



# Suppression of bromate formation in ozonation process by using ferrate(VI): Batch study

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## HIGHLIGHTS

- Bromate can be effectively diminished with the increase of ferrate dosage.
- As [ferrate] = 2.0 mg/L, bromate was diminished completely in certain water quality.
- The mechanism was speculated to be a combined role of ferrate's intermediates.
- Compared to other methods controlling bromate, ferrate was efficient and safe.
- The applying of ferrate to inhibit bromate formation was economic and feasible.

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## ABSTRACT

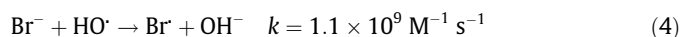
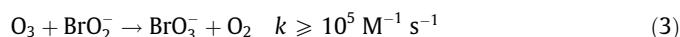
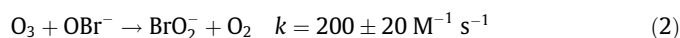
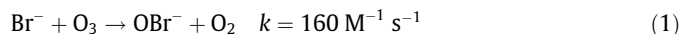
A series of batch experiments were conducted to investigate the effects of ferrate(VI) on bromate formation in a ferrate(VI)–ozone oxidation system under different conditions with varying ozone dosage (1.5–4.0 mg/L), initial bromide concentration (100–1500 µg/L), temperature (5–40 °C), alkalinity (25–250 mg/L) and NOM (0.1–10 mg/L) content of water being treated. The range of ferrate(VI) dosage used was 0–5.0 mg/L. Comparisons with other methods capable of controlling bromate formation (e.g. suppression of pH, addition of ammonia, as well as other ozone-based technologies) were also made. Compared with sole ozonation process, the addition of ferrate(VI) was demonstrated an effective suppression of bromate formation in ferrate(VI)–ozone oxidation process. The required ferrate(VI) dosage to achieve 100% diminishing of bromate formation was 2.0 mg/L, at the conditions of ozone dosage ≤2.5 mg/L, initial bromide concentration ≤200 µg/L, pH ≤9.0 and temperature ≤40 °C. The possible mechanisms responsible for the diminished bromate formation in the ferrate(VI)–ozone oxidation process were speculated to be the combined effects induced by the ferrate(VI) intermediates, such as low valent Fe species and hydrogen peroxide. The additional cost for treating per ton bromide bearing water was only 0.0003–0.006 \$ at ferrate(VI) dosage of 0.1–2.0 mg/L.

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## 1. Introduction

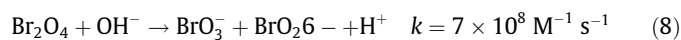
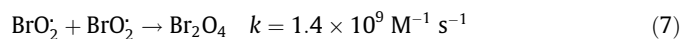
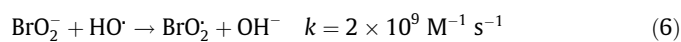
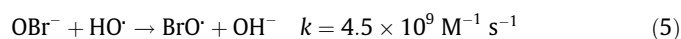
Ozone (O<sub>3</sub>) is widely used as a disinfectant in drinking water treatment by virtue of its high oxidation capacity [1,2], and can successfully degrade many recalcitrant contaminants including endocrine-disrupting chemicals (EDCs) [3–5], flame retardants [6] and pharmaceuticals [7]. However, ozonation of bromide-bearing water is very likely to result in the formation of bromate (BrO<sub>3</sub><sup>−</sup>) through direct oxidation by molecular state ozone or indirect oxidation by hydroxyl radical (OH·) combining with ozone (Eqs. (1)–(8)) [8]. Bromate is one of the undesired disinfection

by-products in drinking water, and could cause severe gastrointestinal irritation, renal failure, hearing loss, and depression of the central nervous system when long-term exposed [9]. Thus, bromate was classified as a potent carcinogen by the “International Agency for the Research on Cancer” (IARC) in 1990s [10]. The maximum contaminant level (MCL) for bromate in drinking water has been set to be 10 µg/L in many countries [11].



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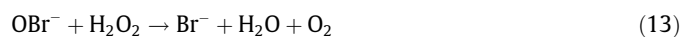
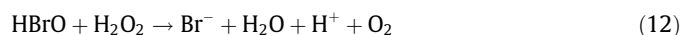
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The formation of bromate through ozonation is reportedly influenced by various conditions. Increasing in ozone dosage, bromide concentration, pH, temperature and contact time would favor bromate formation [12,13]. Some constituents in water, such as alkalinity, ammonia and natural organic matter (NOM), can also affect the formation of bromate. Alkalinity could shift the ionization balance of HOBr/OBr<sup>−</sup> towards OBr<sup>−</sup>, which is more reactive with ozone and leads to more bromate formation. Ammonia can diminish bromate formation by reacting with HOBr/OBr<sup>−</sup> to form bromamines, which in turn reacts with ozone and releases bromide and nitrate ions [14]. NOM in water could inhibit bromate formation by competing with bromide for reacting with ozone and OH<sup>•</sup>, or reducing Br<sup>−</sup> and HOBr/OBr<sup>−</sup> to Br<sup>•</sup> [8,15].

Strategies having been studied for controlling bromate formation in ozonation process include pH suppression, ammonia dosing, and OH<sup>•</sup> and HOBr scavenger dosing [8,15–17]. Amongst them, pH suppression and ammonia dosing were reportedly high-efficient and achieved up to 50% reduction in bromate formation [18]. However, pH suppression favors HOBr formation, and might lead to the generation of more toxic organic bromide compounds (i.e. bromoform and cyanogen bromide) when reacting with NOM. Furthermore, subsequent adjustment of pH is needed to prevent the corrosion of water supply pipes, which is great costly for applying in water with strong buffer capacity. As for ammonia addition, its effectiveness is dependent on the quality of water treated. Moreover, though the addition of ammonia can consume certain amount of ozone, if without sophisticated operation, ammonia is very likely to residue in water as a contaminant [19].

