Bromate ion formation in dark chlorination and ultraviolet/chlorination processes for bromide-containing water

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Abstract

Bormate (BrO_3^-) is a carcinogenic chemical produced in ozonation or chlorination of bromide-containing water. Although its formation in seawater with or without sunlight has been previously investigated, the formation of bromate in dilute solutions, particularly raw water for water treatment plant, is unknown. In this article, the results of bench scale tests to measure the formation rates of bromate formation in dilute solutions, including de-ionized water and raw water from Yangtze River, were presented in dark chlorination and ultraviolet (UV)/chlorination processes. And the effects of initial pH, initial concentration of NaOCl, and UV light intensity on bromate formation in UV/chlorination of the diluted solutions were investigated. Detectable bromate was formed in dark chlorination of the two water samples with a relatively slow production rate. Under routine disinfecting conditions, the amount of formed bromate is not likely to exceed the national standards (10 μg/L). UV irradiation enhanced the decay of free chlorine, and, simultaneously, 6.6%–32% of Br^- was oxidized to BrO_3^-. And the formation of bromate exhibited three stages: rapid stage, slow stage and plateau. Under the experimental conditions (pH = 4.41–11.07, C_{Cl_2} = 1.23–4.50 mg/L), low pH and high chlorine concentration favored the generation of bromate. High light intensity promoted the production rate of bromate, but decreased its total generation amount due to acceleration of chlorine decomposition.

Key words: bromate; chlorination; raw water; Yangtze River; ultraviolet (UV) irradiation

Introduction

Recent interests in ozonation byproducts during drinking water treatment have led to a number of studies on control and removal of bromate (BrO_3^-) in water (von Gunten, 2003). In the United States and the European Union (EU), the maximum acceptable contaminant level of BrO_3^- is 10 μg/L. The World Health Organization (WHO) has proposed a maximum BrO_3^- level of 10 μg/L. Given that the requirement for maximum contaminant level (MCL) of bromate present in drinking water trends to be much strict, many investigations to the formation of bromate in water have been carried out.

Bromate is typically generated in ozonation of water containing bromide ion (Butler *et al.*, 2005). Moreover, bromide during chlorination can also be transformed to bromate (Emmert, 1999). Under alkaline conditions, bromide can be oxidized to hypobromite by hypochlorite. Wong and Davidson (1977) reported that the exchange reaction between hypochlorite and bromide could be rapidly completed within 2.5 min. It has been recognized that the decomposition or disproportionation of hypohalous acid and hypohalite leads to form halate or oxygen. The path-

way and rate of decomposition are related to the factors, such as pH, concentration, temperature, ionic strength, and light. Of interest, Macalady *et al.* (1977) found that considerable bromate was formed from the solutions of chlorinated seawater exposed to sunlight, and less sunlight intensity caused the less production of bromate. And they did not find the formation of bromate in the dark. Wong (1979) also observed that sunlight induced the decomposition of free oxidant in seawater to form bromate. Haag (1981) found that both bromate and chlorate are products of free oxidants in seawater at molar ratios of Cl_2/Br > 1. Chlorinated seawater samples containing mixtures of hypochlorite and hypobromite disproportionated much faster to form halate than separated solutions of hypohalites, which was explained by cross-oxidation reacting ions between hypobromite and hypochlorite. Furthermore, bromate was formed in the dark. Haag (1981) ascribed the observation, different from the results of Macalady *et al.* (1977) or Wong (1979), to the longer reaction times and much higher concentrations used in his experiments.

Bromate formation in seawater during chlorination has been investigated for more than two decades. Macalady *et al.* (1977) used 4.2–4.9 mg/L Cl_2 to seawater, a dosage close to that used in drinking water treatment, to pro-

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duce 65 mg/L bromide, greatly higher than 15–100 μg/L containment level in surface waters. Based on the results, it is likely that bromate produced during outdoor pre-chlorination under sunlight or pre-chlorination prior to an ultraviolet disinfection process leads to violation of the rigid 10 μg/L BrO_3^- regulations in tap water. However, quantitative measurement of the formation rate of bromate in chlorination of a dilute bromide-containing solution, particularly under ultraviolet (UV) irradiation, as well as evaluation of impacts of water quality parameters on its formation, has not been conducted.

