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Bromate formation in bromide-containing waters irradiated by gamma rays[*]

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The formation of bromate, a classified potential carcinogen, is of great concern when disinfection processes are used for treating high-bromide drinking waters. Bromide-containing aqueous solutions with various additives were irradiated by ^{60}Co γ source. With a 2.0 kGy irradiation of N_2O-saturated solutions at initial bromide concentrations of 180.2 μg l^{-1}, 416.9 μg l^{-1}, 663.1 μg l^{-1} and 823.9 μg l^{-1}. 79.5%, 84.0%, 87.3% and 88.3% of bromide ions were transformed to bromate, respectively. Addomg CO_3^{2-}/HCO_3^- or NO_3^- ions into N_2O-saturated bromide solutions, the amount of bromate ions formed decreased with increasing concentrations of the additives. On the other hand, the bromate concentration was all below the detection limit of 1 μg l^{-1} whenever N_2O was not added to quench e_{aq}^- and ·H. The results indicated that γ-rays irradiation could be used as a disinfection process, instead of ozonation, to comply with upcoming more stringent regulations, especially in waters containing high concentrations of bromide.

Keywords: Bromide, Bromate, Gamma irradiation, Disinfection

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I. INTRODUCTION

Bromide (Br^-) is commonly found in water bodies, with concentrations varying from a few μg l^{-1} to several mg l^{-1}. Through oxidative processes, Br^- can be oxidized to bromate (BrO_3^-), which is classified as a possibly carcinogen to humans by the International Agency for Research on Cancer (IARC). The World Health Organization (WHO) recommends a provisional guideline value of 10 μg l^{-1} for drinking water because of limitations in available analytical and treatment methods [1]. The same value has recently been set as the maximum contaminant level (MCL) of bromate in drinking water in many countries, including China [2].

The main source of BrO_3^- in drinking water is the ozonation of bromide-containing waters, which may cause serious bromide levels of over 100 μg l^{-1} [3]. Several authors reported that bromate formation during ozonation is due to three general pathways, the direct pathway, direct-indirect pathway and indirect-direct pathway. The direct pathway involves only molecular ozone (O_3), and in the direct-indirect and indirect-direct pathways, both O_3 and ·OH radicals (produced from O_3 decomposition) participate in bromate formation [4]. Others reported that bromate was formed predominately through the free radical pathway [5, 6]. In a continuous flow reactor, the amount of BrO_3^- formation reduced by 90% in the presence of *tert*-butanol (acted as ·OH scavenger) [6].

Therefore, it is important to investigate the factors affecting the BrO_3^- formation through the free radical pathway without involving any O_3. In this study, aqueous solutions containing bromide and other additives were subjected to γ-rays irradiation, and free radicals were generated. The influence of factors, such as atmospheres (namely N_2O, O_2, N_2 and natural air), absorbed dose, initial bromide concentration, pH, and common inorganic ions (including nitrate, chloride, (bi)carbonate and sulfate) etc, were investigated.

II. EXPERIMENTAL

A. Materials

NaBr of extra pure grade was purchased from Acros Organics. Anion Standards of Br^- and BrO_3^- and other anions were purchased from AccuStandard Inc. N_2O, O_2 and N_2 gases were of high purity (99.99%). All other chemicals were of analytical grade and obtained through J&K Chemical Ltd and used as received. De-ionized water by Millipore Q system was used throughout the experiments.

B. Sample irradiation

The irradiation experiments were performed in a ^{60}Co gamma source at Shanghai Institute of Applied Physics, Chinese Academy of Sciences. Adsorbed doses were measured by a ceric sulfate dosimetry system. Prepared NaBr aqueous solutions under air-equilibration or saturated with N_2, O_2 or N_2O by bubbling for 20 min of high-purity N_2, O_2 or N_2O gases in 80 mL Pyrex glass tubes, were irradiated to 0.5∼10 kGy. Inorganic anions of nitrate, sulfate, chloride, and (bi)carbonate, were added in the form of their stock solutions of sodium salts. The solution pH was adjusted by adding perchloric acid or sodium hydroxide, and was adjusted to 7.0 unless otherwise stated. All experiments were carried out at ambient temperature.

C. Analysis methods

The concentrations of bromate and bromide and other anions were determined by a Dionex ICS-2000 reagent-free

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ion chromatograph, with an IonPac AS19 analytical colum (250 mm × 4 mm ID), using 20 mmol l^{-1} potassium hydroxide eluent at a flow rate of 1 ml min^{-1}. Sample volume loaded for all analysis was 200 µl each. The detection limits of bromate and bromide were below 1 µg l^{-1} and 10 µg l^{-1}, respectively. The pH values were measured by a PHSJ-4A pH meter.

