Formation of Bromate during Ferrate(VI) Oxidation of Bromide in Water

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ABSTRACT:

Ferrate (VI) is traditionally recognized as a safe oxidant without production of disinfection byproducts (DBPs). However, here we detected probable carcinogenic bromate (BrO_3^-) during ferrate(VI) oxidation of bromide (Br^-)-containing water, and evaluated the effects of pH, ferrate(VI) dose, initial Br^- concentration, and co-existing anions on the BrO_3^- formation. BrO_3^- was produced at a moderately–weakly acidic pH condition and in the absence of phosphate that was commonly applied as a buffer and stabilizing agent in previous ferrate(VI) studies. At pH 5.0, the produced BrO_3^- was increased from 12.5 to 273.8 $\mu\text{g/L}$ with the increasing initial Br^- concentration from 200 to 1,000 $\mu\text{g/L}$ at 10 mg/L Fe(VI), corresponding to an increase in the molar conversion ($[\text{BrO}_3^-]/\text{initial } [\text{Br}^-]$) from 2.3% to 10.3%, in a bicarbonate-buffered solution. As pH increased to 7.0, the BrO_3^- concentration gradually dropped. The BrO_3^- production appeared to be associated with the oxidation by high valence iron species (i.e. Fe(VI), Fe(V) and Fe(IV)). Two key intermediate products (i.e. hypobromous acid/ hypobromite (HOBr/OBr^-) and hydrogen peroxide (H_2O_2)) relevant to the bromate formation were identified. The production of HOBr, a requisite intermediate for the ensuing bromate formation, was indirectly validated through identification of bromine-containing trihalomethanes and haloacetic acids during ferrate oxidation in a natural water, though these bromo-organic DBPs produced were insignificant. Furthermore, the inhibition effects of various anions on the formation of BrO_3^- followed chloride < sulfate < silicate < phosphate. More H_2O_2 was detected at higher phosphate concentration. It could reduce HOBr to Br^- , thereby inhibiting the bromate formation.

INTRODUCTION.

Although water disinfection can inactivate pathogenic microorganisms, it can lead to the production of various disinfection by-products (DBPs) of health concerns, such as trihalomethanes, haloacetic acids, N-nitrosodimethylamine, and bromate, as a result of reactions between disinfectants and certain water matrix constituents (Haag and Hoigne, 1983; Mitch et al., 2003; Sedlak and von Gunten, 2011). To minimize the formation of these undesirable compounds, alternative treatment agents are being sought. Recently, ferrate(VI) has gained much attention (Sharma et al., 2005). Ferrate(VI) is the oxyanion FeO_4^{2-} with iron in + 6 oxidation state. FeO_4^{2-} has a tetrahedral structure in which the four Fe-O bonds are equivalent with covalent character (Hoppe et al., 1982). Although the capability of ferrate(VI) for water treatment was early demonstrated in the 1970s (Gilbert et al., 1976; Waite and Gilbert, 1978; Waite, 1979), a large number of studies on ferrate(VI) as a “new” and multi-purpose treatment agent have only emerged over the past one and half decades, partially as a result of recent advances in ferrate synthesis (Waite, 2012). During the oxidation, Fe(VI) is reduced to intermediate high valence iron species – more reactive perferryl (Fe(V)) and ferryl (Fe(IV)) - and eventually to stable Fe(III). The produced Fe(III) precipitates from water in the forms of iron oxides/hydroxides are also expected to remove pollutants via precipitation, coagulation and adsorption (Graham et al., 2010). Previous studies demonstrate that ferrate(VI) effectively inactivates pathogens in water such as virus, *E. Coli.*, and bacteriophage MS2 (Schink and Waite, 1980; Jiang et al., 2006, 2007; Jessen et al., 2008; Hu et al., 2012), as well as remove many other pollutants including natural organic matters (NOM) (Graham et al., 2010; Song et al., 2016), toxic inorganic substances (Fan et al., 2002), and emerging micro-pollutants (Yang et al., 2012). Traditionally, ferrate(VI) is recognized to be a safe disinfecting or oxidizing agent

without production of potentially carcinogenic bromate (BrO_3^-) or any other DBPs (Sharma et al., 2006; Lee and von Gunten, 2010), thereby being advantageous over many existing disinfectants, such as ozone that may suffer from the oxidation of bromide to BrO_3^- (Haag and Hoigne, 1983; Von Gunten and Hoigne, 1994; Pinkernell and von Gunten, 2001).

