



Formation of iodinated trihalomethanes after ferrate pre-oxidation during chlorination and chloramination of iodide-containing water



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ABSTRACT

Iodinated disinfection by-products (I-DBPs) are responsible for taste and odor issues, and more toxic than their brominated and chlorinated analogs. Ferrate salt (Fe(VI)) is green, efficient and multifunctional in drinking water treatment. Iodinated trihalomethanes (I-THMs) formation of iodide containing water pretreated by ferrate during chlorination/chloramination was investigated in this paper. The results indicated that I-THMs can be reduced significantly by ferrate pre-oxidation due to the oxidation of iodide to iodate. During chlorination, no detectable I-THMs were found at pH < 8 after ferrate pre-oxidation. However, I-THMs formation increased significantly at pH 8–9. I-THMs formation decreased drastically with increasing ferrate dosage and no detectable I-THMs were found at high ferrate dosage (>2 mg/L). The presence of high bromide concentration could restrain the transformation from iodide to iodate during ferrate pre-oxidation. However, no obvious changes in the amount and speciation of I-THMs were observed with increasing bromide addition. The yield of I-THMs was within $15 \pm 2 \mu\text{g/L}$ when bromide addition varied. During chloramination, compared to the samples without bromide, the formation of I-THMs was restrained too. However, increasing bromide concentration in chloraminated solutions would lead to significant increase in the I-THMs formation and could contribute to the changes in speciation. The yield of I-THMs increased from 16.11 $\mu\text{g/L}$ to 33.28 $\mu\text{g/L}$ when bromide concentration is 25 μM and 100 μM , respectively. Ferrate pre-oxidation can be employed to reduce the I-THMs formation in drinking water treatment for iodide-containing water.

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1. Introduction

Disinfection is an important part in drinking water treatment processes because it can significantly prevent the outbreaks of diseases which were spread by drinking water [1,2]. To date, a large amount of disinfectants were investigated and put into operation. Among those disinfectants, chlorine and chloramination were widely used in water treatment plants because of their low-cost and favorable disinfection ability. However, disinfection by-products (DBPs) were observed during the chlorination/chloramination of raw water and various studies confirmed that DBPs have cytotoxicity and genotoxicity in mammalian cell assays [3,4]. Over the past several decades, regulated DBPs which contains chlorinated and brominated trihalomethanes (THMs) and haloacetic acids have drawn a lot of attention, and a series of characteristics were exposed to public [2,5,6]. However, iodinated disinfection by-products (I-DBPs) still need a better understanding because they are more toxic than their chlorinated and brominated analogs in terms of cytotoxicity and genotoxicity [7,8]. Besides, io-

idated trihalomethanes (I-THMs) were reported to be responsible for taste and odor issues [9]. A former study showed that as low as 0.02 $\mu\text{g/L}$ iodoform would be sufficient to cause odor issues [2,10]. Thus, it is extremely easy to cause offensive odors in drinking water if I-THMs exist. I-DBPs are derived from the reaction between natural organic matter (NOM) and hypiodous acid (HOI) [8,11]. HOI is believed to be generated by the oxidation of iodide during the treatment processes [12]. In the areas near the sea coast which suffer from seawater intrusion, surface or ground waters usually contain high iodide concentration [13]. A number of former studies have confirmed that the iodinated DBPs would be generated enormously during the disinfection of iodide containing raw water, especially when chlorine or chloramine were used as disinfectant [12,14].

In order to restrain the formation of I-DBPs and improve drinking water quality, pre-oxidation was adopted in the water treatment processes. It was reported that pre-oxidation can eliminate taste, odor, alga as well as dissolved organic matters (DOM), and it can successfully reduce the formation of DBPs [15–17]. For instance, a number of former studies have investigated the effect of various pre-oxidants, such as chlorine [18], chlorine dioxide [16], ozone [18], potassium permanganate [14,19], and UV/H₂O₂ [20]. However, the application of these pre-oxidation processes was limited because of some specific

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reasons. For example, the preparation of chlorine dioxide was complicated and expensive, and it was very hard to store because chlorine dioxide was unstable. Besides, potassium permanganate would result in more formation of iodoform because potassium permanganate could oxidize iodide to iodine [14]. In recent years, ferrate salt has been investigated as an efficient pre-oxidant for water treatment [15,16].