Besides attempts on adjusting operating conditions in ozonation process, some ozone-based technologies, such as UV/O<sub>3</sub>, VUV/O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> and KMnO<sub>3</sub>/O<sub>3</sub>, have been studied to enhance water treatment as well as control bromate formation [20]. As shown in Eqs. (9)–(11), BrO<sub>3</sub><sup>−</sup> formed by ozonation can be reduced to BrO<sub>2</sub><sup>−</sup>, OBr<sup>−</sup>, and finally to Br<sup>−</sup> at the wavelength of 185–254 nm under UV or VUV irradiation [21]. As shown in Eqs. (12) and (13), HBrO and OBr<sup>−</sup> can be directly reduced to Br<sup>−</sup> by co-present H<sub>2</sub>O<sub>2</sub>. In KMnO<sub>3</sub>/O<sub>3</sub> oxidation process, manganese intermediates in low oxidation states (e.g. Mn(V), Mn(IV), Mn(III) and hydrated manganese dioxide) would compete with bromide for reacting with ozone, leading to suppressed bromate formation [23]. Yet, further study is needed for solving the problems limiting engineering application of these ozone-based technologies, such as lower efficiency and toxic residual manganese.



Over the past decade, the use of ferrate(VI) as an oxidant has attracted much attentions in drinking water treatment, since it possesses high redox potential (+2.20 V) in acidic solution, and can avoid the formation of chlorinated DBPs and bromate which

formed during chlorination and ozonation processes [24,25]. It has been reported to be applied in water treatment for inactivation of bacterial community [26] and degradation of various contaminants (i.e. sulfur/nitrogen-bearing pollutants, phenols, chlorophenols, and EDCs) [27–29]. Moreover, the product of ferrate(VI) oxidation reaction is Fe(III) species which is helpful in enhancing the aggregation and settling process of particulate materials, and hence promoting the removal of organic matter, nutrients and some metals [30]. These advantageous properties make ferrate(VI) a green multi-functional chemical capable of performing disinfection, oxidation, and coagulation in drinking water treatment. Nevertheless, due to the high cost of high purity ferrate(VI), its application in water treatment is limited, and hence, ferrate(VI) coupling technologies are paid more and more attention currently [31]. It has been reported that ferrate(VI)-ozone combined oxidation can enhance the degradation of contaminants with low oxidants dosage [32,33] promoting oxidation efficiency and reducing the cost. Furthermore, considering that ferrate(VI) is isostructural with permanganate, it might be able to control bromate formation similarly as permanganate in ozonation process. Yet, information addressing the effects of ferrate(VI) on bromate formation in ozonation process remains little.

This study aims to investigate the effects of ferrate(VI) on bromate formation in a ferrate(VI)-ozone oxidation system under different conditions with varying ozone dosage, and initial bromide concentration, temperature, alkalinity and NOM content of water being treated. Comparisons with other methods capable of controlling bromate formation (e.g. suppression of pH, addition of ammonia, as well as other ozone-based technologies) were made. Possible mechanisms governing how ferrate(VI) behaves in bromate formation, and the economic cost for using ferrate(VI) in engineering settings are discussed.

## 2. Materials and methods

### 2.1. Materials

The chemicals, K<sub>2</sub>FeO<sub>4</sub>, KBr, Na<sub>2</sub>HPO<sub>4</sub>, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, H<sub>2</sub>SO<sub>4</sub>, NaOH, FeCl<sub>3</sub>, NaClO, NaHCO<sub>3</sub>, NH<sub>4</sub>Cl, humic acid, and tertiary butanol, used in this study were commercially purchased from Sigma-Aldrich or Aladdin. The stock solution of ferrate(VI) was prepared immediately prior to the experiments by dissolving potassium ferrate(VI) (K<sub>2</sub>FeO<sub>4</sub>, purity ≥ 99%) in the pH buffer (0.005 M Na<sub>2</sub>HPO<sub>4</sub>/0.001 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·9H<sub>2</sub>O, pH ≈ 9.2). Potassium bromide (KBr, reagent-grade) stock solution was prepared with deionized distilled water and stored in 4 °C cold room. Ozone was generated by an ozone generator (CF-G-3-10G, Qingdao Guolin Industry Co., Ltd., China) at a rate of 10 g/h. Saturated ozone solution was prepared following the method introduced in Ref. [16] by continuously purging the ozone gas into the deionized water for about 3 h before starting the experiments. The ozone concentration dosed in the experimental solutions was varied by adjusting the spiked volume of saturated ozone solution according to its actual saturation concentration measured *in situ*. Solution pH was adjusted by H<sub>2</sub>SO<sub>4</sub> or NaOH solution. The stock solutions of NaHCO<sub>3</sub>, NH<sub>4</sub>Cl, humic acid, and tertiary butanol were prepared by dissolving into deionized distilled water.

### 2.2. Experimental methods

Series of batch experiments were conducted in 500 mL conical beakers sealed with paraffin film for investigating the effects of ferrate(VI) on bromate formation in a ferrate(VI)-ozone oxidation system with varying ozone dosage and ozonation time, and initial bromide concentration, temperature, alkalinity and NOM content

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