

Research Article

Bromate Formation Characteristics of UV Irradiation, Hydrogen Peroxide Addition, Ozonation, and Their Combination Processes

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Bromate formation characteristics of six-physicochemical oxidation processes, UV irradiation, single addition of hydrogen peroxide, ozonation, UV irradiation with hydrogen peroxide addition (UV/H₂O₂), ozonation with hydrogen peroxide addition (O₃/H₂O₂), and ozonation with UV irradiation (O₃/UV) were investigated using 1.88 μM of potassium bromide solution with or without 6.4 μM of 4-chlorobenzoic acid. Bromate was not detected during UV irradiation, single addition of H₂O₂, and UV/H₂O₂, whereas ozone-based treatments produced BrO₃⁻. Hydroxyl radicals played more important role in bromate formation than molecular ozone. Acidification and addition of radical scavengers such as 4-chlorobenzoic acid were effective in inhibiting bromate formation during the ozone-based treatments because of inhibition of hydroxyl radical generation and consumption of hydroxyl radicals, respectively. The H₂O₂ addition was unable to decompose 4-chlorobenzoic acid, though O₃/UV and O₃/H₂O₂ showed the rapid degradation, and UV irradiation and UV/H₂O₂ showed the slow degradation. Consequently, if the concentration of organic contaminants is low, the UV irradiation and/or UV/H₂O₂ are applicable to organic contaminants removal without bromate formation. However, if the concentration of organic contaminants is high, O₃/H₂O₂ and O₃/UV should be discussed as advanced oxidation processes because of their high organic removal efficiency and low bromate formation potential at the optimum condition.

1. Introduction

Nowadays, the world demand for water is growing because of the rapid population growth. Furthermore, pollution of freshwater resources proceeds in all over the world. For instance, China encounters severe water pollution caused by industrial chemicals, heavy metals, and algal toxin with an extraordinary economic growth [1]. Gadgil [2] reported that about half the population in the developing world is suffering from one or more of the six main diseases, diarrhea, ascariis dracunculosis, hookworm, schistosomiasis, and trachoma, which are associated with water supply and sanitation. In the industrialized countries, micropollutants like pharmaceuticals gather much concern as potential contaminants in drinking water [3] and surface water [4]. As a result of this situation, water supply section has made efforts to supply

a plenty of safe drinking water. In this context, various advanced water treatment like UV disinfection, ozonation, and adsorption processes [5–7] have been introduced to water purification plants.

UV irradiation and ozone-based chemical oxidation are widely used as advanced water purification processes. These processes can achieve higher level of disinfection and organic pollutants removal [9, 10]. However, bromate (BrO₃⁻) formation in these chemical oxidation processes may bring a potential health risk, because BrO₃⁻ is a possibly carcinogenic to human [11]. Therefore, it is important to understand BrO₃⁻ formation potential in these processes.

Various knowledge of the BrO₃⁻ formation during UV and ozone-based chemical oxidation processes has been accumulated for past a few decades. For instance, ozonation of bromide-containing water produces BrO₃⁻ via ozone and