Shanghai is a costal city located in the estuary of Yangtze River. In dry seasons, roughly from December to April, seawater frequently intrudes the lower reaches of Yangtze River, that is water sources of local water treatment plants, occasionally considerably increasing the content of bromide in the water. The objective of this study was to investigate the formation of bromate in dilute bromide-containing solutions (de-ionized water and raw water from Yangtze River) in dark chlorination and UV/chlorination processes, and to examine the effects of water quality parameters, including initial pH, initial chlorine concentration, and UV intensity, on the bromate formation.

1 Materials and methods

1.1 Reagents and raw water

All chemicals were at least analytical reagent grade. De-ionized water (conductivity < 1 μS/cm) was obtained through a Milli-Q equipment. Anion solutions were prepared by dissolving certain amounts of sodium and/or potassium salts of the various anions with de-ionized water. The level of bromate in the sodium hypochlorite stock solutions was 0.30–1.18 μg BrO_3^-/mg Cl_2. The "blank values" of bromate in each experiment were theoretically calculated according to the dosage of chlorine (Weinberg et al., 2003).

Raw water was collected from a sedimentation tank (horizontal flow) in Zhabei Water Treatment Plant, Shanghai, China. The water source of this plant is located in the downstream of Yangtze River, close to the estuary. Particles were removed using filtration through a 0.45-μm membrane. Characteristics of the filtered raw water are shown in Table 1. Bromide present in the raw water resulted from sea-water intrusion had a moderate level (56.3 μg/L).

Table 1   Characteristics of the filtered raw water from Yangtze River

Parameter	Value
DO (mg/L)	6.0
pH	7.2
COD_{Mn} (mg/L)	1.1
DOC (mg/L)	1.7
Br^- (μg/L)	56.3
Cl^- (mg/L)	50.1
NH_3-N (mg/L)	0.10

1.2 Experimental procedures

In dark chlorination tests, raw water or de-ionized water solution was dispended in a 250-ml brown glass bottle. Initial Br^- concentration in raw water was 56.3 μg/L. Certain amounts of Br^- were added to the bottles to form the pre-determined concentration. Initial pH was adjusted to a desirable value using 0.1 mol/L HCl and NaOH. Once sodium hypochlorite was introduced to initiate the reactions, the bottle was placed in an incubator at 20°C (dark).

In UV-irradiated chlorination tests, all runs were conducted in a 1.5-L complete-mixing plastic cylinder reactor at room temperature with variations below 2.8°C. A quartz tube was inserted from the top into the center of the reactor. One to three low-pressure mercury lamps (253.7 nm, output power 6 W) were installed into the quartz tube to form different light intensities. The UV lamps were allowed 5 min warm-up prior to UV-irradiated chlorination experiments. The solution was thoroughly mixed by a magnetic stirrer. Initial pH was adjusted using 0.1 mol/L HCl and NaOH. In the tests to investigate the effect of initial pH, 1 mmol/L phosphate buffer solution was added to maintain the desirable pH. The reactor was wrapped by foil during the experiments to increase the UV efficiency and decrease the disturbance of other lights outside. Reactions were initiated by adding certain amounts of sodium hypochlorite.

In all dark chlorination and UV/chlorination tests, 10 ml sample was withdrawn in designated sampling times, of which 5 ml was used for subsequent residual free chlorine measurement through a DPD (N, N-diethyl-p-phenylendiamine) colorimetric method, and the rest 5 ml of which was ready for measurement of bromate and bromide ion after elimination of residual chlorine through the addition of sodium thiosulfate. A control test without bromide ions was conducted to find that sodium thiosulfate did not affect bromate test at neutral pH.

