Study on pathways of bromate formation during bromide-containing lake water ozonation

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ABSTRACT

The pathways of bromate formation during ozonation of bromide-containing lake water were investigated. The results showed that bromate formation was inhibited efficiently by adding t-butanol which is an ·OH scavenger, or promoting (bi)carbonate alkalinity. It was also suggested that addition of H_2O_2 yielded different results. Bromte formation was restricted when H_2O_2/O_3 mole ratio was 0.5:1, while increase of bromate formation occurred when H_2O_2/O_3 mole ratio was more than 1:1. An O_3 dose of 4.5mg/L was applied during such lake water ozonation. It was suggested that the main pathway of bromate formation was indirect pathway, the direct pathway, in contrast, was recognized as a less important pathway due to the bromate formed in this pathway accounted for only 8% of total production.

Key words: Drinking water, Ozone, Bromate, Hydroxyl radical, Alkalinity, Hydrogen peroxide.
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INTRODUCTION

Ozonation considered as the most available strategy to remove micropollutants is commonly applied during drinking water treatment, concern over bromate ion formation during ozonation of bromide-containing water has arisen for bromate is a suspected carcinogen[1].As a result, the proposed maximum contaminant level (MCL）for bromate was set at 10μg/L by the United States Environmental Protection Agency (USEPA)[2]. Many researchers have investigated the characteristics and mechanism of bromate formation, it is claimed that bromate formation through four major pathways [3-5], which are called direct pathway, indirect pathway, direct/indirect　 pathway and indirect/direct pathway. In the direct pathway, basically, ozone oxidized bromide ion to bromate step-by-step: $Br^- \rightarrow OBr^- \rightarrow BrO_2^- \rightarrow BrO_3^-$.The indirect pathway is forming bromate by only hydroxyl radical(·OH) through the reaction (1) to (7)[6]. In the direct/indirect pathway, bromide ion is first oxidized by ozone molecular to form hypobromous acid/hypobromite (HOBr/OBr⁻) . HOBr/OBr⁻ then react with ·OH to form BrO_3^- through the reaction (3) to (7). The last pathway is indirect/direct pathway which is described that ·OH first oxidize bromide ion to HOBr/OBr⁻ through the reaction (1) to (2), further oxidize to BrO_3^- by ozone molecular.

$$Br^- + \cdot OH \rightarrow Br\cdot \;, \qquad\qquad k = 1.1\times10^9 M^{-1}s^{-1} \qquad\qquad (1)$$

$$Br\cdot + Br^- \rightarrow HOBr/OBr^- \;, \qquad\qquad k = 10^{10} M^{-1}s^{-1} \qquad\qquad (2)$$

$$HOBr/OBr^- + \cdot OH \rightarrow BrO\cdot + OH^- \;, \qquad k_{OBr^-} = 4.5\times10^9 M^{-1}s^{-1} \qquad (3)$$

$$2BrO\cdot + H_2O \rightarrow OBr^- + BrO_2^- + 2H^+ \;, \quad k = 5\times10^9 M^{-1}s^{-1} \qquad (4)$$

$$BrO_2^- + \cdot OH \rightarrow BrO_2\cdot + OH^- \;, \qquad\qquad k = 1.9\times10^9 M^{-1}s^{-1} \qquad (5)$$

$$BrO_2\cdot + BrO_2\cdot \rightarrow Br_2O_4 \;, \qquad\qquad k = 1.4\times10^9 M^{-1}s^{-1} \qquad (6)$$

$$Br_2O_4 + OH^- \rightarrow BrO_3^- + BrO_2^- + H^+ \;, \qquad k = 7\times10^8 M^{-1}s^{-1} \qquad (7)$$
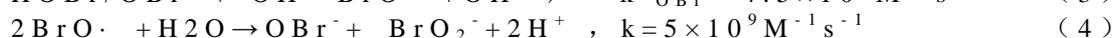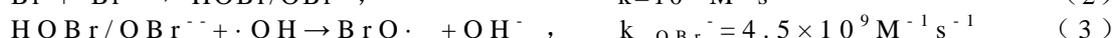
In order to minimize bromate formation, based on improved mechanistic and kinetic understanding, three strategies have been applied to drinking water ozonation: pH depression, ammonia addition and hydrogen peroxide(H_2O_2) addition[7]. pH depression displays the HOBr/OBr⁻ equilibrium further to HOBr, slowing down the oxidation by ozone[8]. Ammonia can react with HOBr to form bromamine, inhibiting the bromate formation by direct pathway[9]. The addition of H_2O_2 may inhibit bromte formation through depressing HOBr [6]. H_2O_2 reacts with ozone to form hydroxyl radical (·OH) , however, promoting the indirect pathways and enhancing bromate formation. ·OH can react bromide to form bromate ion rapidly through indirect pathway. Tadao Mizuno et al. [10]. applied *t*-butanol and decreased bromate formation by 90% All in all, the suppression effects of bromate formation could vary among source waters because of disparities in parameters such as bromide, ammonia, natural organic materials (NOM) and temperature [11].