Bromide (Br^-) concentrations in freshwater range mostly between 14 and 270 $\mu\text{g/L}$, with slightly higher levels in regions with saltwater intrusion, road runoff, dissolution from sedimentary rock, and anthropogenic waste discharge, and may reach a few mg/L in coastal areas (Flury and Papritz, 1993; Butler et al., 2005). BrO_3^- is formed as an undesirable DBP during oxidative treatment of Br^- -containing water with ozone, hydroxyl radicals ($\text{OH}\cdot$), or sulfate radicals ($\text{SO}_4^{\bullet-}$) (Von Gunten and Oliveras, 1998; Fang and Shang, 2012). International Agency for Research on Cancer (IARC) classifies BrO_3^- as a Group 2B or “possible human” carcinogen. The US Environmental Protection Agency (EPA) has a drinking water maximum contaminant level (MCL) of BrO_3^- at 10.0 $\mu\text{g/L}$. Although the commonly accepted viewpoint in literature is that ferrate(VI) is an environmentally friendly alternative oxidant without the production of BrO_3^- (Sharma et al., 2006; Lee and von Gunten, 2010), we noticed that most of these studies were conducted in phosphate-buffered solutions that rarely exists in a real-world potable water treatment scenario or only at an alkaline condition under which Fe(VI) is much less active. The objective of this study was to detect the formation of BrO_3^- under different experimental conditions, and evaluate the effects of key factors including ferrate(VI) dose, solution pH and co-existing anions, during ferrate(VI) oxidation of bromide in water.

1. MATERIAL AND METHODS.

Reagents. All the reagents used were at least analytical grade, except as noted. Potassium bromide (KBr) (99.8%), bromate standard (1,000 mg/L) for ion chromatography (IC), potassium

ferrate(K_2FeO_4) ($> 96\%$), 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), and all the other reagents were purchased from Sigma–Aldrich. A concentrated ferrate(VI) stock solution (200 mg/L as Fe) was prepared by dissolving a certain amount of K_2FeO_4 in deionized (DI) water. Ferrate(VI) concentration in the stock solution was confirmed with the ABTS method (Lee et al., 2005b). Solutions were prepared with DI water ($\geq 18.2 \text{ M}\Omega\cdot\text{cm}$).

Experimental procedures. All the BrO_3^- formation tests were performed in 250-mL amber glass vials on a magnetic stirrer at ambient temperature ($25 \pm 1.5^\circ\text{C}$). Bicarbonate (NaHCO_3) buffer solution (5 mM) was first prepared with an original pH of ~ 9.2 . And then the solution pH was adjusted with 0.05 or 0.5 M nitric acid (HNO_3) to designated pH levels (5.0–7.0). Br^- -containing water was simulated by dissolution of a certain amount of KBr in the bicarbonate buffer solution. The oxidation treatment was initiated through the addition of an aliquot of K_2FeO_4 from the stock solution into 200 mL Br^- -containing water. During the reaction, the solution was rapidly mixed (150 rpm) to ensure a complete mixing state. As the reaction proceeded, the solution pH was not obviously altered. Fifty milliliters of treated samples were collected at 10 min, within which the ferrate(VI) decay was completed under the tested conditions, and immediately filtered through $0.45 \mu\text{m}$ membranes to remove any iron precipitates. The depletion of Fe(VI) was confirmed by quantification of residual ferrate(VI) in water using the ABTS method (Lee et al., 2005b) or measurement of absorbance at 510 nm under which ferrate has an extinction coefficient of $1150 \pm 20 \text{ M}^{-1} \cdot \text{cm}^{-1}$. The filtrate was collected for further analysis. In the tests to examine the formation of bromo-organic DBPs, ferrate(VI) (5 mg/L as Fe) was applied to a rapid sand filter effluent collected from a local water treatment plant ($\text{Br}^-_0=1,250 \mu\text{g/L}$, $\text{DOC} = 3.4 \text{ mg/L}$, and $T=25\pm 1.5^\circ\text{C}$). In the tests to evaluate effects of various anions, appropriate amounts of NaCl, Na_2SO_4 , $\text{Na}_2\text{SiO}_3\cdot 9\text{H}_2\text{O}$, and Na_2HPO_4

