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Bromate removal by gamma irradiation in aqueous solutions

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Abstract Bromate (BrO_3^-) is a disinfection by-product in drinking water, and its removal is very difficult especially at low levels. ^{60}Co gamma rays were used to remove BrO_3^- in aqueous solution in this study. The effects of absorbed doses, BrO_3^- initial concentration, gas saturation, pH value and coexisting anions (Cl^-, NO_3^-, SO_4^{2-} and HCO_3^-/CO_3^{2-}) on BrO_3^- reduction were evaluated. After 4.0-kGy irradiation of air-equilibrated solution of 30.7 μg/L BrO_3^-, the residual BrO_3^- was 8.3 μg/L, which is below the maximum contaminant level of drinking water. The BrO_3^- reduction rate increased with the dose, in the order of $N_2 > \text{air} > O_2 > N_2O$ atmosphere under similar conditions. The results also show that high pH favored the BrO_3^- removal. According to the experimental results, it can be concluded that the efficiency of decomposing BrO_3^- by reactive species followed the order of $\cdot e_{aq}^- > \cdot H > HO_2\cdot > O_2^-\cdot$. Coexisting Cl^-, HCO_3^-/CO_3^{2-} and SO_4^{2-} ions have little effect on BrO_3^- removal, whereas NO_3^- can inhibit its removal as a result of competition with BrO_3^- for $\cdot e_{aq}^-$.

Keywords Gamma irradiation · Bromate · Drinking water · Coexisting anion

1 Introduction

Bromate (BrO_3^-) is classified as a Group 2B substance (possibly carcinogenic to humans) by the International Agency for Research on Cancer. The maximum contaminant level for BrO_3^- ion in drinking water is set in China as 10 μg/L [1], which is the provisional guideline value recommended by the World Health Organization [2]. BrO_3^- is generated by oxidation of bromide in water through disinfection processes such as ozonation processes [3], TiO_2 photo-catalysis [4] and UV/$S_2O_8^{2-}$ processes [5]. In particular, during the ozonation of drinking water, the formation of BrO_3^- becomes a problem for bromide levels of 50–100 μg/L [6]. Therefore, it is desirable to develop effective techniques to control BrO_3^-, especially when the Br level is high in the source water, for instance in regions with saltwater intrusion.

A number of methods were investigated to minimize BrO_3^- generation during ozonation or to remove excessive BrO_3^-. Although pH suppression, ammonia addition and chlorine–ammonia addition are applicable in ozone sterilization plants [3, 6, 7], they are not suitable for source waters with high level of ammonia or alkalinity due to potential side effects [8, 9]. Also, it is difficult to remove BrO_3^- formed during ozonation, especially for low levels. BrO_3^- is non-biodegradable and highly stable in water. Up to now, technologies for BrO_3^- removal include activated carbon adsorption [10], photo-catalytic degradation [11], ion exchange [12], electrochemical reduction [13], etc.. The methods may achieve high removal efficiency of BrO_3^- under certain conditions. For example, at BrO_3^- concentrations of 50, 100 or 200 μg/L, the removal efficiency can be over 90 % by employing an anion-exchange membrane [12].

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However, the approaches are still in the laboratory evaluation and development stages.

Irradiation with gamma rays or electron beam is as a promising and clean approach for environmental protection. Pilot-scale and industrial-scale studies have shown that the ionizing radiations are effective in decomposing toxic and refractory pollutants, and in disinfecting pathogenic micro-organisms in drinking water, wastewater and waste sludge [14, 15]. Radiation technology is advantageous in that it does not use any chemical compounds (this is often cost-effective), hence the attractiveness in treatment of drinking water. While other advanced oxidation processes (AOPs) are based on oxidation of toxic substances just by hydroxyl radicals (·OH) and/or other oxidants, ionizing radiations generate simultaneously ·OH and highly reducing species such as $\cdot e_{aq}^-$, which play an important role in degrading pollutants [16]. Zhou et al. [17] revealed that when bromide-containing water was irradiated by gamma rays, BrO_3^- could be formed only in N_2O-saturated solutions when $\cdot e_{aq}^-$ was converted into ·OH. Inspired by this result and considering that the Br is in its higher oxidation state in BrO_3^-, we carried out this study to investigate the reductive removal of BrO_3^- in water by ^{60}Co γ-rays and to determine the effect of various experimental factors on the efficiency of the removal of bromate.