Nan Si Lake which is a source of drinking water in north of China presents typical particularities, such as high bromide, high ammonia and high NOM. Ozonating this water may have the risk of forming bromate. The object of this paper was investigating the pathways of bromate formation during ozonation of Nan Si Lake water, additionally, providing the strategy of bromate inhibition under such water quality.

EXPERIMENTAL SECTION

2.1 Characteristics of source water
The water sample was taken from Nan Si Lake. The main parameters of the water sample are shown as Table 1.

Table 1 Water quality parameters

TOC(mg/L)	$UV_{254}(cm^{-1})$	pH	NH_4^+(mg/L)	Alkalinity(mg/L)	Br^-(mg/L)
2.40-2.55	0.026-0.034	8.16-8.23	0.20-0.30	114-130	0.23-0.24

2.2 Bench scale experiments and analytical methods
Bench scale ozonation was conducted in an ozone contact tower with water samples. The reactor was a cylinder of which the dimensions were of 50mm in OD, 200mm in height. Cylinder bottom was loaded with the titanium alloy microporous aerator. Pure oxygen was applied to an ozone generator (Triogen, UK), which provided a 40ml/min gas flow rate ozone into the batch reactor. Ozone influent was then introduced into the reactor through a aeration at the bottom to start the reactor. The effluent gas was absorbed through an absorption bottle at the top of reactor. Water samples were withdrawn at desired time which was 9.5min. To stop ozone reaction, water samples were purged with nitrogen gas.

2.3 Analytical methods
Bromide and bromte concentrations were determined by using an ion chromatographer (Metrohm 883 Basic IC plus, with column Supp-7, Switzerland) with a detection limit of 2μg/L for both bromide and bromate. Carbonate alkalinity and bicarbonate alkalinity was determined by pH indicator titration. Dissolved organic carbonate (DOC) concentrations were determined by high-temperature catalytic oxidation with a Shimadzu TOC-V$_{CSH}$ analyzer. Ozone concentrations in gas were analyzed by using iodometry.

RESULTS AND DISCUSSION

3.1 Effect of Hydroxyl radical scavenger (t-butanol) on bromate formation
To investigate the pathways of bromate formation, the hydroxyl radical scavenger was applied to inhibit the indirect pathway under the condition of O_3 dosage of 4.5mg/L, reaction time of 9.5min and pH value of 8.2. Result of this experiment is shown in Fig. 1.

Fig.1 shows that the amount of bromate ion formed decreased with increasing amount of *t*-butanol added. When *t*-butanol was added at 20mg/L, the concentration of bromate ion formed decreased by 64% (from 39μg/L in the absence of *t*-butanol to 14μg/L). When the amount of *t*-butanol applied achieved 100mg/L, the concentration of bromate ion formed decreased by 90%. The ·OH can react with bromide to form bromate ion through the reaction (1) to (7)[6], and these reaction are quite rapid. The ·OH scavenger, *t*-butanol, can deplete ·OH and has very slow rate of reaction with ozone[12]. Therefore, addition of *t*-butanol blocks the indirect pathway of bromate formation efficiently. The experiment results suggest that when the indirect pathway was blocked, bromate formation through the direct pathway accounted for only 8% of total production. That is to say, the reaction with ·OH is the main pathway to form bromate ion under the water quality parameters of Nan Si Lake.
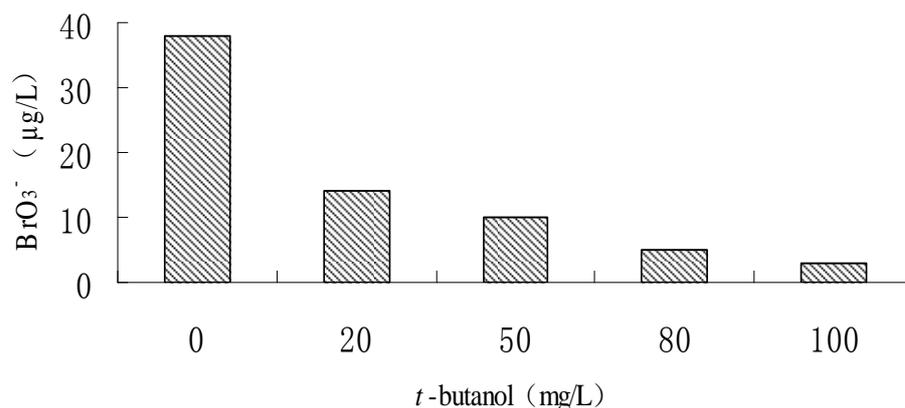
Fig.1 Effect of *t*-butanol on bromate formation