hydroxyl radical pathways [8], but pH depression [12] and ammonia addition [12, 13] successfully decrease BrO_3^- formation. The pH depression decreased 50–63% in BrO_3^- formation per a decline in one-pH-unit [12] because of a depression of hydroxyl radical generation and a decrease in hypobromite (BrO^-), which is a key intermediate of BrO_3^- formation. The inhibition effect of ammonia addition on BrO_3^- formation is caused by bromamines formation from the reaction of HOBr with ammonia [14]. The effective ammonia dose for BrO_3^- depression was limited to 200 $\mu\text{g/L}$ and further increase in ammonia addition did not enhance the BrO_3^- minimization [14]. Effect of hydrogen peroxide (H_2O_2) in ozonation on BrO_3^- formation is complicated. As H_2O_2 can reduce BrO^- into bromide (Br^-) [15], it seems to be useful to depress the BrO_3^- formation. However, ozone reacts with hydroperoxide anion (HO_2^-) and produces hydroxyl radicals ($\cdot\text{OH}$) [16], which promotes oxidation of Br^- [8]. Ozekin et al. [13] reported that an increase in H_2O_2 dose in ozonized water enhanced BrO_3^- formation at pH 6.5, though the BrO_3^- formation at pH 8.5 did not depend on the H_2O_2 dose and was smaller than that of ozone alone. Kim et al. [17] pointed out the importance of molar ratio of $\text{H}_2\text{O}_2/\text{O}_3$ for BrO_3^- formation during ozonation with H_2O_2 addition; the molar ratio of $\text{H}_2\text{O}_2/\text{O}_3$ above 0.5 and the dissolved ozone concentration below 0.1 mg/L successfully depress the BrO_3^- formation. The inconsistent results between Ozekin et al. [13] and Kim et al. [17] may be caused by the difference in their experimental designs: H_2O_2 was injected during ozonation [17] or after ozonation [13]. But, both research groups suggested that the $\cdot\text{OH}$ generation under a certain concentration of dissolved ozone enhanced the BrO_3^- formation during ozone/ H_2O_2 treatment [13, 17]. UV light is known to decompose BrO_3^- into BrO^- and/or Br^- [18]. As the result, Collivignarelli and Sorlini [19] reported that BrO_3^- formation during ozonation with UV 254 nm irradiation (O_3/UV) was about 40% lower than that during conventional ozonation. However, Ratpukdi et al. [20] showed that the BrO_3^- formation potential of O_3/UV was similar to ozonation alone, though ozonation combined with vacuum UV irradiation could decrease the BrO_3^- formation. Thus, the BrO_3^- formation mechanisms of UV and ozone-based chemical oxidation processes have been explored extensively. However, each research was performed using different reactors, different procedures, and different water matrices. Therefore, it is not easy to judge which process should be selected for BrO_3^- control.

In this study, BrO_3^- formation in UV irradiation, H_2O_2 addition, ozonation, and their combination processes, UV irradiation with H_2O_2 addition (UV/ H_2O_2), ozonation with H_2O_2 addition ($\text{O}_3/\text{H}_2\text{O}_2$), and ozonation with UV irradiation (O_3/UV), were discussed using the same reactor and the same water matrix to provide comparable information of their features of BrO_3^- formation and its control.

2. Experimental

2.1. Material and Experimental Conditions. A low-pressure mercury vapor lamp (20W, UVL20PH-6, Sen Lights, Japan)

was used as a UV light source. Ozone gas was generated from analytical grade oxygen gas with a silent discharge ozonizer (ED-OG-R3Lt, Eco Design, Japan). Hydrogen peroxide was purchased from Nacalai Tesque, Japan as about 35% aqueous solution (extra pure grade) and used without further purification. The accurate H_2O_2 concentration was checked just before an experiment and final concentration was set at 10, 100, or 1,000 μM . Figure 1 shows the experimental setup. The reactor was made of glass with a volume of 1.9 L. The UV lamp in a duplex quartz jacket was installed in the center of the reactor. Ozone was injected through two gas diffusers made of glass at the injection rate of about 20 mg/min. Inlet and outlet ozone gas concentration was monitored with two ozone monitors (EG-600, Ebara Jitsugyo, Japan). The exhaust ozone gas was dried with a gas dryer (DH106-1, Komatsu Electronics, Japan) before ozone monitoring, because water vapor biases the ozone concentration. Oxygen gas flow rate was regulated with a mass flow controller (CMQ9200, Yamatake, Japan) at 500 mL/min. Test solution was 1.9 L of 1.88 μM potassium bromide (KBr, Nacalai Tesque, Japan) solution with or without 6.4 μM of 4-chlorobenzoic acid (4-CBA, Wako Chemicals, Japan). The 4-CBA was used as a model compound of organic scavengers of hydroxyl radical ($\cdot\text{OH}$), because it was unreactive with ozone [21]. The solution pH was adjusted by addition of sulfuric acid or sodium hydroxide at around 2.5 or 7. An experimental run continued for 10 or 30 minutes and solution in the reactor was sampled every two or five minutes for chemical analyses of BrO_3^- , bromide ion (Br^-), dissolved ozone, H_2O_2 , 4-CBA, and pH.