1.3 Analytical methods

The pH of samples was determined with Thermo Orion CHN818. Free chlorine concentrations were determined with a pocket colorimeter (HACH test kits, Cat No. 46700-00). Linear range of free chlorine concentrations in these experiments was from 0.2 to 2 mg/L. Samples were diluted to meet the linear range demand prior to analysis. Hypochlorite was measured by the DPD method. Although this method is used to measure the sum of all hypohalites, effects of other hypohalites present in the samples could be ignored because the hypobromite level is greatly lower than the chlorine level in the tests. Anions were analyzed using an ICS1000 ion chromatograph (Dionex Corporations, USA), equipped with an IonPacAS19 anion column and suppressed EDC detector using 20 mmol/L potassium hydroxide eluent. The detection limit of bromate was 1.2 μg/L, based on the slope of the calibrations curve and the reproducibility of analysis at low concentrations.

1.4 Data analysis

Pseudo-first-order reaction kinetics was used to fit free chlorine reduction by UV irradiation:

$$- dC_{Cl_2}/dt = k_{obs} \times C_{Cl_2} \tag{1}$$

where, C_{Cl_2} is the free chlorine concentration at time t and k_{obs} is the observed rate constant.

2 Results and discussion

### 2.1 Bromate formation in dark chlorination

Figure 1 shows the decomposition of hypochlorite and the formation of bromate in de-ionized water and raw water as a function of time. Background bromide level in raw water was moderate (56.3 µg/L, Table 1), and additional potassium bromide was added to simulate high concentrations of bromide present in raw water.

As shown, the chlorine in the experiments exhibited a rapid decay within the first several days followed a leveling off, a pattern similar to that reported by others (Macalady *et al.*, 1977; Haag, 1981). The decomposition of sodium hypochlorite is involved in a series of reactions that can be affected by hypochlorite concentration, pH, temperature, and light. In the experiments, the pseudo-first-order rate constants of chlorine decomposition were greatly higher than those reported by Liu *et al.* (2003) (2×10^{-4}–4×10^{-4}/h for 1.2–2.0 mol/L sodium hypochlorite), probably due to the existence of bromide ion in the solutions. Bromide is quantitatively oxidized by hypochlorite to hypobromite in alkaline conditions through the following reaction:

$$HOCl + Br^- \longrightarrow HOBr + Cl^- \tag{2}$$
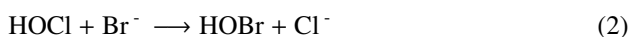
Furthermore, chlorate and bromate may be produced through a series of oxidation-reduction reactions in the mixture of hypobromite and hypochlorite (Lewin and Avrahami, 1955).

$$2HOCl + HOBr \longrightarrow BrO_3^- + 3H^+ + 2Cl^- \tag{3}$$

$$3HOCl \xrightarrow{HOBr} ClO_3^- + 3H^+ + 2Cl^- \tag{4}$$
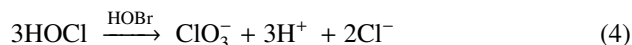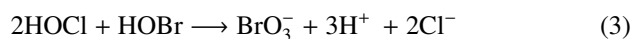
These reactions may, to a certain degree, explain that the chlorine in raw water with higher bromide concentration (151.3 µg/L) decomposed more quickly than that with lower one (56.3 µg/L) (Fig.1a).