III. RESULTS AND DISCUSSION

A. Effect of atmosphere and initial concentration

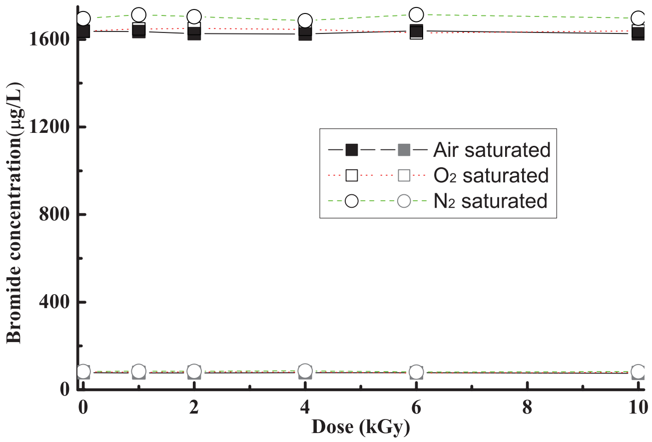

Fig. 1. (Color online) Br^- concentration as a function of absorbed dose and atmosphere. The datum points in square (□) and circle (○) are of initial Br^- concentration of approximately 80 µg l^{-1} and 1650 µg l^{-1}, respectively.

The results from samples saturated with air, N_2, or O_2 and without other additives, are illustrated in Fig. 1. For both initial Br^- concentration of approximately 80 µg l^{-1} and 1650 µg l^{-1}, the concentration of Br^- almost remained unchanged for all samples, and the BrO_3^- concentrations were all below the detection limit. It could be conclude from Fig. 1 that Br^- could not be oxidized into BrO_3^- under such conditions. In Ar saturated solutions with initial Br^- concentrations from 800 µg l^{-1} to 80 µg l^{-1}. LaVerne *et al.* [7] found that the Br^- concentrations kept constant up to 100 kGy.

It is well known that ·OH radicals could oxidize Br^- to $BrOH^-$·, which then transforms to Br·, Br_2^-· and other bromine species [8–10]. From Fig. 1, the oxidized bromine species could be reduced effectively by e_{aq}^-, H· and/or O_2^-·/HO_2· andBr^- reformed. Possible reactions are listed below [7, 9]:

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

$$\cdot OH + Br^- \leftrightarrow BrOH^- \cdot \quad (2)$$

$$BrOH^- \cdot \leftrightarrow OH^- + Br \cdot \quad (3)$$

$$BrOH^- \cdot + Br^- \leftrightarrow OH^- + Br_2{}^- \cdot \quad (4)$$

$$Br \cdot + Br^- \leftrightarrow Br_2{}^- \quad (5)$$

$$e_{aq}{}^- + Br_2{}^- \rightarrow 2\,Br^- \quad (6)$$

$$H \cdot + Br_2{}^- \cdot \rightarrow 2\,Br^- + H^+ \quad (7)$$

$$e_{aq}{}^- + O_2 \rightarrow O_2{}^- \cdot \quad (8)$$

$$H \cdot + O_2 \rightarrow HO_2 \cdot \quad (9)$$

$$O_2{}^- \cdot (HO_2 \cdot) + Br_2{}^- + O_2(+H^+) \quad (10)$$

The numbers in Eq. (1) are called G-values, defined as the number of formed or decomposed molecules per 100 eV absorbed energy. The reactions in Eqs. (8) – (10) take place in aqueous solutions saturated with air or O_2.

On the other hand, as shown in Fig. 2, the majority of bromide was oxidized to bromate in N_2O saturated solutions even at 0.5 kGy. The formation of bromate increased with increasing doses and initial bromide concentrations. At 2.0 kGy, for initial bromide concentrations of 180.2 µg l^{-1}, 416.9 µg l^{-1}, 663.1 µg l^{-1} and 823.9 µg l^{-1} approximately 79.5%, 84.0%, 87.3% and 88.3% of bromide ions were transformed to bromate, respectively. And the analysis of bromide indicated that over 95% of the oxidized bromide was transformed to bromate for all the samples in Fig. 2. This means that the concentrations of intermediates were low.

In the irradiating N_2O-saturated solutions, the primary reactive radicals were ·OH radicals due to reactions (11) and (12).

$$e_{aq}{}^- + N_2O + H_2O \rightarrow \cdot OH + OH^- + N_2 \quad (11)$$

$$H \cdot + N_2O \rightarrow \cdot OH + N_2 \quad (12)$$

When *tert*-butanol (acted as an ·OH scavenger) was added to the solution of 0.1–25 mM concentration, no bromate was detected after 4.0 kGy irradiation for N_2O saturated solutions with 823.9 µg l^{-1} Br^-. From the results, one knows that ·OH radicals can oxidize bromide to bromate. Von Gunten and Oliveras reported that bromate formed with ·OH radicals being the only oxidants and HOBr/OBr^- are requisite intermediates [11].

