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The control of bromate formation in ozonation of bromide-containing water

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ABSTRACT

Bromate formation under different conditions of ozone-based treatment for bromide-containing water was investigated. The paper not only presented common influencing factors such as temperature, pH, addition of ammonia or hydrogen peroxide, but also explored the effect of utilization of metallic compounds containing magnesium oxide, titanium oxide, potassium permanganate, and copper sulfate. The results showed that bromate formation could be significantly inhibited by increasing acidity, addition of ammonia or permanganate. And cooling the ozonation system is an alternative to control bromate formation.

Keywords: Ozonation; Bromate formation; Control; Bromide-containing water

1. Introduction

Because of the scarcity of fresh water resources and the need for additional water supplies, the treatment of converting seawater into drinking water has attracted great attention. Chemical disinfection is necessary to inactivate pathogens for desalination systems and ozone is one of efficient disinfectants for water treatment. However, bromide in seawater or desalinated product water will be oxidized to form bromate. In the process of ozonation [1–5], bromide is oxidized by ozone and/or hydroxyl radicals, through combining oxidation of intermediate species (e.g. HOBr, OBr^-, $Br^{\bullet}$, $BrO^{\bullet}$), and eventually to bromate. Up to now, it is generally supposed that bromate forms through the following three pathways:

(1) Direct(D)

$$Br^- \xrightarrow{O_3} HOBr/OBr^- \xrightarrow{O_3} OBr_2^- \xrightarrow{O_3} BrO_3^-$$

(2) Direct/Indirect(D/I)

$$Br^- \xrightarrow{O_3} HOBr/OBr^- \xrightarrow{^{\bullet}OH} BrO^{\bullet} \xrightarrow{\text{disproportionation}} OBr_2^- \xrightarrow{O_3} BrO_3^-$$

(2) Indirect/Direct(I/D)

$$Br^- \xrightarrow{^{\bullet}OH} Br^{\bullet} \xrightarrow{O_3} BrO^{\bullet} \xrightarrow{\text{disproportionation}} OBr_2^- \xrightarrow{O_3} BrO_3^-$$

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Bromate is a probable human carcinogen classified by the International Agency for the Research on Cancer in 1990. And the World Health Organization has set a limit of 10 μg/L of bromate in drinking water [6]. It is, therefore, desirable to develop effective methods to remove bromate from desalinated water. Literature search revealed that there are three kinds of ways to reduce the amount of bromate in water. The first is to remove the bromate precursors, such as bromide before ozone treatment [7,8]. The second is to control parameters, such as temperature, pH, adding ammonia or hydrogen peroxide, and modifying disinfection operation, during ozonation process [9,10]. The third is using physical and chemical methods [11–13], such as activated carbon adsorption/reduction and photocatalysis, to remove bromate after ozonation. Considering low-cost and simplified treatments, the work aimed at exploring effective treatment conditions to control bromate formation during ozonation operation.

2. Experimental

2.1. Preparation of ozone-saturated water

Ozone used in the experiment was generated in an ozonator (made by Nanjing Wuhuan Electric Light Source Plant, oxygen as source), and then piped into an reactor with 200 mL ultrapure water. At the same time, the solution was stirred continuously with a magnetic stirrer. The concentration of ozone [$\lambda = 258$ nm, $\xi = 3{,}100$ L (mol cm)$^{-1}$] in water was determined by an ultraviolet spectrophotometer (Shanghai Jinghua No. 725) at intervals. The result showed that the concentration of ozone would be balanced at 0.4 mg/L in 30 min. Thus it took 30 min to prepare ozone-saturated water in subsequent work.

2.2. The formation and determination of bromate

200 mL of newly prepared ozone-saturated water was transferred into a 500 mL round-bottomed flask, then stirred and recorded the reaction time immediately after 1 mL of potassium bromide (10 g/L) was added; and 30 min later, the solution was vortexed continuously for 3 min to remove residual ozone. And then 5 mL of the obtained solution was transferred into a 10 mL volumetric flask, and then 1.00 mL of KBr (15.0 g/L), 0.20 mL of H_2SO_4 (5 M) and 0.12 mL of phenol (0.4 M) were added in turn. The mixture was then incubated in water bath of 70℃ for an hour. Diluted to the mark with ultrapure water, the final solution was thereby ready for the determination of potassium bromate by HPLC.