Ferrate salt (Fe(VI)) is a green, multifunctional chemical which can be used as an oxidant and a subsequent coagulant as ferric hydroxide [21–24]. It was reported that in alkaline solutions, the oxidation reduction potential (ORP) of ferrate was 0.70 V and in acidic solutions, the ORP of ferrate reached up to 2.20 V which was higher than other pre-oxidants [25,26]. Due to its remarkable oxidation power, ferrate has a high efficiency of sterilization over a wide pH range. In addition to the ferrate's outstanding performance in disinfection, its decomposition product is an environmentally friendly coagulant as well. When ferrate was added to the acidic solutions, the oxygen ligands of ferrate exchanged rapidly with water and Fe(III) can be generated that can enhance the coagulation efficiency [23]. The reaction products including Fe(III) and molecular oxygen are both nontoxic to aquatic and humans [23]. Over the past few years, the DBPs formation during ferrate pre-oxidation of NOM and model compounds was investigated [15]. It was reported that both hydrophilic and hydrophobic fractions of NOM was reduced and a decrease in THMs formation was observed during the pre-oxidation and post-chlorination of most of model compounds except amines and glycine [15]. This indicated that ferrate pre-oxidation and post-chlorination/chloramination can efficiently restrain the formation of DBPs. However, only a limited number of studies have investigated the effect of ferrate pre-oxidation on DBPs formation and to the best of our knowledge, the effect of ferrate pre-oxidation on I-THMs formation potential has not been reported [15–17].

The objectives of this study were to investigate the impacts of initial concentration of ferrate, bromide concentration and solution pH on the formation of I-THMs during ferrate pre-oxidation and post-chlorination/chloramination of natural water spiked with iodide, and four chlorine- and bromine-containing THMs (THM4) were studied incidentally.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals were at least of analytical grade except as noted and were used without further purification. Calibration standards including dichloromethane (CHCl_2 , 95+%), chlorodiodomethane (CHClI_2 , 90–95%), dibromiodomethane (CHBr_2I , 90–95%), bromodiodomethane (CHBrI_2 , 90–95%), bromochloriodomethane (CHBrClI , 95+%), chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl) and bromoform (CHBr_3) were purchased from CanSyn chemical Corp. (Toronto, ON, Canada). Commercial 4–4.99% sodium hypochlorite (NaOCl), iodoform (CHI_3 , 99.0%), and potassium bromide (KI , 99.0+%) were purchased from Sigma-Aldrich. Methyl *tert*-butyl ether (MtBE) was received from J.T. Baker (USA). H_2SO_4 , NaOH , and $\text{Na}_2\text{S}_2\text{O}_3$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

Potassium ferrate (K_2FeO_4 , Fe(VI)) of >95% purity was prepared by the hypochlorite oxidation of ferric nitrate, according to the wet chemical synthesis method [27]. Stock solutions of potassium ferrate (100–300 μM) were prepared by adding solid K_2FeO_4 to Milli-Q water buffered with 5 mM phosphate / 1 mM borate at $\text{pH} \approx 9.1$ where ferrate is reported to be most stable [24,28,29]. The concentration of Fe(VI) was determined by the molar absorption coefficient of $\varepsilon_{510 \text{ nm}} = 1150/\text{M cm}$ [24,30]. All solutions were prepared with ultra-pure water produced from a Milli-Q water purification system (Millipore, USA).