were introduced to achieve the desirable chloride, sulfate, silicate and phosphate levels, respectively. All the tests were carried out in triplicates. All analytical results reported represent the mean of three replicate samples, with error bars corresponding to ± 1 x standard deviation, except as noted.

Analytical methods. Solution pH was measured with a pH meter (A310, ORION). BrO_3^- and Br^- in water were quantified by an ion chromatograph (MIC-2, Metrohm) with a 100- μL loop and a conductivity measurement after suppression was used. The eluent was 3.2 mM carbonate/1.0 mM hydrogen carbonate. The detection limit of BrO_3^- was 1.8 $\mu\text{g/L}$, which was 3.14 fold of the standard deviation of seven replicated analyses of 5 $\mu\text{g}\cdot\text{L}^{-1}$ sample. H_2O_2 was measured with horseradish peroxidase (HRP)-catalyzed oxidation of ABTS by H_2O_2 (Lee et al., 2014). Bromine-containing trihalomethanes (i.e., bromoform, bromodichloromethane, and dibromochloromethane) and haloacetic acids (i.e., bromochloroacetic acid, monobromoacetic acid, and dibromoacetic acid) in water were analyzed in the water quality analysis laboratory of American Water Corp. using Standard Method 6200C and 6251B (APHA, 2012), respectively. Dissolved organic matter (DOC) was quantified using a total organic carbon (TOC) analyzer (TOC-VCPH, Shimadzu).

2. RESULTS AND DISCUSSION

We first detect bromate after ferrate oxidation of Br^- -containing water under different reaction conditions, as shown in **Table 1**. Results in the control groups 1-4 showed that traceable bromate did not exist in the impurities of the ferrate(VI) reagent or any other used chemicals. As seen, 48.0 and 273.0 $\mu\text{g/L}$ BrO_3^- were produced at pH 5.0 for 10.0 mg/L Fe(VI) oxidation of 200 and 1,000 $\mu\text{g/L}$ Br^- in 5 mM bicarbonate buffer solution, respectively. In contrast, under identical conditions, 11.0 $\mu\text{g/L}$ and undetectable BrO_3^- were observed in the phosphate buffer solution,

respectively. These findings suggest that part of bromide was oxidized into bromate in the presence of ferrate(VI) at an acidic condition, and the buffer species play a role in the bromate formation.

Table 1 Bromate formed after ferrate(VI) oxidation of bromide in water (pH = 5, no ferrate(VI) was applied in the control groups)

Group	Experimental Conditions	BrO ₃ ⁻ (μg/L)
Control	1 1,000 μg/L Br ⁻ in 5 mM bicarbonate solution	ND*
	2 1,000 μg/L Br ⁻ in 5 mM phosphate solution	ND
	3 10.0 mg/L Fe(VI) in 5 mM bicarbonate solution	ND
	4 10.0 mg/L Fe(VI) in 5 mM phosphate solution	ND
Treatment	1 10.0 mg/L Fe(VI) oxidized 200 μg/L Br ⁻ in 5 mM bicarbonate solution	48.0
	2 10.0 mg/L Fe(VI) oxidized 200 μg/L Br ⁻ in 5 mM phosphate solution	ND
	3 10.0 mg/L Fe(VI) oxidized 1,000 μg/L Br ⁻ in 5 mM bicarbonate solution	273.0
	4 10.0 mg/L Fe(VI) oxidized 1,000 μg/L Br ⁻ in 5 mM phosphate solution	11.0

*ND, not detectable (< 1.8 μg/L)