The chromatographic conditions: column (Hanbang ODS, 4.6 mm × 150 mm × 5 μm), column temperature (30℃), mobile phase (H_2O–CH_3OH 40:60), flow rate (1 mL min^{-1}), detection wavelength (225 nm), inject volume 20 μL.

Batch experiments were conducted at different temperatures and pH. Different amounts of aqueous ammonia, hydrogen peroxide, and diverse metallic compounds were separately added into the oxidization system to investigate their effects on bromate formation by ozonation.

3. Results and discussion

3.1. Effect of ozonation time on bromate formation

Once 200 mL of ozone-saturated water and 1 mL of potassium bromide solution (10 g/L) were poured into a round-bottomed flask (500 mL), the reaction time was recorded and the reaction solution was stirred. And 10 mL of the reaction solution was then pipetted into a colorimetric cylinder at different reaction times (2, 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, 60 min). The superfluous ozone was immediately removed to terminate the reaction by vortexing (XW-80A vortex, Instrument Factory of Shanghai Medical University) for 3 min. And all these solutions were preserved in a refrigerator (4℃) for bromate determination by HPLC.

As shown in Fig. 1, the oxidization of potassium bromide by ozone was near the end point in 15 min, and the yield of potassium bromate increased slowly afterward. To reach the end point at utmost, the oxidization time was set at 30 min in our study.

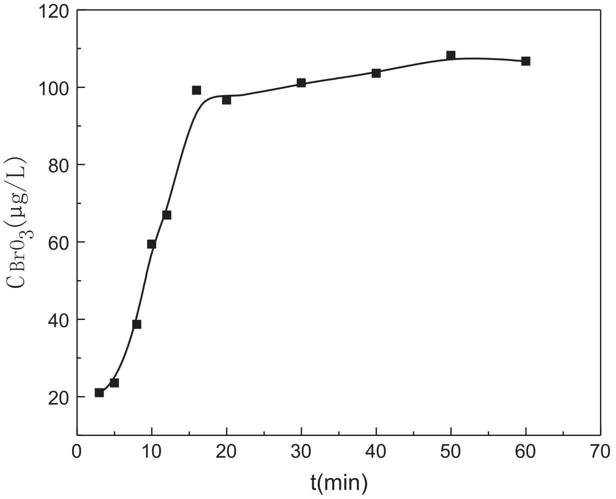

Fig. 1. Concentration of potassium bromate formed at different contact times (C_{ozone}: 0.4 mg/L, $C_{bromide}$: 50 mg/L).

3.2. Effect of reaction temperature on bromate formation

The ozonation systems were separately conducted at 5, 15, 25, 35, 50℃. Fig. 2 illustrates that the higher the temperature, as it was below 25℃, the more the bromate formation, which was in conformity with the report by Croue [14]. The increase of bromate formation was attributed to the increase in $OBr^-/HOBr$ ratio that played an important role in BrO_3^- formation. It was reported that the rate of OBr^- oxidation to $BrO^\bullet$ is faster than that of HOBr [1,3]. However, the bromate formation decreased with continued temperature rise after the temperature exceeding 25℃. At relatively high temperature (>25℃), the ozone stability became a major factor. According to Henry's law, ozone tends to be released from the system with the temperature increased, which might bring the ozone concentration even below the threshold concentration required for bromate formation. However, the disinfection would be inefficacious for the decreased concentration of ozone dissolved in water. Thus it is undesirable to control the formation of bromate in drinking water by heating. Cooling down the disinfection system may serve as an auxiliary way to control bromate formation if there is adequate cooling apparatus.

3.3. Effect of pH on bromate formation

The formation of bromate was easily affected by pH, as shown in Fig. 3. The impact of pH can be explained by the change of the ratio of $OBr^-/HOBr$ ($HOBr \Leftrightarrow OBr^- + H^+$, pka = 8.86 at 20℃). The decline of pH impelled the equilibrium $HOBr/OBr^-$ towards HOBr, slowing down the rate of bromate formation in D and D/I pathways since there is a distinction of four magnitudes [15] between the reaction rate constants of OBr^- and HOBr with ozone. In addition, the amount of $^\bullet OH$ decreased as the acidity increased. Pumping carbon dioxide is an effective way to lowering the pH value for low alkali water but not for high alkali water. Thus acidity regulators, for instance, citric acid, malic acid, and tartaric acid, are additional choices to strengthen acidity.