Another evidence to support occurrence of the above-mentioned reactions is that detectable bromate was observed during chlorination both in de-ionized water and raw water (Fig.1b). Increasing chlorine or bromide content kinetically enhanced the formation rate of bromate, which could be explained sensibly from Eqs. (2)–(4). However, the positive effect of bromide ion in raw water on bromate formation was not significant when comparing the two curves in Fig.1b ($C_{O(Br^-)} = 151.3$ µg/L and $C_{O(Br^-)} = 56.3$ µg/L). This observation may be due to the substitutive reactions between HOBr and organic matters present in raw water, which inhibited the reaction rates of Eqs. (3) and (4). The amount of bromate produced in raw water with 1.23 mg/L Cl_2 and 56.3 µg/L Br^- was slightly higher than that produced in de-ionized water with similar chlorine dose (1.03 mg/L) and higher bromide concentration (151.3 µg/L), because the disproportionation reactions of hypohalites are strongly influenced by pH, and the pH of raw water in the experiment was close to pH 7.4, where the maximum rate of hypobromite occurs (Wong and Davidson, 1977). Hypobromite, oxidized from bromide by hypochlorite (Eq. (2)), is more reactive than hypochlorite (Nobukawa and Sanukida, 2001; Duong *et al.*, 2003). Hence, once formed, it both reacts with organic matters in water and participate oxidation reactions to produce chlorate or bromate (Eqs. (3) and (4)). The durations of chlorination tests were 96 h, the longest hydraulic retention time of the local water supply pipeline network. The pH variations in the solutions were below 0.3 during the experiments, because the hypochlorite and hypobromite in
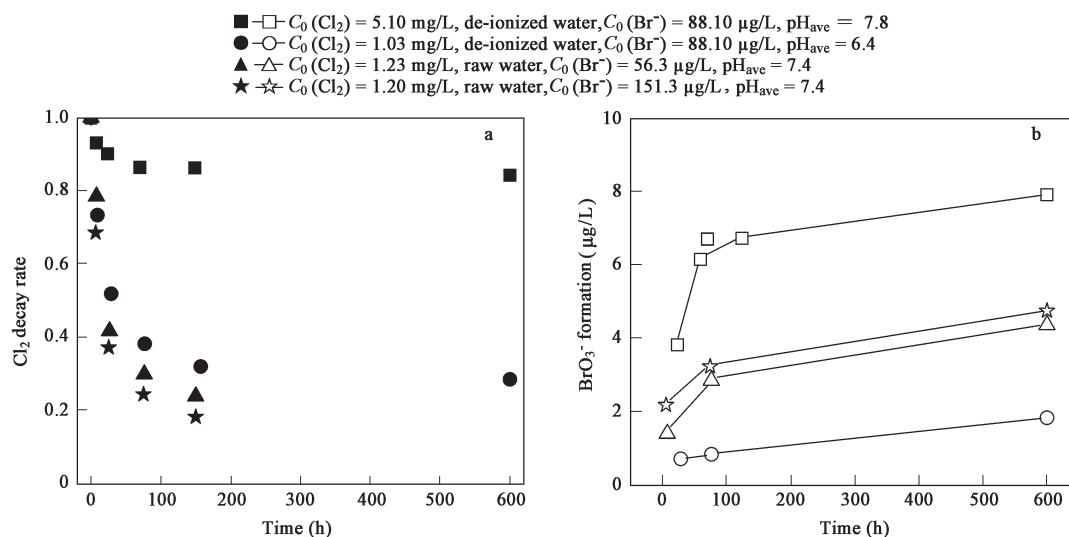

■ –□– C_0 (Cl_2) = 5.10 mg/L, de-ionized water, C_0 (Br^-) = 88.10 µg/L, pH$_{ave}$ = 7.8
● –○– C_0 (Cl_2) = 1.03 mg/L, de-ionized water, C_0 (Br^-) = 88.10 µg/L, pH$_{ave}$ = 6.4
▲ –△– C_0 (Cl_2) = 1.23 mg/L, raw water, C_0 (Br^-) = 56.3 µg/L, pH$_{ave}$ = 7.4
★ –☆– C_0 (Cl_2) = 1.20 mg/L, raw water, C_0 (Br^-) = 151.3 µg/L, pH$_{ave}$ = 7.4

Fig. 1 Chlorine (Cl_2) decay (a) and bromate (BrO_3^-) formation (b) during chlorination in de-ionized water and raw water from Yangtze River.

the pH 7–10 maintained the concentration of hydrogen ion (Lewin and Avrahami, 1955).

2.2 Bromate formation in UV-induced chlorination

Figure 2 shows the dissipation of free chlorine concentration and the formation of bromate under UV irradiation as a function of time. The decay rates of chlorine and the initial concentration of chlorine were similar in de-ionized water and raw water. The aqueous free chlorine concentration decreased continuously over time. The dissipation of residual chlorine followed pseudo-first-order reaction kinetics well under the irradiation (de-ionized water $k = 0.00138/h$, $R^2 = 0.998$; raw water $k = 0.0015/h$, $R^2 = 0.996$). This observation suggested that the decay of chlorine by UV irradiation in the solution is the dominant reaction, compared with other possible procedures (e.g., Eqs. (2)–(4) and halogen substitution). A relatively slow depression of pH was observed in the experiments (de-ionized water: from 7.94 to 7.72, raw water: from 7.51 to 7.44).