The pH-dependence of the BrO₃⁻ formation at different initial Br⁻ concentrations is shown in **Figure 1**. We did not find any significant BrO₃⁻ production at pH 7, regardless of the initial Br⁻ concentration. However, nearly linear relationships were observed between concentrations of the initial bromide and the produced bromate at pH 5.0 and 6.0 with the slopes of 0.164 ± 0.004 and 0.034 ± 0.002 μM BrO₃⁻/μM Br⁻, respectively. The constant slopes in **Figure 1** suggested that the bromate conversions ($[\text{BrO}_3^-]/[\text{Br}^-]_0$, here [Br⁻] indicates the initial molar concentration of Br⁻) were 16.4 and 3.4% at the pH of 5 and 6 (ferrate(VI) = 10 mg/L as Fe), respectively. As seen, a significant bromate formation occurred only at an acidic condition. At the tested conditions, the BrO₃⁻ yields at pH = 5.0 or at > 200 μg/L Br₀⁻ and pH = 6.0 exceeded 10.0 μg/L, which is the bromate MCL of the United States drinking water.

Figure. 1 BrO_3^- formation at different initial pH during Fe(VI) oxidation of Br^- ($\text{Br}^-_0 = 50\text{--}1,000$ $\mu\text{g/L}$, $\text{Fe(VI)}_0 = 10.0$ mg/L , $[\text{NaHCO}_3]_0 = 5$ mM , and $T = 25 \pm 1.5^\circ\text{C}$)

The formation of bromate during ferrate(VI) oxidation of bromide is of great interest, because ferrate(VI) has long been recognized as an oxidant without any significant production of unwanted DBPs. Two previous studies (Lee and von Gunten, 2010; Sharma, 2010) reported that the reaction of Br^- with ferrate(VI) was very slow in water. Lee and von Gunten (2010) obtained a second order reaction rate constant of the reaction between bromide and ferrate(VI) below $0.1 \text{ M}^{-1} \cdot \text{s}^{-1}$ at pH 8. Sharma (2010) found that ferrate(VI) decay was not significantly different with and without 1.4 mM Br^- at pH 8.5. Of note, both of the studies were conducted at an alkaline condition. Generally, ferrate(VI) exists in four individual protonated forms (H_3FeO_4^+ , H_2FeO_4 , HFeO_4^- , and FeO_4^{2-}) with $\text{pK}_1 = 1.65$, $\text{pK}_2 = 3.55$, and $\text{pK}_3 = 7.35$ (Rush et al., 1996b). Under an alkaline condition, ferrate only has a reduction potential as low as 0.70 V ($\text{FeO}_4^{2-}/\text{Fe(OH)}_3$) with

respect to SHE (Wood, 1958; Cyr and Bielski, 1991; Lee et al., 2005a), and the dominant FeO_4^{2-} is the least reactive. Therefore, the studies only suggest that ferrate(VI) is not reactive toward Br^- at an alkaline environment, in agreement with our finding (**Figure 1**) that undetectable bromate was produced at a high pH. In contrast, we observed the BrO_3^- formation at a moderately–weakly acidic environment that was not tested in the previous studies. General speaking, under an acidic environment, ferrate(VI) is much more reactive with a reduction potential up to 2.20 V ($\text{H}_3\text{FeO}_4^+/\text{Fe}^{3+}$) with respect to SHE. Besides high valence iron species (i.e. Fe(VI) and its intermediate reduction iron species - perferryl (Fe(V)) and ferryl (Fe(IV))), hydroxyl radicals ($\text{OH}\cdot$) were present during the Fe(VI) reduction (Lee et al., 2014), which has a potential to oxidize bromide to bromate. The hydroxyl radicals were produced likely through the classical Fenton- and/or Fenton-like chemistry because Fe(II)/Fe(III) and H_2O_2 (the Fenton/Fenton-like's reagents) were the intermediate and/or final products during the Fe(VI) reduction in water. To identify the oxidant species for the bromate formation, we conducted a set of tests to oxidize Br^- with Fe(VI) in the presence and absence of *tert*-butanol (a $\text{OH}\cdot$ scavenger) at pH 5.0-7.0. Results showed that the BrO_3^- production due to $\text{OH}\cdot$ was insignificant (data not shown here). In addition, Lee et al. (2014) experimentally verified that the $\text{OH}\cdot$ yields ($\Delta[\text{OH}\cdot]/\Delta[\text{Fe(VI)}]$) during the Fe(VI) self-decay was very low (<5%). Hence, the principal role of $\text{OH}\cdot$ in the BrO_3^- formation was ruled out under the studied conditions, and the high valence iron species appeared to be responsible for the bromate production.