2.2. Chemical Analysis. The Br^- concentration was analyzed using an ion chromatography system with a conductivity detector (DX-500, Dionex, USA). Analytical conditions were as follows. Column: Dionex IonPac AS12A with a suppressor (Dionex ASRS-ULTRA 4 mm); mobile phase: aqueous solution with 2.7 mM sodium carbonate and 0.3 mM sodium bicarbonate; flow rate: 1.0 mL/min; sample injection volume: 100 μL ; oven temperature: 40°C. The BrO_3^- concentration was determined by the ion chromatography coupled with a postcolumn system (Dionex BRS-500) [22]. Reaction conditions were as follows, reactant A: 1.5 M potassium bromide and 1.0 M sulfuric acid; reactant B: 1.2 mM sodium nitrite; flow rate: 0.4 mL/min for reactant A and 0.2 mL/min for reactant B; reaction temperature: 40°C; detection: absorbance at 268 nm. The determination limit was estimated to be 0.050 μM . Dissolved ozone and H_2O_2 were analyzed by indigo-colorimetric method [23] and DMP method [24], respectively. The 4-CBA concentration was determined by the high-performance liquid chromatography (LV-10ADVP, Shimadzu, Japan) [21]. Analytical conditions were as follows: column: ODS-80TM (4.6 \times 250 mm, Tosoh, Japan); mobile phase: acetonitrile (70%) and 0.1% phosphoric acid (30%); flow rate: 1.0 mL/min; sample injection volume: 200 μL ; oven temperature: 40°C; detection: absorbance at 234 nm. The solution pH was measured with a pH meter (Twin pH B-212, Horiba, Japan).

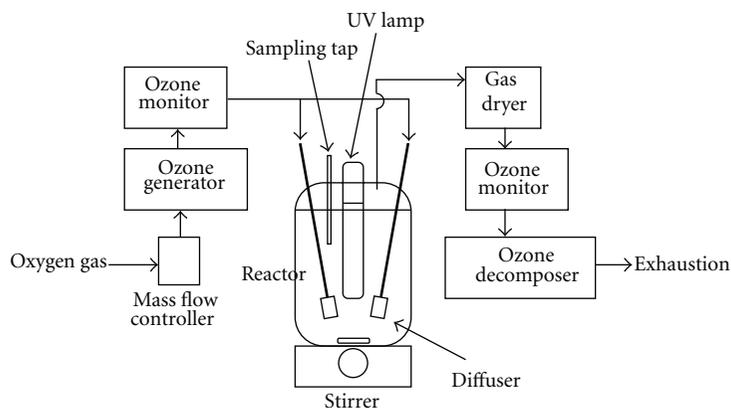
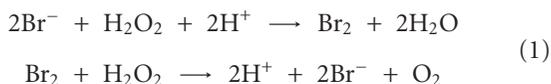


FIGURE 1: Experimental setup.

3. Results and Discussion

3.1. UV Irradiation, H₂O₂ Addition, and UV/H₂O₂ Process.

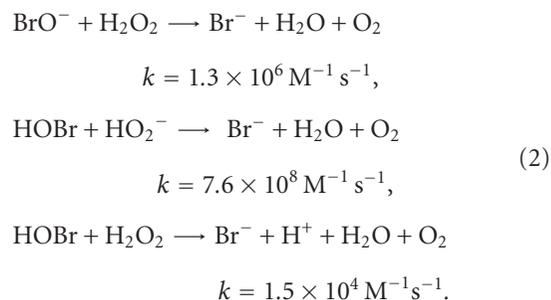
The H₂O₂ addition did not change concentrations of BrO₃⁻, Br⁻, and 4-CBA under both acid and neutral pH conditions (data not shown). Although H₂O₂ is an oxidant, H₂O₂ is nucleophilic too. Therefore, H₂O₂ can oxidize Br⁻ into bromine (Br₂), but Br₂ is reduced into Br⁻ by H₂O₂ as follows [25]:



Accordingly, Br⁻ concentration did not change because of the catalytic behavior of Br⁻ as shown in reactions (1). On the reactivity of 4-CBA with H₂O₂, Dionysiou et al. [26] also observed that H₂O₂ did not decompose 4-CBA under the dark condition. Since the standard electrode potential of H₂O₂ (1.736 V versus standard hydrogen electrode (SHE)) is lower than that of ozone (2.07 V versus SHE) and •OH (2.38 V versus SHE) [25], the low oxidation potential of H₂O₂ may be responsible for the low reactivity with 4-CBA.