3.2 Effect of (bi)carbonate alkalinity on bromate formation

To study the roll of (bi)carbonate which can react with ·OH in bromate formation, a 4.5mg/L O_3 was applied at the reaction time of 9.5min, adjust pH of 8.2 by phosphate buffer. The alkalinity was adjusted to 170mg/L, 190mg/L, 220mg/L as $CaCO_3$. Result of this experiment is shown in Fig. 2.
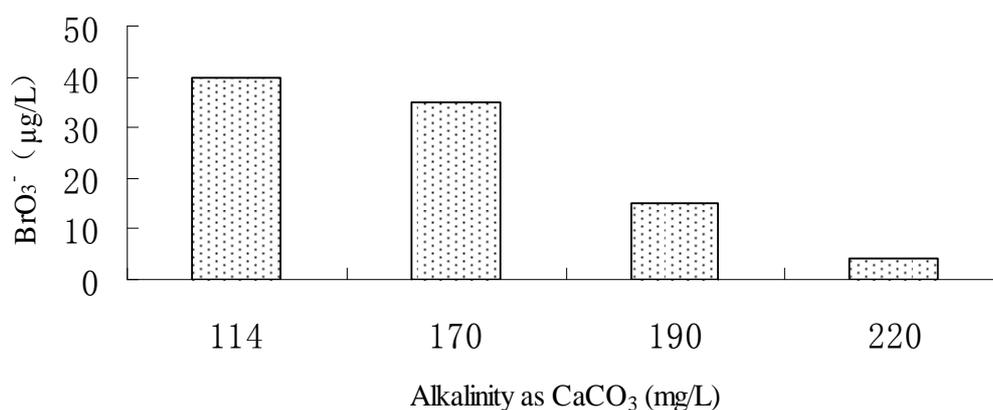
Fig.2 Effect of alkalinity on bromate formation

As it can be seen from Fig.2, bromate formation decreased with increasing amount of alkalinity. A decrease of 55% bromate formation was achieved when alkalinity was increased from 114mg/L as $CaCO_3$ to 190mg/L. When the alkalinity increased to 220mg/L as $CaCO_3$, there was a decrease of 92% bromate formation. Bicarbonate and carbonate are ·OH scavengers due to they can react with ·OH through the reaction (8) and (9) [3]. Ron Hofman et al. [13] indicated that during ozonation of raw water containing ammonia, ammonia blocks the direct/indirect pathway while (bi)carbonate should scavenge the ·OH that is required by the indirect/direct pathways. These experiment results also suggest that it is efficient rising (bi)carbonate alkalinity during ozonation of Nan Si Lake water to control bromate formation.

$$CO_3^{2-}+·OH \rightarrow OH-+ CO_3^-, \qquad k^0=3.7\times10^8 M^{-1}s^{-1} \qquad (8)$$
$$HCO_3^-+·OH \rightarrow H_2O+ CO_3^-, \qquad k^0=8\times10^6 M^{-1}s^{-1} \qquad (9)$$
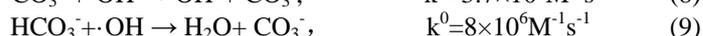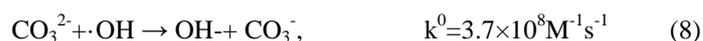
3.3 Effect of H_2O_2 on bromate formation

In order to investigate the effect of H_2O_2 on bromate formation, H_2O_2 was applied and adjust H_2O_2/O_3 mole ratio of 0.5:1, 1:1, 1.5:1, 2:1. The experiment was conducted under the condition of O_3 dosage of 4.5mg/L, reaction time of 9.5min, alkalinity of 114mg/L as $CaCO_3$, and pH value of 8.2. The result is shown in Fig. 3.

$$HOBr+HO_2^- \rightarrow Br^-+O_3+H_2O，\qquad k^0=7.6\times10^8 M^{-1}s^{-1} \qquad (10)$$

From Fig. 3 it is observed that effects of H_2O_2 addition on bromate formation were mixed. Compare with applying