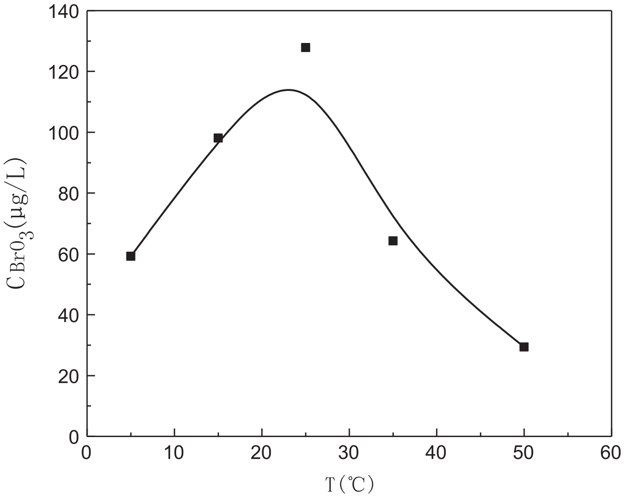

Fig. 2. Formation of bromate at different temperatures (C_{ozone}: 0.4 mg/L, $C_{bromide}$: 50 mg/L).

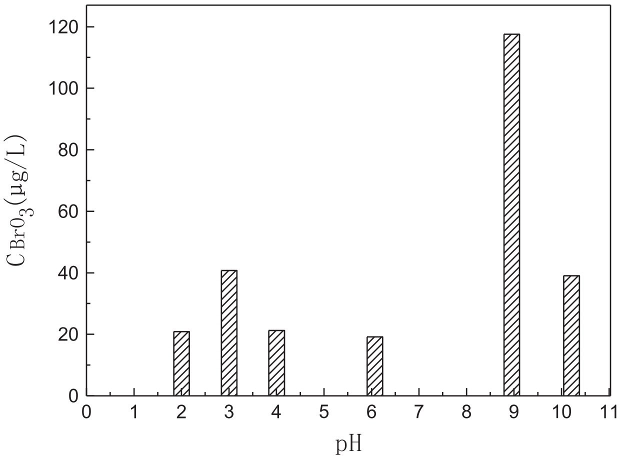

Fig. 3. Formation of bromate at different pH values (pH was adjusted by acetic acid and sodium hydroxide, C_{ozone}: 0.4 mg/L, $C_{bromide}$: 50 mg/L).

3.4. Bromate control by ammonia addition

It has been proved that bromate formation can be inhibited by ammonia [16]. To investigate the effect of the addition of ammonia on the control of bromate formation, several treatments were conducted upon different volumes of ammonia that were 0, 0.05, 0.2, 0.4, 0.6, and 0.8 mL respectively. The results depicted in Fig. 4 show that almost no bromate was found upon the addition of 0.05 mL of ammonia, indicating that high dosages of ammonia were needed to inhibit the formation of bromate.

Ammonia could scavenge hypobromous acid as shown by reaction (1), blocking the D and D/I bromate formation pathways. However, the I/D pathway did not require HOBr, and was therefore not significantly affected. So bromate formation might be reduced, but would not be completely eliminated upon addition of ammonia. And it was supported by previous reports that 80% reduction of bromate formation could be achieved by adding ammonia at pH 8.5 [17].

$$\mathrm{HOBr} + \mathrm{NH_3} \rightarrow \mathrm{NH_2Br} + \mathrm{H_2O} \tag{1}$$

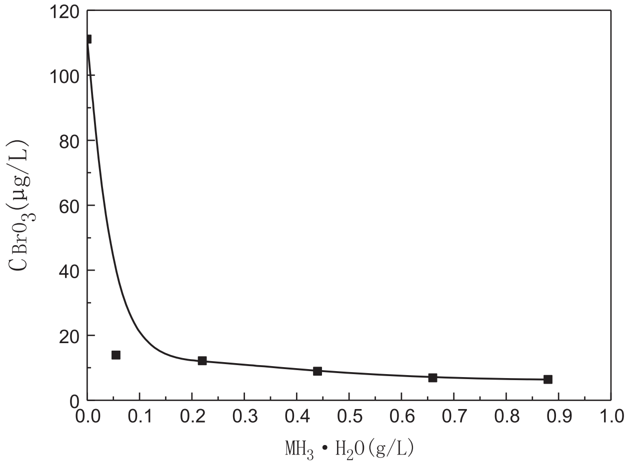

Fig. 4. Formation of bromate upon addition of ammonia (C_{ozone}: 0.4 mg/L, $C_{bromide}$: 50 mg/L).