Besides bromate, we are also interested in the formation of bromo-organic DBPs. We performed another set of tests using the water collected after the sand filtration in a local water treatment plant (**Table 2**). Results showed that, at a maximum, only 0.8 $\mu\text{g/L}$ bromoform, 2.3 $\mu\text{g/L}$ monobromoacetic acid and 8.6 $\mu\text{g/L}$ dibromoacetic acid were detected at 1,250 $\mu\text{g/L}$ Br^-

when 5 mg/L Fe(VI) was applied. Because the initial Br⁻ concentration was much greater than a typical Br⁻ level in natural fresh waters and the produced bromo-organic DBPs were low, the formation of bromo-organic DBPs is not of great concern during Fe(VI) applications. Moreover, the formation of these bromo-organic DBPs observed from the tests indirectly indicate that HOBr (the dominant species of HOBr and OBr⁻ at the tested pH conditions; pK_a = 8.8-9.0) was produced in the ferrate(VI)-Br⁻ system. Previous studies demonstrated that hypobromous acid and hypobromite (HOBr/OBr⁻) were key intermediates for the BrO₃⁻ formation in an oxidation treatment system (Von Gunten and Hoigne, 1994; Von Gunten and Oliveras, 1998).

Table 2. Formation of bromo-organic disinfection byproducts during ferrate(VI) oxidation of Br⁻ in the effluent of a sand filter from a local drinking water treatment plant. (Br₀=1,250 µg/L, DOC = 3.4 mg/L, Fe(VI)₀=5 mg/L, and T=25±1.5°C)

pH	Bromoform (µg/L)		Monobromacetic acid (µg/L)		Dibromoacetic acid (µg/L)	
	Ave.	Std.	Ave.	Std.	Ave.	Std.
6.5	0.8	0.0	1.9	0.1	6.6	0.1
7.5	N.D.	/	2.3	0.4	8.6	2.4

The effects of different anions on the BrO₃⁻ formation in the bicarbonate-buffered solution at pH 5 and 6 are shown in **Figure 2**. In order to more readily compare their different roles on the bromate formation, an initial Br⁻ concentration (1,000 µg/L) greater than a typical Br⁻ range in freshwater was used with a high ferrate dose (Fe(VI) = 10.0 mg/L). At the either initial pH, the four anions obeyed the same order in terms of their inhibition degrees: control ≈ chloride < sulfate < silicate < phosphate. At pH 5, the bromate concentrations in the presence of

chloride, sulfate, silicate and phosphate were 97.7, 74.9, 28.4, and 22.2% of that in the control, respectively. When pH went up to 6.0, the concentrations correspondingly dropped to 86.3, 47.9, 26.1, and 9.7% of their respective control concentrations. Of extreme interest, phosphate, which was the most commonly used as a buffer and complex chemical in previous ferrate(VI) water treatment studies, caused the most significant inhibition among the tested anions. Phosphate used in the previous ferrate(VI) treatment tests is to maintain the solution pH, and/or serve as a complexing agent for Fe(III) (the final product after Fe(VI) reduction) to prevent ferric precipitation that may interfere with the optical monitoring of Fe(VI) reactions and accurate determination of reaction rate constants, as well as accelerate spontaneous decomposition of Fe(VI) due to surface catalysis (Sharma et al., 2001; Lee et al., 2005a; Jiang et al., 2015). Several efforts attempted to demonstrate the impact of phosphate buffer upon ferrate(VI) stability. An early study (Deyrup and Mills, 1956) reported that phosphate provided a marked Fe(VI) stabilization at pH 8.0-10.0. Jiang et al. (2015) also found that the presence of phosphate could retard ferrate(VI) decay at pH 7.5, because it was able to sequester or complex Fe(III) (the product of ferrate(VI) reduction) and thus prevent the growth of Fe(III) solid products that could catalyze Fe(VI) decay.