Multi-phase production of bromate was observed (Fig.3a). Bromate was rapidly produced within the initial 5 min when residual chlorine was > 3.8 mg/L (stage

1). Subsequently, its formation rate decreased, and the concentration of formed bromate showed a good linear relationship with the time t until chlorine concentration was around 1 mg/L (stage 2). Finally, a plateau followed (stage 3) when chlorine concentration was below 1 mg/L. The observation implied that chlorine concentration played a critical role in the formation rate of bromate. Since UV is capable of reducing bromate to bromide ion, the amount of bromate formed depends on the balance between reactions of its formation and reduction.

2.2.1 Effect of water quality parameters on the production of bromate

Effect of pH on the rates of chlorine decay and bromate formation is shown in Fig.3. Without adding any buffer solution or acid, the pH ranged within 11.07–11.04. The concentration of residual chlorine in the solution decreased from 4.5 to 1.03 mg/L along with UV irradiation. One mmol/L phosphate buffer solution using de-ionized water was used to control the pH, and 0.1 mol/L HCl was pre-added to adjust the initial pH. As shown in Fig.3, the rate of chlorine dissipation increased moderately with the pH decrease, and stabilized once the pH remained constant (k_{obs}
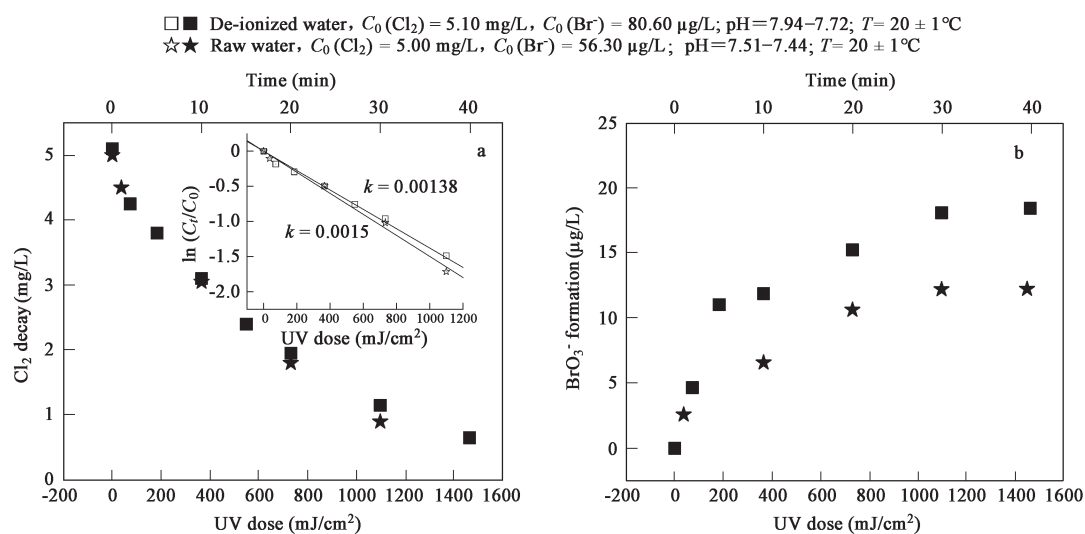

□ ■ De-ionized water，C_0 (Cl$_2$) = 5.10 mg/L，C_0 (Br⁻) = 80.60 μg/L；pH＝7.94−7.72；T= 20 ± 1℃
☆ ★ Raw water，C_0 (Cl$_2$) = 5.00 mg/L，C_0 (Br⁻) = 56.30 μg/L；pH＝7.51−7.44；T= 20 ± 1℃

Fig. 2   Chlorine (Cl$_2$) decay (a) and bromate (BrO$_3^-$) formation (b) during UV/chlorination process in bromide-containing water samples.