2 Experimental

2.1 Reagents

$NaBrO_3$ and NaBr from Acros Organics were of extra pure grade. Anion standards of Br^- and BrO_3^-, and other anions, for uses in ion chromatography, were purchased from AccuStandard Inc. All other chemicals were of analytical grade and used without further purification. N_2O, O_2 and N_2 gases were of high purity (99.99 %). De-ionized water produced by Millipore Q system was used throughout the experiments.

2.2 Irradiation

Bromate solutions in 80-mL sealed Pyrex glass tubes were irradiated at ambient temperatures in a ^{60}Co γ-ray source at Shanghai Institute of Applied Physics, Chinese Academy of Sciences. Adsorbed doses were measured by the ceric sulfate dosimetry system. A series of $NaBrO_3$ aqueous solutions were prepared by dissolving certain amount of $NaBrO_3$ into de-ionized water to predetermined concentrations. Inorganic anions of nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-) and carbonate (HCO_3^-/CO_3^{2-}) were added to the solution if necessary in the form of their stock solutions of sodium salts. The pH value was adjusted by adding perchloric acid or sodium hydroxide, and the initial pH was 7.0 unless otherwise stated. The solutions were air-equilibrated or bubbled with high-purity N_2, O_2 and N_2O for 20 min, respectively, and were irradiated to 1–10 kGy.

2.3 Analysis methods

Concentrations of bromate and bromide were determined by a Dionex ICS-2000 reagent-free ion chromatograph with an IonPac AS19 analytical column (250 mm × 4 mm ID), using 20 mmol/L potassium hydroxide eluent at a flow rate of 1 mL/min. The detection limits of BrO_3^- and Br^- were 1 and 10 μg/L, respectively. All the experiments were duplicated, and the results were averaged.

3 Results and discussion

3.1 Effect of dose and initial concentration

Air-equilibrated solutions with initial BrO_3^- concentrations of 30–210 μg/L and with dissolved oxygen of about 8 mg/L were irradiated to 1–10 kGy. The removal rates of BrO_3^- are illustrated in Fig. 1a, and percentage of bromine recovery (considering only BrO_3^- and Br^- in the reaction systems) is shown in Fig. 1b.

From Fig. 1, BrO_3^- was degraded effectively by gamma rays. The removal rate of BrO_3^- increased with the dose and decreased with increasing initial BrO_3^- concentrations. At 30.7 μg/L and 4.0 kGy, 73 % BrO_3^- was decomposed and the residual was 8.3 μg/L, which is below the maximum contaminant level of 10 μg/L. Figure 1 shows that at a given dose, the BrO_3^- recovery increased with the initial concentration, but the removal rates did not change significantly. At higher BrO_3^- levels, there were less recombination of reactive radicals (such as $\cdot e_{aq}^- + \cdot OH \rightarrow OH^-$, $\cdot OH + \cdot OH \rightarrow H_2O_2$, etc.) with more radicals reacting with BrO_3^-. However, the formation of intermediate compounds, and the oxidation of Br^- and the intermediates by ·OH radicals, made the reaction system complicated [17–19]. It was reported that bromide could be oxidized to BrO_3^- when ·OH radicals acted as the only oxidant and that $HOBr/OBr^-$ are the requisite intermediates [18]. $HBrO_2/BrO_2^-$ may exist in our reaction systems because of the oxidation of $HOBr/OBr^-$ by ·OH radicals [3]. In Fig. 1b, at 30.7 μg/L and 86.2 μg/L of BrO_3^-, the Br recovery decreased at first and then increased with the dose, indicating that the amount of bromine intermediates would agree with the opposite tendency. On the other hand, Zhou et al. [17] and LaVerne et al. [19] reported that Br^-

