Bromate formation in bromide-containing waters irradiated by gamma rays (Postprint)

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Abstract

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 a ^{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. Adding CO_3^{2-}/HCO_3^- or NO_3^- ions to 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 remained 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-ray 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.

Full Text

Preamble

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 a ^{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. Adding $CO_3{}^{2-}$ to N_2O-saturated bromide solutions caused the amount of bromate ions formed to decrease with increasing concentrations of the additive. On the other hand, the bromate concentration was below the detection limit of 1 µg l^{-1} whenever N_2O was not added to quench e q^{-} and $\cdot$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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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 possible 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 bromate 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 $\cdot$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 (acting as $\cdot$OH scavenger) [6].

Therefore, it is important to investigate the factors affecting $BrO_3{}^-$ 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) was 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 from a 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. Absorbed 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 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 set to 7.0 unless otherwise stated. All experiments were carried out at ambient temperature.

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C. Analysis Methods

The concentrations of bromate, bromide and other anions 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^{-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

The results from samples saturated with air, N_2, or O_2 and without other additives are illustrated in Fig. 1 [Figure 1: see original paper]. For both initial Br^- concentrations 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 concluded 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 remained constant up to 100 kGy.

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

$$
\begin{aligned}
BrOH^- \cdot + Br^- &\leftrightarrow OH^- + Br_2^- \cdot \\
Br \cdot + Br^- &\leftrightarrow Br_2^- \cdot \\
Br_2^- \cdot + Br_2^- \cdot &\rightarrow 2Br^- \\
H \cdot + Br_2^- \cdot &\rightarrow 2Br^- + H^+ \\
Br_2^- \cdot + O_2 &\rightarrow O_2 + 2Br^- \\
H \cdot + O_2 &\rightarrow HO_2 \cdot \\
HO_2 \cdot (O_2^- \cdot) + Br_2^- \cdot &\rightarrow 2Br^- + O_2(+H^+)
\end{aligned}
$$

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 [Figure 2: see original paper], 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. Analysis of bromide indicated that over 95% of the oxidized bromide was transformed to bromate for all the samples in Fig. 2, meaning that the concentrations of intermediates were low.

In the irradiating N_2O-saturated solutions, the primary reactive radicals were $\cdot$ OH radicals due to reactions (11) and (12):

$$
\begin{aligned}
e_{aq}^- + N_2O + H_2O &\rightarrow \cdot OH + OH^- + N_2 \\
\gamma\text{-rays} &\rightarrow [2.7] \cdot OH + [2.6] e_{aq}^- + [0.6] \cdot H + [2.6] H_3O^+ + [0.7] H_2O_2 + [0.45] H_2 + \cdots \\
\cdot OH + Br^- &\leftrightarrow BrOH^- \cdot \\
BrOH^- \cdot &\leftrightarrow OH^- + Br \cdot \\
H \cdot + N_2O &\rightarrow \cdot OH + N_2
\end{aligned}
$$

When tert-butanol (acting as an $\cdot$OH scavenger) was added to the solution at 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 these results, one knows that $\cdot OH$ radicals can oxidize bromide to bromate. Von Gunten and Oliveras reported that bromate formed with $\cdot OH$ radicals being the only oxidants and $HOBr/OBr^-$ are requisite intermediates [11].

B. Effect of pH

Figure 3 [Figure 3: see original paper] 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 pH 10.8, however, the bromate concentration decreased to 46.0 µg l^{-1} from about 550 µg l^{-1} under neutral conditions.

This shows the pH value dependence of G-values of the species formed in water radiolysis [12]. While the G-values of $\cdot OH$, e q$^-$ and $\cdot H$ are almost constant in near-neutral conditions, H^+ in higher concentration can react with e q$^-$ (H^+ + e q$^-$ $\rightarrow$ $\cdot H$), hence decreasing the concentration of $\cdot OH$ 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 $\cdot OH$ radicals decreases as they are transformed to less reactive $\cdot O^-$ species, and more reductive species like e q$^-$ 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 matrices 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 with initial bromide concentrations of 81.7 µg l^{-1} and 1636.6 µg l^{-1}.

Figure 4 [Figure 4: see original paper] 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 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 µg l^{-1} from 554.0 µg l^{-1} when 1 mM was added after 4.0 kGy irradiation. The bromate concentration decreased significantly only at high NO_3^- concentrations, as depicted in Fig. 4. While the bromate concentration was not substantially affected by 1 mM NO_3^- addition, it decreased from 554.0 µg l^{-1} to 190.1 µg l^{-1} when 10 mM NO_3^- was added.

Cl^- ions could react with $\cdot OH$ radical quickly to form $ClOH\cdot$ (k = 4.3 × 10^9 mol^{-1} s^{-1}), but $ClOH^-\cdot$ may reform $\cdot OH$ radical by the fast reverse reaction (k = 6.1 × 10^9 s^{-1}) in neutral solutions [13]. The slightly increased bromate formation in the presence of Cl^- ion might be due to less radical recombination of $\cdot OH$ radicals (such as $\cdot OH + \cdot H \rightarrow H_2O$, $\cdot OH + \cdot OH \rightarrow H_2O_2$, etc.). Both ${CO_3}^{2-}$ and ${HCO_3}^-$ react with $\cdot OH$ radicals and form ${CO_3}^- \cdot$ radicals [13]. The results in Fig. 4 indicated that the ${CO_3}^- \cdot$ radical alone cannot oxidize Br^- and other bromine species to bromate. In the ozonation process, however, ${CO_3}^- \cdot$ 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].

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

IV. Conclusion

γ-rays irradiation of bromide-containing aqueous solutions under different conditions was investigated. It was found that bromate can be formed only in N_2O-saturated solutions, in which the primary reactive radicals were $\cdot OH$ radicals. Adding ${CO_3}^{2-}/{HCO_3}^-$ or ${NO_3}^-$ ions to N_2O-saturated bromide solutions can decrease bromate formation. Bromide concentrations were found to remain constant in irradiated N_2, O_2 or air-saturated bromide solutions irradiated to 0.5–6 kGy. When ${CO_3}^{2-}/{HCO_3}^-$ 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 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 current detection limits.

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Note: Figure translations are in progress. See original paper for figures.