Figure 2 shows the time-course changes in Br⁻, BrO₃⁻, and 4-CBA concentrations during UV irradiation and UV/H₂O₂ at neutral pH. The concentration changes at acidic condition were almost the same at neutral pH, though the H₂O₂ accumulation was enhanced at acidic condition. The low-pressure mercury vapor lamp emits vacuum UV light of 185 nm, which can photolyze water molecules into hydrogen atoms and •OH [27]. Therefore, H₂O₂ accumulation was caused by H₂O₂ production via the combination of two •OH [28]. The concentrations of Br⁻ and 4-CBA declined during the UV irradiation and UV/H₂O₂, though BrO₃⁻ was not generated (Figure 2). No BrO₃⁻ formation during UV irradiation and UV/H₂O₂ was also reported by Kruihof et al. [29]. The H₂O₂ concentration in the both treatment increased with the passage of time, and the final concentration in UV irradiation reached over 10 μM, which was the initial concentration in UV/H₂O₂. The 4-CBA degradation in UV irradiation slightly delayed in comparison with that in UV/H₂O₂, but the degradation was enhanced with the accumulation of H₂O₂. Accordingly, •OH generation via

UV photolysis of H₂O₂ [27] was believed to contribute to the 4-CBA degradation during the UV irradiation and UV/H₂O₂. The decline in Br⁻ concentration without BrO₃⁻ accumulation indicates the formation of intermediates. Von Gunten and Oliveras [8] reported that ozone and •OH oxidized Br⁻ to BrO₃⁻ (Figure 3). In this mechanism, hypobromite ion (BrO⁻) and bromite ion (BrO₂⁻) are the critical intermediates, which participate in all BrO₃⁻ formation pathways. Accordingly, UV irradiation and UV/H₂O₂ were thought to produce BrO⁻ and/or BrO₂⁻. The H₂O₂ can reduce hypobromous acid (HOBr) and BrO⁻ as follows [15]:



Therefore, the accumulation of H₂O₂ was inferred to contribute partly to the prevention of BrO₃⁻ formation in UV irradiation and UV/H₂O₂. Phillip et al. [30] reported that low-pressure mercury vapor lamps decayed free bromine into Br⁻ (major) and BrO₃⁻ (minor). Thus, the photo-degradation of HOBr/BrO⁻ might conduce to the prevention of BrO₃⁻ formation too.

3.2. Ozonation. In ozonation, BrO₃⁻ formation was correspondent to a decrement in Br⁻ at neutral pH without 4-CBA. However, the BrO₃⁻ formation was much lower than Br⁻ removal at acidic pH or coexistence of 4-CBA (Figure 4). Although both ozone and •OH promote the oxidation of Br⁻ to BrO₃⁻ via BrO⁻ and BrO₂⁻ (Figure 3), our experimental results shown in Figure 4 indicated that contribution of •OH to BrO₃⁻ evolution was relatively large. Because acidic pH restrains •OH generation via self-decomposition of ozone [31], and 4-CBA is a •OH radical scavenger with low reactivity with ozone [21]. Since HOBr has a pKa of 8.8–9.0 [32],