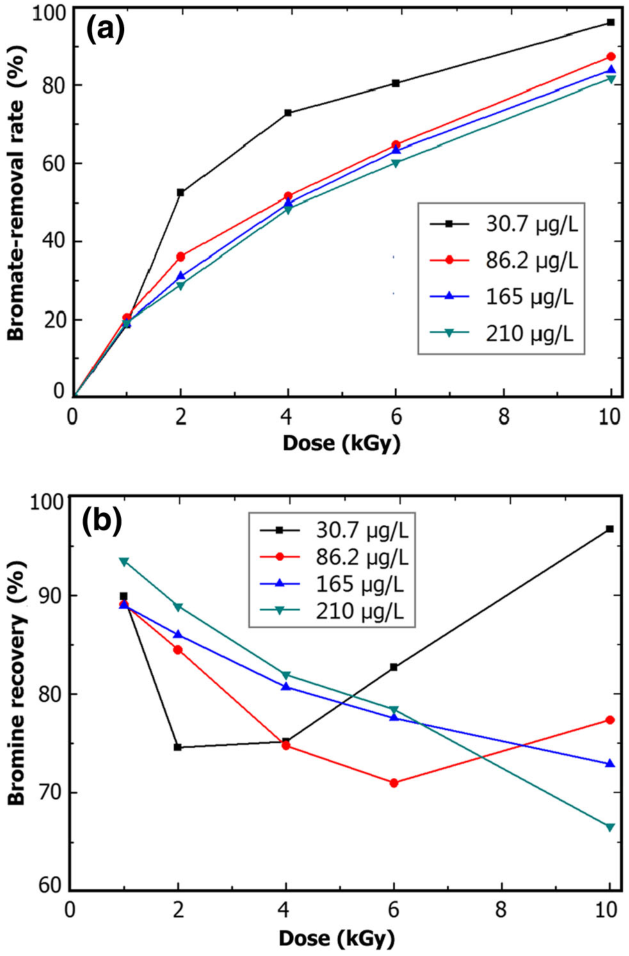

Fig. 1 (Color online) Effect of dose and initial content on bromate removal (**a**) and bromine recovery (**b**), irradiated under air-saturated condition

could not be oxidized to BrO_3^- by irradiating air-equilibrated NaBr solutions due to recycling of the oxidized species of bromine element by $\cdot e_{aq}^-$, $\cdot H$ and/or $HO_2\cdot/O_2^-\cdot$, which implies that the reduction of BrO_3^- and bromine intermediates is inevitable under similar operation condition. Therefore, we can infer that the amount of intermediates at 165 μg/L and 210 μg/L BrO_3^- follows a similar tendency to that at 30.7 μg/L and 86.2 μg/L BrO_3^-, and that all the BrO_3^- and the intermediates are reduced to Br^- at sufficiently higher absorbed doses.

3.2 Effect of saturated atmosphere

In order to explore the atmosphere effect, aqueous solutions with high level BrO_3^- and saturated with air, N_2, O_2 or N_2O were irradiated to 1–10 kGy. As shown in Fig. 2, for the solution degassed by N_2, the removal rate of BrO_3^- was near 98 % and its concentration reduced remarkably to 7.6 μg/L at 4.0 kGy. At a given irradiation dose, the removal efficiency of BrO_3^- decreased in the order of N_2, air, O_2 and N_2O.

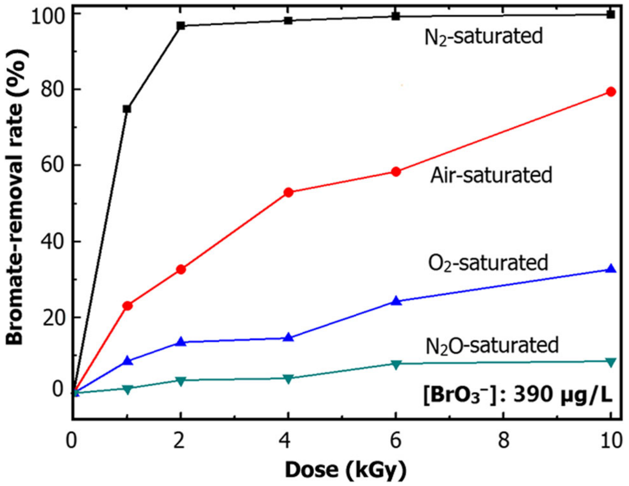

Fig. 2 (Color online) Effect of atmosphere on BrO_3^- removal by γ-rays

The general reaction of radiolysis of N_2-saturated water can be written as Eq. (1) [20, 21], where the numbers are G-values, which are defined as the number of formed or decomposed molecules per 100 eV absorbed energy.