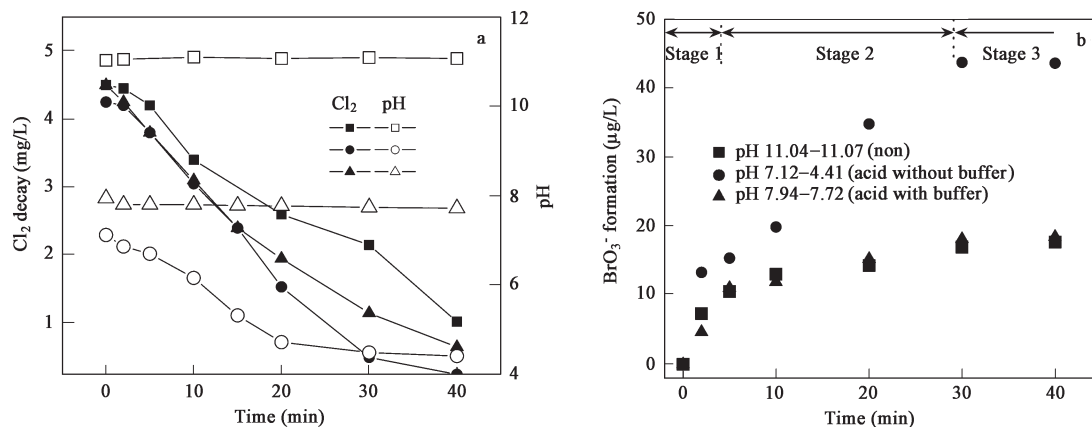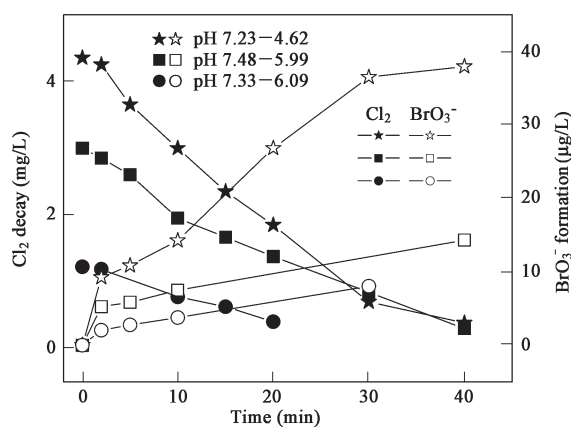**Fig. 3**   Effect of pH on bromate (BrO$_3^-$) formation (a) and chlorine (Cl$_2$) decay (b). Conditions: C_{0Br^-} = 85 μg/L; I = 610 μW/cm^2.

= 0.0261 at pH 11.04–11.07, R^2 = 0.9775; k_{obs} = 0.0587 at pH 7.12–4.41, R^2 = 0.8985; k_{obs} = 0.0505 at pH 7.94–7.72, R^2 = 0.9913). The decomposition rate of chlorine did not follow pseudo-first-order reaction behavior when the pH ranged widely during the experiments.

Similar multi-phases of bromate production were observed in these experiments. The production curves have an initial quick-forming stage followed by a relatively slow-forming stage and then a plateau stage. Generally, the amount of formed bromate increased with the pH decrease. As shown, little difference between formation rates of bromate among alkaline conditions was observed, whereas the formation rate was significantly high in acidic conditions during stage 2. At the plateau stage (stage 3), bromate concentration in the solutions remained constant or even decreased slightly, probably because an equilibration was reached, between its yield rate due to chlorine decomposition and its loss rate caused by UV photo-reduction. In brief, neutral and/or acidic condition favored bromate formation in the UV/chlorine process.