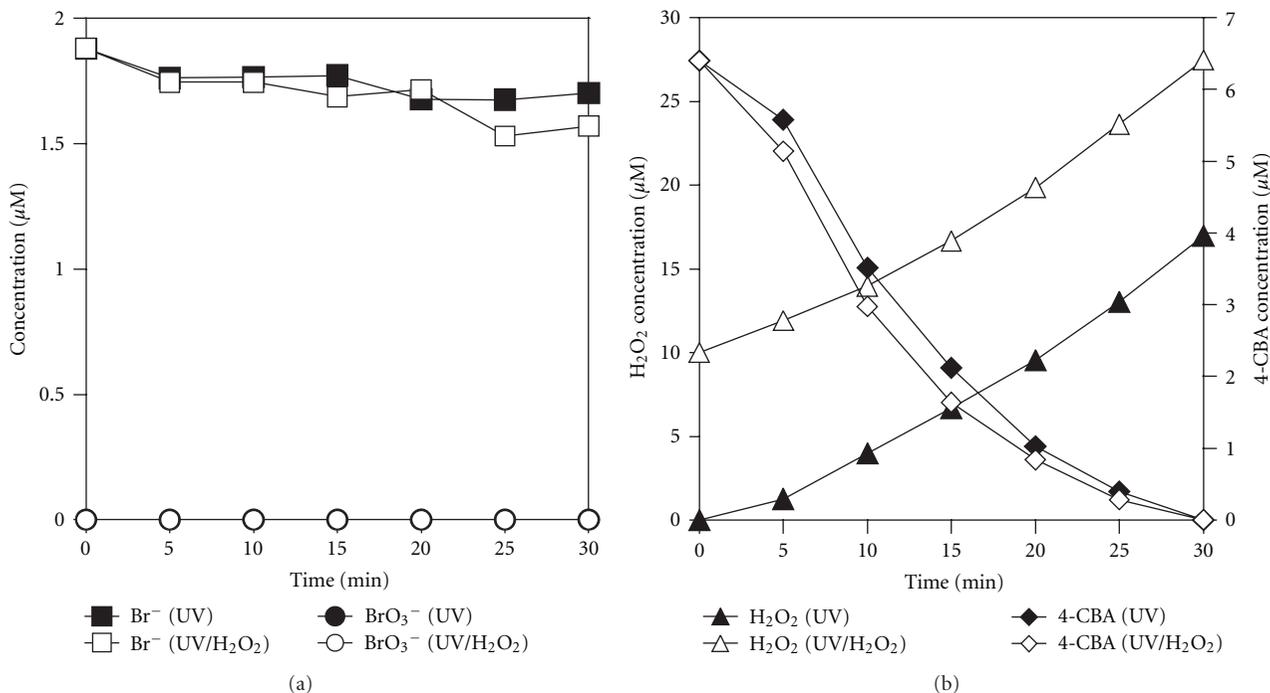


FIGURE 2: Changes in concentrations of Br^- , BrO_3^- , H_2O_2 , and 4-CBA during UV irradiation (UV) and UV/ H_2O_2 treatment at neutral pH. The initial H_2O_2 concentration for UV/ H_2O_2 was $10 \mu\text{M}$.

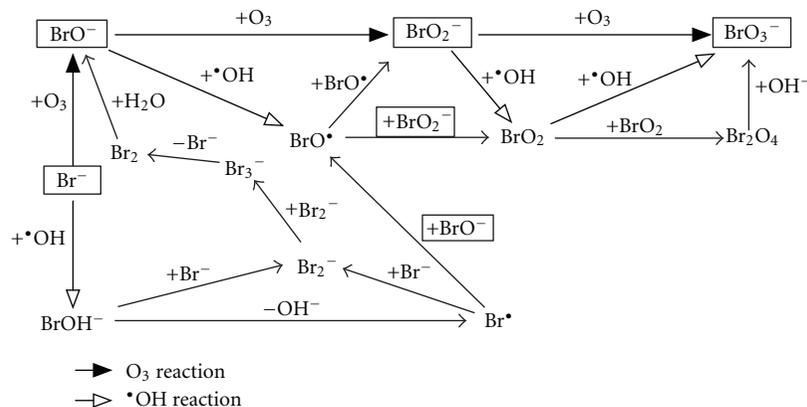


FIGURE 3: BrO_3^- formation pathways illustrated on the basis of Von Gunten and Oliveras [8].

acidification decreases the percentage of BrO^- . The decrease in BrO^- at acidic pH also contributed to the decrease in BrO_3^- formation [33]. In addition, the discordance of a decrement in Br^- and an increment in BrO_3^- at acidic pH in Figure 4 suggested the accumulation of HOBr .

