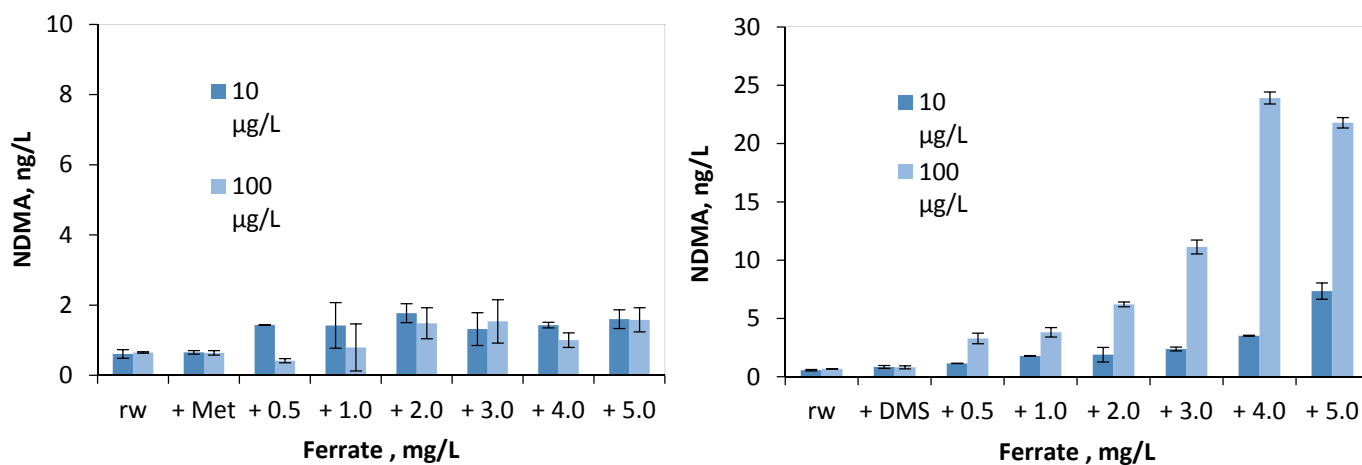


Fig. 2. NDMA formation in Lake Constance water spiked with metformin (Left) and DMS (Right) (10 and 100 µg/L, respectively) and treated with ferrate(VI) (0.1 mg/L dose)

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 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 FeCl₃ with ozonation can't. Moreover, ferrate(VI) treated water did not 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 H₂O₂ and achieve the same task. Figure 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 minutes, which is satisfied by 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 equality compare with 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 pH.

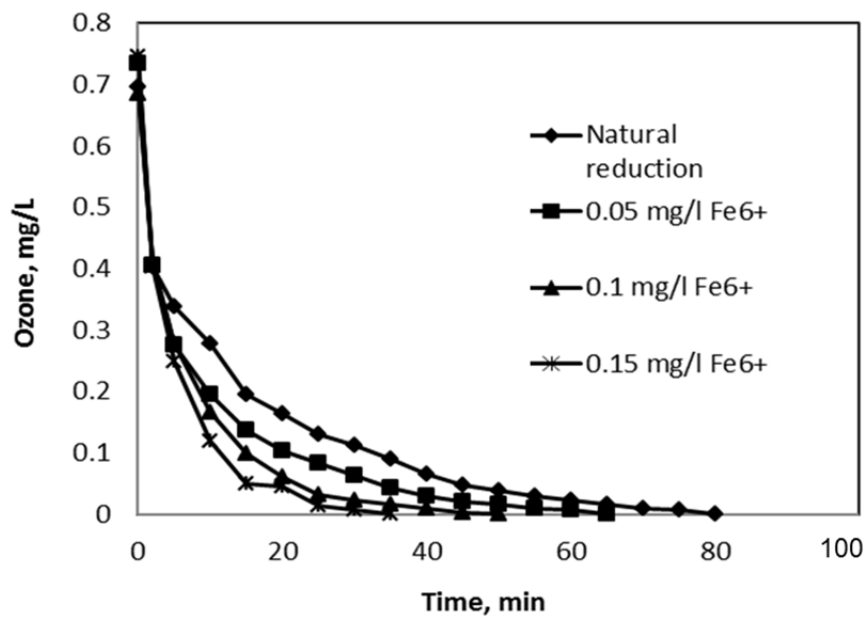


Fig. 3 Ozone reduction by ferrate(VI)

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	%	~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	

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 of 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.

Table 4.

Summarized results of the genotoxicity testing

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

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 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) has the additional benefits; it did not significantly result in the formation of N-Nitroso-dimethylamine (NDMA) after the treatment and can remove 10% metformin, benzotiozole and acesulfam but FeCl₃ with ozonation can't. 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 were observed.

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