ozone alone, there was a decrease of 70% bromate formation was at H_2O_2/O_3 mole ratio of 0.5:1 while the bromate formation rose up at H_2O_2/O_3 mole ratio of more than 1:1. 8. When H_2O_2/O_3 mole ratio was 0.5:1, $HOBr/OBr^-$ might be reduced by H_2O_2 through reaction (10) [5] inhibiting bromate formation. However, H_2O_2 may enhance the bromate formation due to high concentration of $\cdot OH$ formed by catalyzing O_3 with H_2O_2, and that promote the indirect pathway.
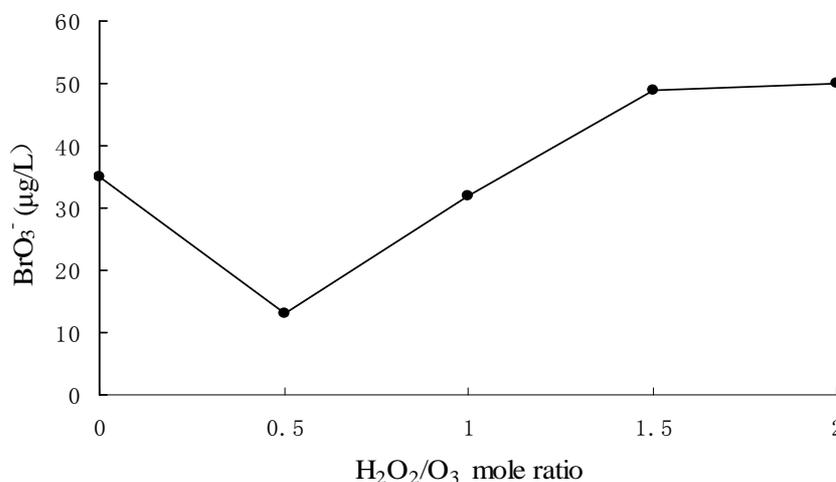
Fig.3 Effect of H_2O_2/O_3 mole ratio on bromate formation

To demonstrate the theory that high concentration of H_2O_2 enhances indirect pathway of bromate formation, another two experiments were conducted named group A and group B respectively. An 100mg/L *t*-butanol was applied 6min after the start of group B while group A was conducted without addition of *t*-butanol. Both groups were conducted under the condition of O_3 dosage of 4.5mg/L, reaction time of 9.5min, alkalinity of 114mg/L as $CaCO_3$, H_2O_2/O_3 mole ratio of 1.5:1, and pH value of 8.2.The result is shown in Fig. 4.
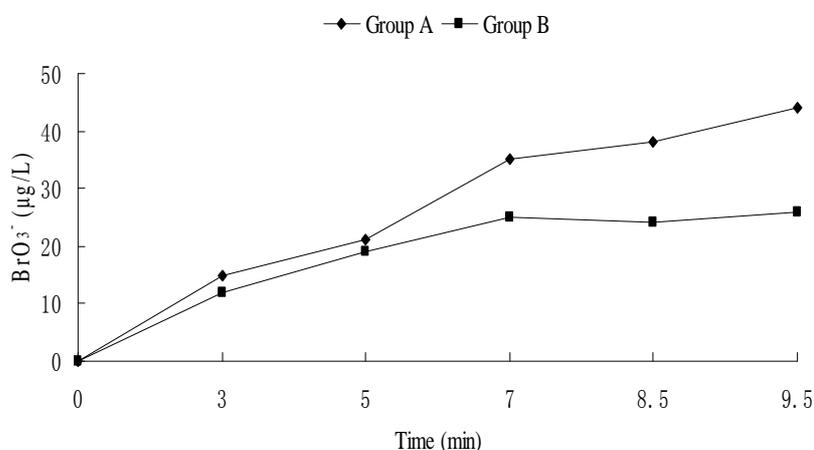
Fig.4 Effect of *t*-butanol on bromate formation with H_2O_2/O_3 mole ratio of 1.5:1

Results from these experiments are shown in Fig.4 note that in the first 5 min a total of about 18μg/L bromate formed in both groups. After addition of *t*-butanol the bromate formation of group B increased slowly around 7min, and at last was maintained at 22μg/L. While the bromate formation of group A increased to 40μg/L. The results suggest that addition of *t*-butanol inhibited bromate formation through indirect pathways efficiently. That is to say excess H_2O_2 may catalyze O_3 to form high concentration of $\cdot OH$ enhancing bromate formation.

CONCLUSION

Experiment to study the pathway of bromate formation during ozonation of Nan Si Lake water was conducted, and several conclusions can be drawn from this work. (1) The direct pathway may be inhibited efficiently by the condition of this raw water due to bromate formed in this pathway accounted for only about 8% of total production. (2) The indirect pathway may be a dominated pathway of bromate formation due to there is a certain decrease by

90% of bromate formation after addition of 100mg/L t-butanol. Moreover, increasing (bi)carbonate alkalinity from 114mg/L to 220mg/L (as $CaCO_3$) reduced bromate formation by 92% which supports this theory. (3) Effects of H_2O_2 addition on bromate formation are mixed and strongly depend on the water quality parameters. During ozonation of Nan Si Lake water, H_2O_2 may inhibit bromate formation through reducing $HOBr/OBr^-$ at H_2O_2/O_3 mole ratio of 1.5:1. However, excess H_2O_2 may catalyze O_3 to form high concentration of $\cdot OH$ enhancing bromate formation. Therefore, when H_2O_2/O_3 process is applied to control bromate formation the H_2O_2/O_3 mole ratio should be considered.

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