3.3. $\text{O}_3/\text{H}_2\text{O}_2$. Figure 5 shows the changes in concentrations of Br^- , BrO_3^- , and 4-CBA during $\text{O}_3/\text{H}_2\text{O}_2$ at various H_2O_2 doses and pHs. The $\text{O}_3/\text{H}_2\text{O}_2$ processes showed additional effect on lowering BrO_3^- formation, especially at higher H_2O_2 dose. Bromate ion was not detected in $\text{O}_3/\text{H}_2\text{O}_2$ at the H_2O_2 dose of $1,000 \mu\text{M}$. When the H_2O_2 dose was

lowered to 100 or $10 \mu\text{M}$, rapid BrO_3^- formation was observed (Figure 5). As H_2O_2 can reduce HOBr/BrO^- into Br^- , the excess H_2O_2 was believed to restrain BrO_3^- formation. The behavior of BrO_3^- formation in $\text{O}_3/\text{H}_2\text{O}_2$ at the H_2O_2 dose of $10 \mu\text{M}$ (Figure 5) was similar to that in ozonation (Figure 4), since H_2O_2 concentration in ozonation increased to around $10 \mu\text{M}$, which was nearly equal to H_2O_2 concentration in $\text{O}_3/\text{H}_2\text{O}_2$ at the H_2O_2 dose of $10 \mu\text{M}$ (Figure 6). Thus, the initial H_2O_2 dose of $10 \mu\text{M}$ was too low to restrain the BrO_3^- formation in this study.

When acidification was applied, BrO_3^- was not detected in $\text{O}_3/\text{H}_2\text{O}_2$ at the H_2O_2 dose of $100 \mu\text{M}$ or higher. This effect was caused by both the HOBr/BrO^- reduction by H_2O_2

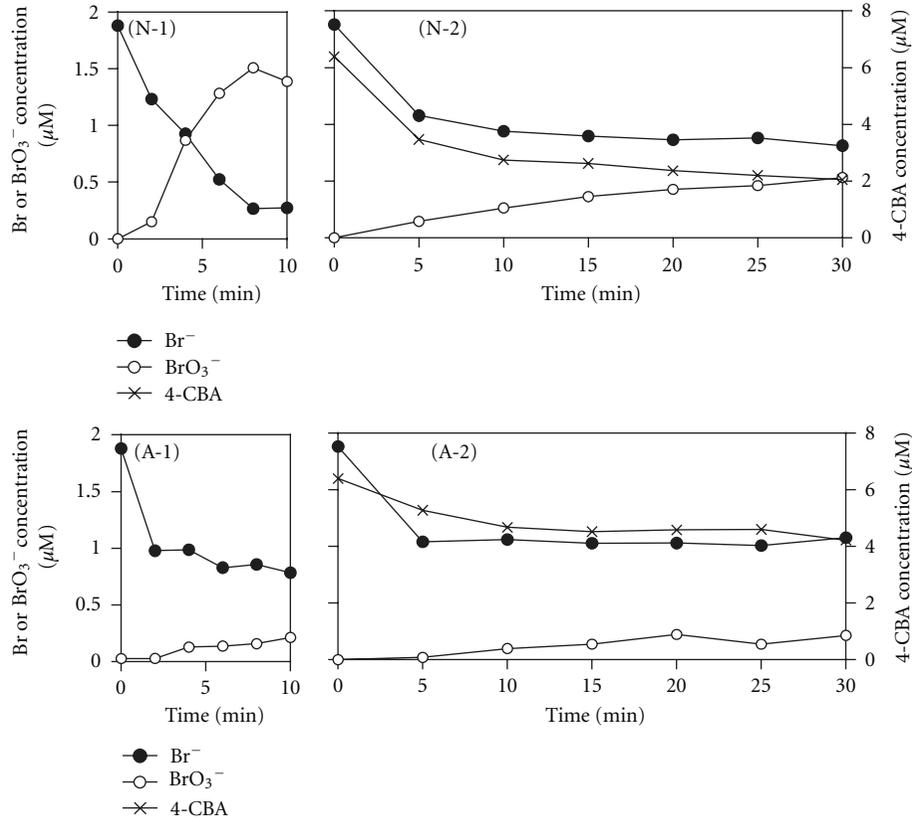
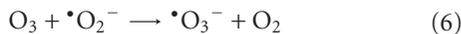
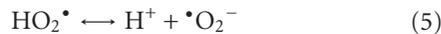
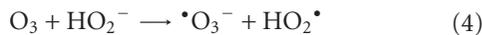
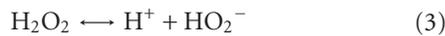