2.2. Experimental and procedures

Natural surface water was collected from Huangpu River in Shanghai, China, and then filtered through 0.45- μm membrane filters (Millipore Corp., USA) immediately to obtain the raw water samples which were used to conduct subsequent experiments. Dissolved organic carbon (DOC), specific ultraviolet absorbance (SUVA, defined as ultraviolet absorbance at the wavelength of 254 nm (UV_{254}) divided by the DOC concentration) and bromide concentration was measured as 3.83 mg/L, 2.38 L/mg m, 0.88 μM , respectively.

Experiments were conducted in duplicate under headspace-free conditions in 40 mL glass screw-cap amber vials with PTFE-lined septa at room temperature (25 ± 1 °C). During the pre-oxidation experiments, chlorination and chloramination of raw water spiked with 10 μM iodide ions (I^-) and buffered with 10 mM phosphate were conducted 30 min after adding the ferrate in order to make sure that ferrate was completely depleted. After that, the samples were stored at 25 ± 1 °C in the dark and incubated for 72 h. The effects of reaction pH, initial dosage of ferrate, and bromide concentration were investigated. Solution pH was adjusted with either 0.01, 0.1, 1 M NaOH or H_2SO_4 and the amount of pH drift was controlled within ± 0.02 . The pre-oxidation and chlorination/chloramination were conducted at the same pH. After pre-oxidation, solution pH would be adjusted again to the specific value before chlorination/chloramination. After the designed reaction time, aliquots of the reacted solution were withdrawn and quenched for remaining disinfectant using sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) with 20% excess of initial disinfectant dose [21].

Chloramination experiments were carried out with preformed monochloramine (NH_2Cl) prepared by adding NaOCl solution slowly into a stirred ammonium chloride (NH_4Cl) solution with the N/Cl molar ratio of 1.2 at pH 8.5 [31], and preformed NH_2Cl was prepared freshly before each test. Chlorine and NH_2Cl concentration were determined using the *N,N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method [32].

2.3. Analytical methods

UV absorption at 254 nm and 510 nm were measured by a UV/Vis spectrophotometer (SQ-4802, UNICO, Shanghai) with a 1-cm quartz cell at the wavelength of 254/510 nm. A Shimadzu TOC-VCSH analyzer (Shimadzu, Japan) was used to detect the concentration of dissolved organic carbon (DOC) and its detection limit was 0.1 mg-C/L. The pH was analyzed with a pH meter (FE20-FiveEasy, Mettler Toledo, Switzerland) calibrated regularly with standard buffer solutions. The concentration of Br^- was measured using an ion chromatography (Dionex ICS-2000, CA, USA), which was equipped with a conductivity detector, a Dionex AS11-HC analytical column (250 mm \times 4.0 mm i.d.) and a Dionex AG11-HC guard column (50 mm \times 4.0 mm i.d.). The concentration of iodide and iodate were detected by UPLC (Waters, USA) equipped with a XTerra[®] MS C18 column (4.6 \times 250 mm i.d., 5 μm film thickness, Waters, USA) by a UV detector at the wavelength of 209 and 223 nm, respectively [33–35].

According to our previous research with some modifications [12,36], method for quantifying I-THMs was adopted in the experiments. After the designed reaction time, 10 mL of samples were quenched and quantified by liquid/liquid extraction with 2 mL MtBE immediately which was followed by a gas chromatography (GC-2010, Shimadzu, Japan) equipped with an electron capture detector (GC/ECD, GC-2010, Shimadzu, Japan) and a HP-5 capillary column (30 m \times 0.25 mm i.d., 0.25 μm film thickness, J&W, USA). The detection limit of CHI_3 , CHBrI_2 , CHClI_2 , CHBr_2I , CHBrClI and CHCl_2I was 0.08, 0.05, 0.05, 0.08, 0.09 and 0.10 $\mu\text{g/L}$, respectively. THM4 was determined by GC/ECD according to USEPA Method 551.1 [37], and the detection limit of CHCl_3 , CHCl_2Br , CHClBr_2 and CHBr_3 was 0.09, 0.03, 0.03 and 0.05 $\mu\text{g/L}$, respectively.

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