



# Formation of bromate during ferrate(VI) oxidation of bromide in water



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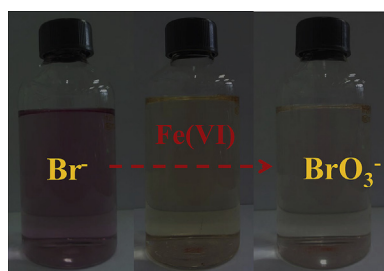
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## HIGHLIGHTS

- Ferrate(VI) has a potential to oxidize bromide to bromate at an acidic condition and without phosphate.
- Lower pH, higher Fe(VI) dose and higher Br<sup>-</sup> concentrations favor the bromate production.
- More H<sub>2</sub>O<sub>2</sub> is observed at a higher phosphate concentration during Fe(VI) oxidation of bromide.
- Phosphate inhibits the bromate formation, probably because H<sub>2</sub>O<sub>2</sub> can reduce HOBr to Br<sup>-</sup>.
- The formation of bromo-organic disinfection byproducts is of minor concern during Fe(VI) oxidation in natural waters.

## GRAPHICAL ABSTRACT



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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<sub>3</sub><sup>-</sup>) during ferrate(VI) oxidation of bromide (Br<sup>-</sup>)-containing water, and evaluated the effects of pH, ferrate(VI) dose, initial Br<sup>-</sup> concentration, and co-existing anions on the BrO<sub>3</sub><sup>-</sup> formation. BrO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> was increased from 12.5 to 273.8 μg/L with the increasing initial Br<sup>-</sup> concentration from 200 to 1000 μg/L at 10 mg/L Fe(VI), corresponding to an increase in the molar conversion ([BrO<sub>3</sub><sup>-</sup>]/initial [Br<sup>-</sup>]) from 2.3% to 10.3%, in a bicarbonate-buffered solution. As pH increased to 7.0, the BrO<sub>3</sub><sup>-</sup> concentration gradually dropped. The BrO<sub>3</sub><sup>-</sup> 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<sup>-</sup>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)) 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<sub>3</sub><sup>-</sup> followed chloride < sulfate < silicate < phosphate. More H<sub>2</sub>O<sub>2</sub> was detected at higher phosphate concentration. It could reduce HOBr to Br<sup>-</sup>, thereby inhibiting the bromate formation.

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## 1. 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  $\text{FeO}_4^{2-}$  with iron in +6 oxidation state.  $\text{FeO}_4^{2-}$  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 ferryl (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 removes 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 micropollutants (Yang et al., 2012). Traditionally, ferrate(VI) is recognized to be a safe disinfecting or oxidizing agent without production of potentially carcinogenic bromate ( $\text{BrO}_3^-$ ) 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  $\text{BrO}_3^-$  (Haag and Hoigne, 1983; Von Gunten and Hoigne, 1994; Pinkernell and von Gunten, 2001).

Bromide ( $\text{Br}^-$ ) concentrations in freshwater range mostly between 14 and 270  $\mu\text{g/L}$ , with slightly higher levels in the 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).  $\text{BrO}_3^-$  is formed as an undesirable DBP during oxidative treatment of  $\text{Br}^-$ -containing water with ozone, hydroxyl radicals ( $\text{OH}\cdot$ ), or sulfate radicals ( $\text{SO}_4\cdot^-$ ) (Von Gunten and Oliveras, 1998; Fang and Shang, 2012). International Agency for Research on Cancer (IARC) classifies  $\text{BrO}_3^-$  as a Group 2B or “possible human” carcinogen. The US Environmental Protection Agency (EPA) has a drinking water maximum contaminant level (MCL) of  $\text{BrO}_3^-$  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  $\text{BrO}_3^-$  (Sharma et al., 2006; Lee and von Gunten, 2010), we noticed that most of these studies were conducted in phosphate-buffered solutions that rarely exist 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  $\text{BrO}_3^-$  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.

## 2. Material and methods

### 2.1. Reagents

All the reagents used were at least analytical grade, except as noted. Potassium bromide (KBr) (99.8%), bromate standard (1000 mg/L) for ion chromatography (IC), potassium ferrate ( $\text{K}_2\text{FeO}_4$ ) (>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  $\text{K}_2\text{FeO}_4$  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 ( $\geq 18.2 \text{ M}\Omega \text{ cm}$ ).

### 2.2. Experimental procedures

All the  $\text{BrO}_3^-$  formation tests were performed in 250-mL amber glass vials on a magnetic stirrer at ambient temperature ( $25 \pm 1.5 \text{ }^\circ\text{C}$ ). Bicarbonate ( $\text{NaHCO}_3$ ) buffer solution (5 mM) was first prepared with an original pH of  $\sim 9.2$ . And then the solution pH was adjusted with 0.05 or 0.5 M nitric acid ( $\text{HNO}_3$ ) to designated pH levels (5.0–7.0).  $\text{Br}^-$ -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  $\text{K}_2\text{FeO}_4$  from the stock solution into 200 mL  $\text{Br}^-$ -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  $1150 \pm 20 \text{ M}^{-1} \text{ cm}^{-1}$ . 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 ( $\text{Br}^-_0 = 1250 \mu\text{g/L}$ ,  $\text{DOC} = 3.4 \text{ mg/L}$ , and  $T = 25 \pm 1.5 \text{ }^\circ\text{C}$ ). In the tests to evaluate effects of various anions, appropriate amounts of NaCl,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{Na}_2\text{HPO}_4$  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  $\pm 1 \times$  standard deviation, except as noted.

### 2.3. Analytical methods

Solution pH was measured with a pH meter (A310, ORION).  $\text{BrO}_3^-$  and  $\text{Br}^-$  in water were quantified by an ion chromatograph (MIC-2, Metrohm) with a 100- $\mu\text{L}$  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  $\text{BrO}_3^-$  was 1.8  $\mu\text{g/L}$ , which was 3.14 fold of the standard deviation of seven replicated analyses of 5  $\mu\text{g L}^{-1}$  sample.  $\text{H}_2\text{O}_2$  was measured with horseradish peroxidase (HRP)-catalyzed oxidation of ABTS by  $\text{H}_2\text{O}_2$  (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

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