$$\cdot H_2O \xrightarrow{\gamma\text{-rays}} [2.7]\cdot OH + [2.6]\cdot e_{aq}^- + [0.6]\cdot H + [2.6]H_3O^+ + [0.7]H_2O_2 + [0.45]H_2 + \cdots \tag{1}$$

As a powerful reducing agent with a standard reduction potential of −2.9 V, hydrated electron ($\cdot e_{aq}^-$) reacts quickly with BrO_3^- , as shown in Eq. (2), while $\cdot H$ reacts in a much slow rate with BrO_3^-, as shown in Eq. (3) [21].

$$e_{aq}^- + BrO_3^- + 2H^+ \rightarrow BrO_2\cdot + H_2O \tag{2}$$

$$H\cdot + BrO_3^- + H^+ \rightarrow BrO_2\cdot + H_2O \tag{3}$$

The reactions of $\cdot H$ and $\cdot e_{aq}^-$ with O_2 produce $HO_2\cdot$ and $O_2^-\cdot$ as shown in Eqs. (4) and (5), respectively [20], which also reduce BrO_3^- possibly via Eqs. (6) and (7). However, according to Fig. 2, it is reasonable to infer that the reduction of BrO_3^- by $HO_2\cdot/O_2^-\cdot$ is slower than that by $\cdot e_{aq}^-$.

$$H\cdot + O_2 \rightarrow HO_2\cdot \tag{4}$$

$$\cdot e_{aq}^- + O_2 \rightarrow O_2^- \tag{5}$$

$$HO_2\cdot + BrO_3^- \rightarrow BrO_2\cdot + OH^- + O_2 \tag{6}$$

$$\cdot O_2^- + BrO_3^- + H_2O \rightarrow BrO_2\cdot + 2OH^- + O_2 \tag{7}$$

On the other hand, the BrO_3^- concentration decreased just slightly and no Br^- ion was detected in the N_2O-saturated solutions, when $\cdot e_{aq}^-$ and $\cdot H$ generated through Eq. (1) were effectively converted into $\cdot OH$ radicals by N_2O, as shown in Eqs. (8) and (9) [21]. It was reported that

BrO_3^- could react with $\cdot OH$ radical and form BrO_3^- radical, which was further dissociated to BrO. radical, as shown in Eqs. (10) and (11) [22]. However, BrO^- radicals could be disproportionate to $HBrO_2/BrO_2^-$ and $HOBr/OBr^-$ and then reform BrO_3^- through oxidation by $\cdot OH$ radicals. As a result, the variation of the BrO_3^- concentration was small in the N_2O-saturated solutions (Fig. 2).

$$e_{aq}^- + N_2O + H_2O \rightarrow \cdot OH + OH^- + N_2 \quad (8)$$

$$H\cdot + N_2O \rightarrow \cdot OH + N_2 \quad (9)$$

$$\cdot OH + BrO_3^- \rightarrow OH^- + BrO_3\cdot \quad (10)$$

$$BrO_3\cdot \rightarrow BrO\cdot + O_2 \quad (11)$$

3.3 Effect of pH

To further elucidate efficiency of different reactive radicals in reducing BrO_3^-, air- and N_2-saturated solutions of different pH values were irradiated. Figure 3 shows the results. The pH increase had a positive impact on BrO_3^- removal in the N_2-saturated conditions, with the BrO_3^- removal rate being 88 % at pH 11 and only 28 % at pH 3.3. By radiolysis of N_2-saturated water, the concentrations of $\cdot H$ and $\cdot e_{aq}^-$ radicals generated varied with the pH value, with more $\cdot e_{aq}^-$ but less $\cdot H$ formed under high pH conditions [20]. The amount of $\cdot e_{aq}^-$ was negligible at pH 3.3, and $\cdot H$ almost disappeared at pH 11, while the generation of $\cdot OH$ radicals remains nearly constant in the pH range studied [20]. Therefore, from Fig. 3, $\cdot e_{aq}^-$ is much more effective than $\cdot H$ in reducing BrO_3^-, and $\cdot e_{aq}^-$ is the main reactive radical account for the removal of BrO_3^-.