Figure. 2 Effects of different anions on the BrO_3^- formation during ferrate(VI) oxidation of Br^-

($\text{Br}^-_0 = 1,000 \text{ } \mu\text{g/L}$, $\text{Fe(VI)}_0 = 10.0 \text{ mg/L}$, $[\text{NaHCO}_3] = 5 \text{ mM}$, anion = 10.0 mg/L , and

$T = 25 \pm 1.5^\circ\text{C}$)

To further understand the role of phosphate in the $\text{Fe(VI)}\text{-Br}^-$ system, the produced bromate and residual H_2O_2 were monitored at different phosphate levels, as shown in **Figure 3**. The bromate level was $61.8 \text{ } \mu\text{g/L BrO}_3^-$ in the bicarbonate buffer solution alone. However, it sharply dropped to $27.4 \text{ } \mu\text{g/L}$ and $9.1 \text{ } \mu\text{g/L}$ at 1.0 and 5.0 mg/L P , and then gradually reached 3.5 and below detection limits with 15.0 and $155.0 \text{ mg/L (5 mM) P}$, respectively. In contrast, the H_2O_2 produced exhibited an opposite trend. The H_2O_2 concentration was dramatically increased from $5.2 \text{ } \mu\text{M}$ in the absence of phosphate to $46.9 \text{ } \mu\text{M}$ at 5.0 mg/L P , and then slowly increased to 58.6 mM when the phosphate augmented to 155 mg/L P . It is well known that H_2O_2 is an important inhibitor for the bromate formation through reduction of hypobromous acid (HOBr) (a key intermediate for the ensuing bromate formation) to bromide during ozonation of bromide-containing water (Eq. (1) and (2)) (Staehelin and Hoigne, 1982; Von Gunten and Oliveras, 1998).

Although we did not unravel the detailed mechanisms of the bromate formation after Fe(VI) oxidation of Br^- , the yielded HOBr might serve as a key intermediate that was later transformed to BrO_3^- , in a similar fashion in the $\text{O}_3\text{-Br}^-$ system. Our findings in **Figure 3** clearly show a positive relationship between the applied phosphate concentration and the produced H_2O_2 level.

In practices, H_2O_2 has been successfully applied as an additive for O_3 -based treatments to reduce the formation of bromate and bromo-organic DBPs (Zhang et al., 2005; Echigo et al., 2009). Whether the external introduction of H_2O_2 can similarly prevent or minimize the formation of BrO_3^- during Fe(VI) oxidation of Br^- is also of interest. As aforementioned, H_2O_2 has a potential to reduce HOBr to Br^- . Moreover, it can directly react with Fe(VI), thereby reducing the Fe(VI) exposure (Rush et al., 1996a). The both reasons would inhibit the production of BrO_3^- . However, the reduced Fe(VI) exposure may lead to the lower removal efficiencies of target pollutants, so that a higher Fe(VI) dose, which would favor the formation of BrO_3^- , is required to ensure an equivalent treatment effect. Another concern is that the added H_2O_2 can improve the reaction rate of H_2O_2 with Fe(II)/Fe(III) to increase the $\text{OH}^\cdot$ yield through the Fenton and Fenton-like chemistry, potentially producing more bromate through the hydroxyl radical oxidation pathway. Therefore, further investigation is needed to quantitatively evaluate whether the addition of H_2O_2 is technically feasible to control the bromate formation in practices.

Figure. 3 Effect of phosphate on the formation of BrO_3^- and H_2O_2 ($\text{Br}^-_0 = 1,000 \text{ } \mu\text{g/L}$, $\text{Fe(VI)}_0 = 10.0 \text{ mg/L}$, $[\text{NaHCO}_3] = 5 \text{ mM}$, $\text{pH}_0 = 6.0$, and $T = 25 \pm 1.5^\circ\text{C}$)