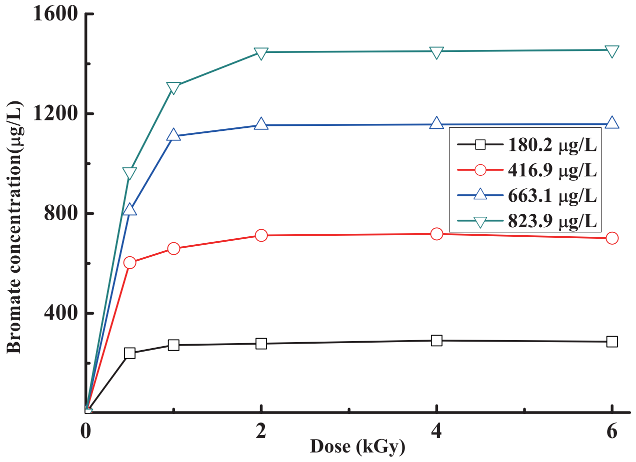

Fig. 2. (Color online) Effect of initial Br^- concentration and absorbed dose on bromate formation in N_2O saturated bromide solutions.

B. Effect of pH

Figure 3 shows the effect of pH value on the formation of bromate in N_2O saturated bromide-containing waters. The formation of bromate was nearly the same at pH 3.5–7.0, and decreased by about 5% at pH 2.5. At the pH 10.8, however, the bromate concentration decreased to $46.0\,\mu g\,l^{-1}$ from about $550\,\mu g\,l^{-1}$ in neutral conditions.

This shows the pH value dependence of G-values of the species formed in water radiolysis [12]. While the G-values of ·OH, e_{aq}^- and ·H are almost constant in near neutral conditions, the H^+ in higher concentration can react with $e_{aq}{}^-$($H^+ + e_{aq}{}^- \to \cdot H$), hence the decreased concentration of ·OH radicals according to Eq. (11) [12], which resulted in a small decrease of bromate concentration compared to neutral conditions. In alkaline conditions, the G-value of ·OH radicals decreases as they are transformed to less reactive $\cdot O^-$ species, and more reductive species, like $e_{aq}{}^-$ and less reactive $HO_2{}^-\cdot$, were formed [12]. The oxidized bromide ions may be reduced by these reductive species. Therefore, the bromate formed at pH 10.8 was much less than that at lower pH values.

C. Effect of common anions

Natural waters are complex matrixes, containing anions that may interfere with the oxidation of bromide by competing with the free radical species. To investigate the influence of common anions in drinking waters, 0.1–25 mM of Cl^-, $CO_3{}^{2-}$/$HCO_3{}^-$, $NO_3{}^-$ or $SO_4{}^{2-}$ were added to bromide-containing solutions. The results from solutions saturated with air, N_2 or O_2 showed that no bromate was found at 0.5–6.0 kGy for solutions in initial bromide concentrations of $81.7\,\mu g\,l^{-1}$ and $1636.6\,\mu g\,l^{-1}$.

Figure 4 depicts the influence of the selected common anions on the formation of bromate in N_2O saturated waters. The amounts of bromate ion formed were unaffected by $SO_4{}^{2-}$ ion, and increased slightly with the Cl^- ions. However, in the presence of $CO_3{}^{2-}$/$HCO_3{}^-$ (predominantly $HCO_3{}^-$ when the solution was neutral), the bromate concentration decreased notably to $44.2\,\mu g\,l^{-1}$ from $554.0\,\mu g\,l^{-1}$ added with 1 mM $CO_{32}{}^-$/$HCO_3{}^-$ after 4.0 kGy irradiation. The bromate concentration decreased significantly only at high $NO_3{}^-$ concentrations, as depicted in Fig. 4. This shows that the bromate concentration was not substantially affected by 1 mM $NO_3{}^-$ addition, whereas added with 10 mM $NO_3{}^-$, it decreased from $554.0\,\mu g\,l^{-1}$ to $190.1\,\mu g\,l^{-1}$.