On the other hand, the removal rate of BrO_3^- in air-saturated solutions was lower and it increased a bit with the pH value. According to Eqs. (1), (4) and (5), the main reactive species formed under these conditions were $O_2^-\cdot/HO_2\cdot$ and $\cdot OH$, with more $O_2^-\cdot$ radicals, and less $HO_2\cdot$ radicals formed at high pH values, but amount of $\cdot OH$ radicals was nearly constant. Therefore, it can be sure that $O_2^-\cdot$ radicals are less powerful than $HO_2\cdot$ radicals in reducing BrO_3^-. Based on the results of Figs. 2 and 3, the efficiency of decomposing BrO_3^- by reactive species was in the order of $\cdot e_{aq}^- > \cdot H > HO_2\cdot > O_2^-\cdot$.

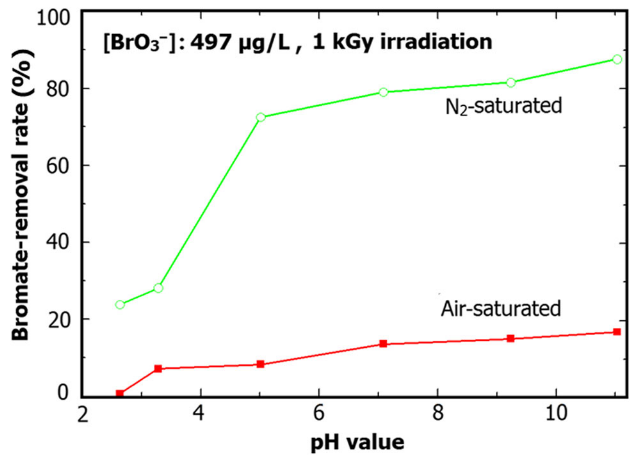

Fig. 3 (Color online) Removal rate of BrO_3^- at various pH values

3.4 Effect of coexisting anions

The presence of coexisting anions in water is known to affect the radiolytic degradation of pollutants [21]. The effects of 1 mmol/L Cl^-, NO_3^-, SO_4^{2-} or HCO_3^-/CO_3^{2-} anions on the radiolytic degradation of BrO_3^- solutions are shown in Fig. 4a. For N_2O-saturated solutions, they had little effect on degradation of BrO_3^-, as they could neither compete with N_2O for reacting with $\cdot e_{aq}^-$ or $\cdot H$, nor act as effective scavengers of the main existing radical (namely $\cdot OH$). For similar reason, the addition of Cl^- or SO_4^{2-} anions showed little influence, too, on BrO_3^- removal under N_2^- or air-saturated conditions.

The effects of CO_3^{2-}/HCO_3^- anions on BrO_3^- removal are more complex. On the one hand, CO_3^{2-}/HCO_3^- anions

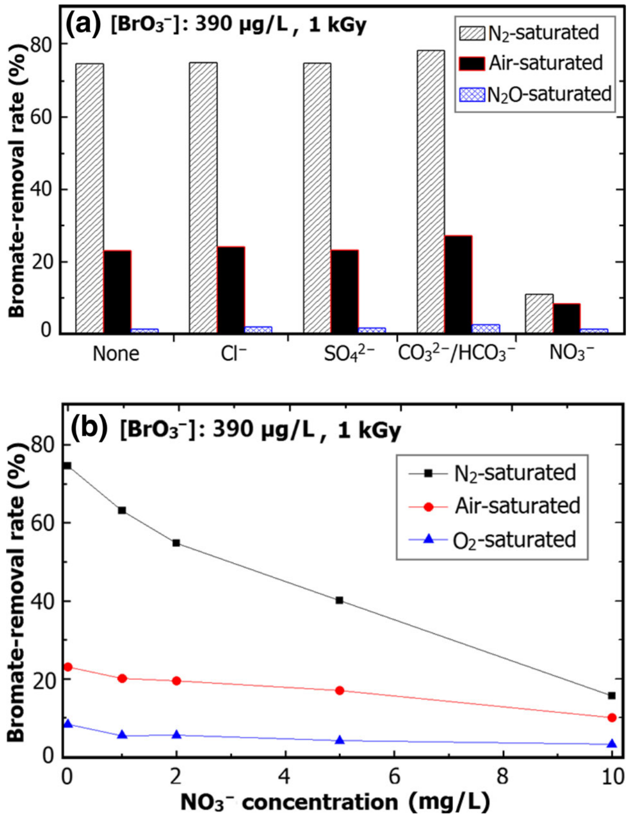

Fig. 4 (Color online) Effect of anions (**a**) and NO_3^- concentration (**b**) on BrO_3^- removal