Concentrations of H_2O_2 produced in the phosphate and bicarbonate buffer systems are compared during ferrate(VI) oxidation of Br^- , as shown in **Figure 4**. In the phosphate buffer solution, the H_2O_2 level slightly decreased from 74.3 to 55.4 μM , from 67.1 to 50.9 μM , and from 64.5 to 49.1 μM at 5-40 min at pH 5.0, 6.0 and 7.0, respectively. The effect of solution pH on the hydrogen peroxide formation was limited. In contrast, at any specific time and pH, the H_2O_2 concentration in the presence of bicarbonate was much lower. For example, H_2O_2 dropped from 5.6 to 4.6 μM at 5-10 min, almost regardless of pH. Results again indicate that more H_2O_2 was accumulated in the presence of phosphate than with bicarbonate. The H_2O_2 could reduce HOBr produced from a ferrate(VI)-bromide water system and thus limit the BrO_3^- formation, in accordance with our finding that more bromate was formed with bicarbonate than with phosphate (**Table 1**).

Figure. 4 Concentrations of H_2O_2 produced over time during ferrate(VI) oxidation of bromide with different buffer species ($\text{Br}^-_0 = 1,000 \mu\text{g/L}$, $\text{Fe(VI)}_0 = 10.0 \text{ mg/L}$, and $T=25\pm 1.5^\circ\text{C}$)

Based on the aforementioned findings, the inhibition effect of phosphate is very likely associated with the enhanced H_2O_2 formation during ferrate(VI) treatment. Lee et al. (2014) proposed the formation pathways of H_2O_2 during ferrate(VI) decay. Ferrate(VI) self-decomposition first generates Fe(IV) and H_2O_2 via a two-electron transfer process. Afterwards, Fe(V) , another intermediate Fe(VI) reduction product, can also decompose into H_2O_2 and Fe(III) at an acidic condition. Although the detailed mechanisms remains unknown, we presume that the adsorption of phosphate to iron precipitates and/or complexation of phosphate with Fe(III) and even high valence iron species may play a key role. It was previously reported that freshly produced iron hydroxides could rapidly adsorb phosphate (Lijklema, 1980). Such binding could prevent the adsorption of targeted pollutants (e.g. arsenite) in water because phosphate occupied active site (Jain et al., 2009). Jiang et al. (2015) also found that the presence of phosphate could

increase the fractions of small iron particles due to complexation and sequestration. Consequently, surface properties of the iron precipitates produced were accordingly modified by the adsorbed phosphate, likely altering the surface-catalyzed Fe(VI) decomposition as well as the following H₂O₂ production/scavenging. On the other hand, the complexes of phosphate with ferrate reduction products (e.g. Fe(III) and Fe(II)) and even high valence iron species are formed during ferrate treatment. The complexes with different reactivity would finally lead to accumulation of more H₂O₂ and/or production of less reactive species, which slowed down the bromate formation.

3. CONCLUSION

This study provides new information on the production of potentially cancerogenic BrO₃⁻ during ferrate(VI) oxidation of Br⁻ in water. Ferrate(VI) is traditionally believed to be a safe water treatment chemical without production of unwanted DBPs. Our results indicate that BrO₃⁻ exceeding the US drinking water MCL might be produced when ferrate(VI) oxidizes Br⁻ in the absence of phosphate and under a moderately–weakly acidic condition. In previous studies, phosphate was commonly used as a buffer and stabilizing agent. This is likely a major reason why bromate was not detected in these studies with phosphate, which was demonstrated to significantly inhibit the bromate formation in this study. In practices, the inhibition effect of phosphate is minimal, because phosphate does not abundantly exist in natural waters. The other reason why the bromate formation was not observed in prior studies is that an alkaline environment was used in the ferrate(VI) oxidation of bromide under which the principal ferrate(VI) species (FeO₄²⁻) is the least reactive. In practices, care should be taken when ferrate(VI) is applied at an acidic condition and a high chemical dose considering that bromate formation potentially occurs. Particularly, some natural water sources may be acidic themselves,

or water is purposely adjusted to an acidic condition in order to maximize the oxidation power of Fe(VI) for the degradation of target pollutants. Compared with bromate, the formation of bromo-organic DBPs is of minor concern. Further investigations are needed to advance our understanding of the ferrate-induced bromate formation mechanisms and effects of water matrix constituents.

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