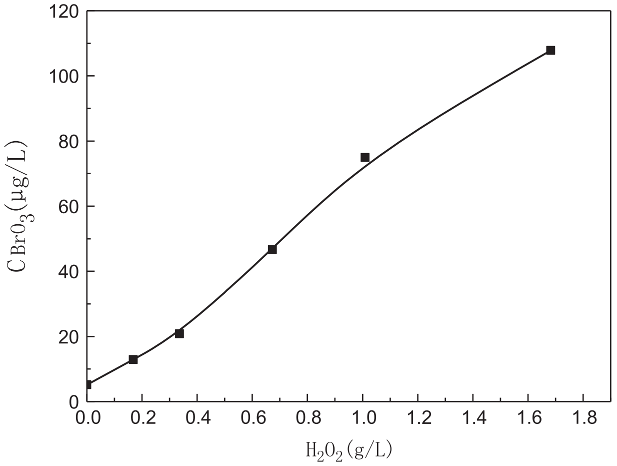

Fig. 5. Formation of bromate by the addition of hydrogen peroxide (C_{ozone}: 0.4 mg/L, $C_{bromide}$: 50 mg/L).

3.5. *Effect of hydrogen peroxide on bromate formation*

Previous investigations concerning the effect of hydrogen peroxide (H_2O_2) on bromate formation have reported mixed results [18,19] are probably because of the conflicting behavior of H_2O_2: it inhibits the D and D/I pathways by scavenging free bromine, while enhances the I/D pathway through $^{\bullet}OH$ production. Combining ozone with hydrogen peroxide accelerates the production of hydroxyl free radicals, which oxidizes bromide as the first step in the I/D pathway. But there ever appeared another consideration that H_2O_2 reduces free bromine to bromide very quickly [20].

To find out the exact effect of H_2O_2 on bromate formation, different volumes of H_2O_2 were applied into the system. The result in Fig. 5 shows that the addition of H_2O_2 promoted the formation of bromate. It was supposed that the enhancement of the I/D pathway was predominant.

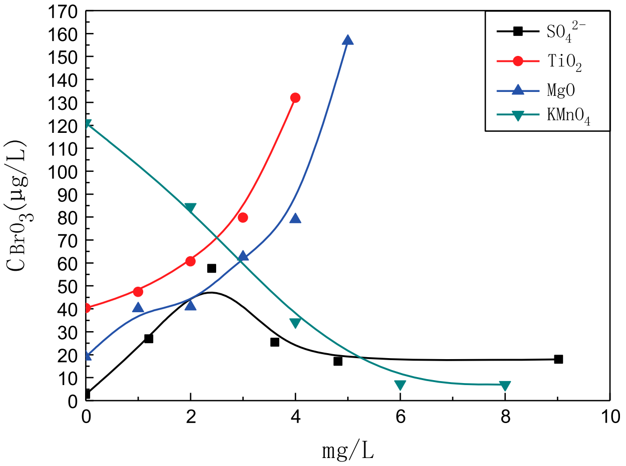

Fig. 6. Effect of metallic compounds on bromate formation (C_{ozone}: 0.4 mg/L, $C_{bromide}$: 50 mg/L).

3.6. *Bromate formation during catalytic ozonation*

The results in Fig. 6 show that the addition of magnesium oxide or titanium oxide promoted the formation of bromate while potassium permanganate inhibited. And the formation of bromate was promoted by a small amount of copper sulfate but inhibited with more addition of copper sulfate. Increased hydroxyl radicals by the catalysis of magnesium or oxide titanium oxide facilitated bromate formation. The decomposition of ozone was promoted by potassium permanganate, which resulted in the increase of $^{\bullet}OH$ and in the decrease of ozone. And the total oxidation ability had been damped. It was reported that sulfate ion accelerates bromate formation [21] Hence the formation of bromate could be promoted obviously at low concentrations of sulfate.

4. Conclusions

The extent of BrO_3^- formation was significantly affected by the temperature of the ozonation system. High temperature brought reduction of the dissolved ozone, resulting in the attenuation of the disinfection. But cooling is an alternative to control bromate formation. And bromate formation decreased at low pH ($pH < 6.0$). Pumping carbon dioxide or employing acidity regulators is advisable to increase acidity. H_2O_2 promoted the formation of bromate by the enhancement of the I/D pathway. Ammonia effectively blocked the D/I and D bromate formation pathways, indicating that the addition of ammonia is one of advisable ways to control the formation of bromate. A significant inhibition of bromate formation was also achieved by potassium permanganate.

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