Results with addition of different initial chlorine doses were shown in Fig.4. The initial pH values with initial chlorine concentrations of 1.23, 3.0, and 5.0 mg/L were similar (7.23–7.48), although significant different production of bromate was observed. At 5 min, the concentrations of bromate were 2.75, 5.84 and 10.84 µg/L, respectively, again suggesting the important role of the chlorine concentration. At stage 2, the formation was primarily controlled by pH. Samples with initial Cl$_2$ of 3.0 and 1.23 mg/L showed similar pH variation, and nearly parallel curves of bromate production and Cl$_2$ decomposition. However, the sample with initial Cl$_2$ of 5.0 mg/L had a higher formation rate of bromate and higher decomposition rate of Cl$_2$ at stage 2 when pH was greatly lower than those in the other two groups. Therefore, bromate formation was strongly influenced by the photo-dissipation of free chlorine and the pH in solution. The pre-chlorination dose is around 1–12 mg/L (Ormeci *et al.*, 2005). Hence, the risk of exceeding set standards of bromate during pre-chlorination exists only if sunlight irradiation is sufficient.

The role of light intensity may be extremely complicat-

ed. Theoretically, almost all bromine and chlorine related species would be photolyzed under UV irradiation in the H$_2$O-NaOCl-Br system, including reactant ClO$^-$, product BrO$_3^-$ and other potential intermediates, such as BrO$_2^-$ and BrO$^-$ (Phillip *et al.*, 2006).

One, two, and three lamps were used, respectively, to form the intensities of 610, 1210, and 1896 µW/cm^2 in the middle of reactor. As shown in Fig.5, the dissipation of chlorine was aggravated with the increase of light intensity. Rate constants k_{obs} of the three experiments were found to follow a linear relationship quite well with the intensity (R^2 = 0.9993):
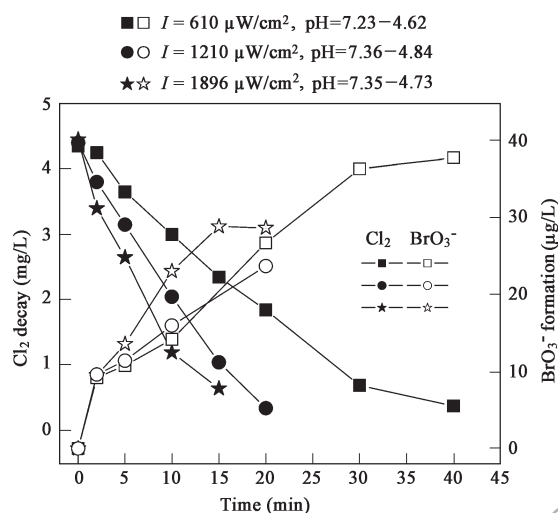
$$k_{obs} = -6 \times 10^{-5} \times I - 0.0218 \qquad R^2 = 0.9993 \qquad (5)$$

where, I is the light intensity (µW/cm^2), k_{obs} is the pseudo-first-order rate constant.

Slight difference in the three groups was found in bromate formation at stage 1. At stage 2, initial pH and free chlorine concentrations in the three experiments were similar. Although high light intensity causes a quick formation of bromate in a short time, the total amount of bromate produced in high intensity was below that in low intensity, because high UV intensity caused rapid decomposition of chlorine so that the duration at stage 2 was shortened. On the other hand, UV photolysis of bromate cannot be ignored. The complicated contribution of light intensity might be explained as the synergistic results of the photolysis of chlorine and bromate.

3 Conclusions

In conclusion, bromate was slowly formed in the studied water in dark chlorination. The residual chlorine of distribution system in Shanghai is maintained at 1.0 mg/L. Hence, the amount of bromate under normal chlorine-disinfecting conditions will not exceed the regulatory level of drinking water standards (10 µg/L). The generation of bromate was enhanced by UV irradiation during chlorination, which was primarily controlled by the concentration of residual chlorine and pH in solutions. The bromate

Fig. 4 Effect of initial concentration of sodium hypochlorite on chlorine (Cl$_2$) decay and bromate (BrO$_3^-$) formation. Conditions: C_{0Br^-} = 85 µg/L; I = 610 µW/cm^2.

Fig. 5 Effect of UV light intensity on chlorine (Cl$_2$) decay and bromate (BrO$_3^-$) formation. Condition: C_{0Br^-} = 85 µg/L.

formation was favored by low pH and high chlorine concentration. Enhancing UV light intensity also increases the forming rate of bromate, and, therefore, shortens the generating time.

Acknowledgements

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