react with ·OH and play a role as ·OH scavenger, as shown in Eqs. (12) and (13) [21], hence the indirect promotion of BrO_3^- removal [17, 19]. On the other hand, the formed active carbonate radicals (CO_3^-.) through Eqs. (12) and (13) can oxidize the intermediates of bromine and form BrO_3^- precursors again, as shown in Eqs. (14) and (15) [23]. In Fig. 4a, adding CO_3^{2-}/HCO_3^- slightly increased the removal of BrO_3^-.

$$HCO_3^- + \cdot OH \rightarrow H_2O + CO_3^- \qquad (12)$$

$$CO_3^{2-} + \cdot OH \rightarrow OH^- + CO_3^- \qquad (13)$$

$$CO_3^- \cdot + BrO^- \rightarrow CO_3^{2-} + BrO \qquad (14)$$

$$CO3^- \cdot + BrO_2^- \rightarrow CO_3^{2-} + BrO_2 \qquad (15)$$

However, it was observed that the presence of NO_3^- anion suppressed significantly the BrO_3^- reduction in both N_2^-- and air-saturated solutions. As shown in Fig. 4a, the removal rate of BrO_3^- decreased from 74.7 % to 10.9 % by adding 1 mmol/L NO_3^- in the N_2-saturated atmosphere. By adding 1 to 10 mg/L nitrate (measured on basis of nitrogen content), the results of BrO_3^- removal under N_2-, O_2- or air-saturated conditions are shown in Fig. 4b. In all the three atmospheres, there existed an inhibition effect, which was enhanced with increasing concentrations of NO_3^-. For example, in air-saturated solutions, the removal rate decreased more than a half when 10 mg/L NO_3^- was added (the drinking water standard of nitrate in China is 10 mg/L). The reason of inhibition can be attributed to the scavenging of $\cdot e_{aq}^-$ by NO_3^- ions, as shown in Eq. (16),

$$e_{aq}^- + NO_3^- \rightarrow \cdot NO_3^{2-} \qquad (16)$$

and the reaction rate is very fast according to Ref. [21]. From Fig. 4, we know that the product of $\cdot e_{aq}^-$ and NO_3^-, namely $\cdot NO_3^{2-}$, and its further decay products are incapable or ineffective in decomposing BrO_3^-. As a result, the efficiency of BrO_3^- removal is reduced, so the operation cost shall be carefully considered in irradiation removal of BrO_3^- from water of high nitrate levels.

4 Conclusion

Bromate removal by γ-irradiations process was investigated, on influence factors of the absorbed dose, BrO_3^- initial concentration, gas saturation, pH value and coexisting anions in aqueous solution. The main results are as follows:

(1) Gamma irradiations are efficient in removing BrO_3^- at neutral conditions in air-saturated atmosphere (normal condition of drinking water).

(2) The efficiency of BrO_3^- removal decreased in the order of $N_2 \gg \text{air} > O_2 > N_2O$ atmosphere at a given dose, and higher pH value was beneficial for BrO_3^- removal.

(3) BrO_3^- was removed by reactive species such as $\cdot e_{aq}^-$, ·H, HO_2. and O_2^-., following by the order of $\cdot e_{aq}^- > \cdot H > HO_2. > O_2^-.$, and $\cdot e_{aq}^-$ played the main role in BrO_3^- decomposing.

(4) Coexisting anions (Cl^-, HCO_3^-/CO_3^{2-} and SO_4^{2-}) exerted little effect on BrO_3^- removal. However, NO_3^- can significantly suppress BrO_3^- removal due to the scavenging of $\cdot e_{aq}^-$ by NO_3^-.

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