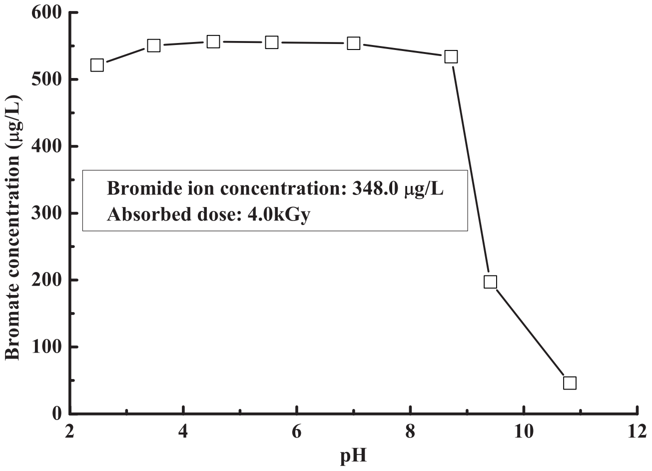

Fig. 3. Effect of pH on bromate formation for N_2O saturated bromide-containing waters.

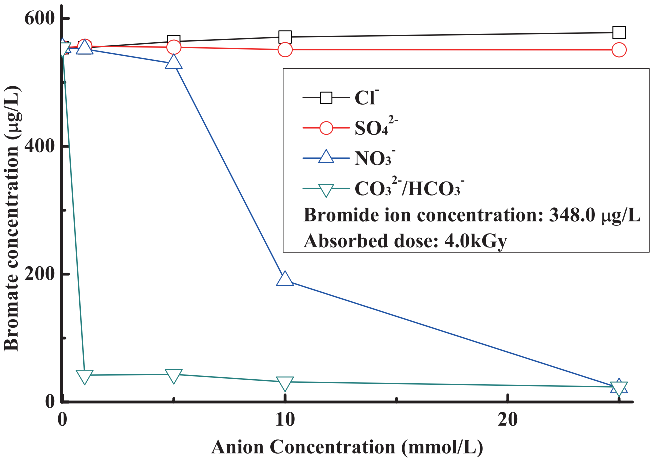

Fig. 4. (Color online) Effect of common anions on bromate formation for N_2O saturated bromide-containing waters.

Cl^- ions could react with ·OH radical quickly to form ClOH·($k = 4.3 \times 10^9\,mol^{-1}\,s^{-1}$), but $ClOH^-\cdot$ may reform ·OH radical by the fast reverse reaction($k = 6.1 \times 10^9\,s^{-1}$) in neutral solutions [13]. Then, the slightly increased bromate formation in the presence of Cl^- ion might be due to less radical recombination of ·OH radicals (such as $\cdot OH + \cdot H \to H_2O$, $\cdot OH + \cdot OH \to H_2O_2$, etc.)

Both $CO_3{}^{2-}$ and $HCO_3{}^-$ react with ·OH radicals and form $\cdot CO_3{}^-$ radicals [13]. The results in Fig. 4 indicated that the $\cdot CO_3{}^-$ radical only cannot oxidize Br^- and other bromine species to bromate. In the ozonation process, however, $\cdot CO_3{}^-$

radicals, which are also produced from $\cdot$ OH, can oxidize BrO$^-$ to BrO$\cdot$ ($k = 4.3 \times 10^7$ mol L^{-1} s^{-1}) and potentially lead to an increase in bromate due to the presence of O_3 [14].

NO_3^- ion is not as efficient an ·OH scavenger as CO_3^{2-}/HCO_3^-, as revealed in Fig. 4, but for higher NO_3^- ion concentrations, NO_3^- ion can compete with N_2O for $\cdot e_{aq}^-$($NO_3^- + \cdot e_{aq}^- \rightarrow NO_3^{2-}$, $k = 9.7 \times 10^9$ mol L^{-1} s^{-1}), resulting in the notably decrease of ·OH concentration and then the decrease of bromate formed.

IV. CONCLUSION

γ -rays irradiation of bromide-containing aqueous solution in different conditions was investigated. It is found that bromate can be formed only in N_2O saturated solutions, in which the primary reactive radicals were ·OH radicals. Adding CO_3^{2-}/HCO_3^- or NO_3^- ions to N_2O saturated bromide solutions can decrease the bromate formation. Bromide concentrations are found to remain constant in irradiated N_2, O_2 or air saturated bromide solutions irradiated to 0.5–6 kGy. When NO_3^-, Cl$^-$, CO_3^{2-}/HCO_3^-, SO_4^{2-} or tert-butanol was added, no bromate was found in the irradiated bromide solutions saturated by N_2, O_2 or air. This study indicated that, instead of ozonation, γ -rays irradiation can be used as a disinfection process especially in high-bromide waters, because of a continuous pressure from regulators to further lower bromate drinking water standards, and the fact that few practical methods can be used to reduce bromate formation in ozonation or remove bromate after its formation to levels well below 10 µg L^{-1} or even below the current detection limits.

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