FIGURE 4: Changes in concentrations of Br⁻, BrO₃⁻, and 4-CBA during ozonation at neutral pH without 4-CBA (N-1), ozonation at neutral pH with 4-CBA (N-2), ozonation at acidic pH without 4-CBA (A-1), and ozonation at acidic pH with 4-CBA (A-2).

and inhibition of $\cdot\text{OH}$ generation in $\text{O}_3/\text{H}_2\text{O}_2$. Because $\cdot\text{OH}$ generation in $\text{O}_3/\text{H}_2\text{O}_2$ is expressed by the following reactions [16] and the acidification inhibits the dissociation of H_2O_2 and HO_2 (reactions (3) and (5)) as follows:



The inhibition of $\cdot\text{OH}$ generation in $\text{O}_3/\text{H}_2\text{O}_2$ was also confirmed by a slow decrease in 4-CBA at acidic pH (Figure 5).

3.4. O_3/UV . Figure 7 shows changes in Br⁻, BrO₃⁻, and 4-CBA concentrations during O_3/UV . The O_3/UV increased BrO₃⁻ concentration rapidly, even at the acidic pH. However, the addition of 4-CBA successfully decreased the BrO₃⁻ formation regardless of the pH condition. Collivignarelli and Sorlini [19] also observed lower BrO₃⁻ formation in O_3/UV than that in ozonation. As mentioned in the Section 3.2, the acidification decreases BrO₃⁻ formation by the inhibition of $\cdot\text{OH}$ generation via the self-decomposition of ozone. Accordingly, it was thought that $\cdot\text{OH}$ generated by the

self-decomposition of ozone did not contribute to BrO₃⁻ formation very much in O_3/UV . This discussion was supported by the lower concentration of dissolved ozone in O_3/UV (Figure 8). The low dissolved ozone concentration also brought the negligible contribution of molecular ozone to BrO₃⁻ formation. The decrease in BrO₃⁻ formation by the addition of 4-CBA indicated the contribution of $\cdot\text{OH}$ to BrO₃⁻ formation. Accordingly, it is suggested that the main oxidant in O_3/UV was $\cdot\text{OH}$, which mainly generated via UV photolysis of ozone [16]. The first step of $\cdot\text{OH}$ generation in O_3/UV is the production of H_2O_2 [16]. Then the H_2O_2 generates $\cdot\text{OH}$ through UV photolysis [16] and the same reactions as $\text{O}_3/\text{H}_2\text{O}_2$ (reactions (3)–(7)). As the coexistence of dissolved ozone and $\cdot\text{OH}$ favors BrO₃⁻ formation [13, 17], low dissolved ozone concentration in O_3/UV was thought to be advantageous to the depression of BrO₃⁻ formation. Moreover, strong H_2O_2 accumulation was observed during O_3/UV (Figure 9). Therefore, the reduction of intermediates by H_2O_2 [15] and UV photolysis [30] was also inferred to contribute to the decline in the BrO₃⁻ formation potential.

3.5. Strategy for Organic Contaminants Removal with Preventing BrO₃⁻ Formation. The aim of advanced oxidation processes is organic contaminants removal from a water stream. Therefore, it is important to remove organic contaminants without BrO₃⁻ formation. In this context, H_2O_2 addition

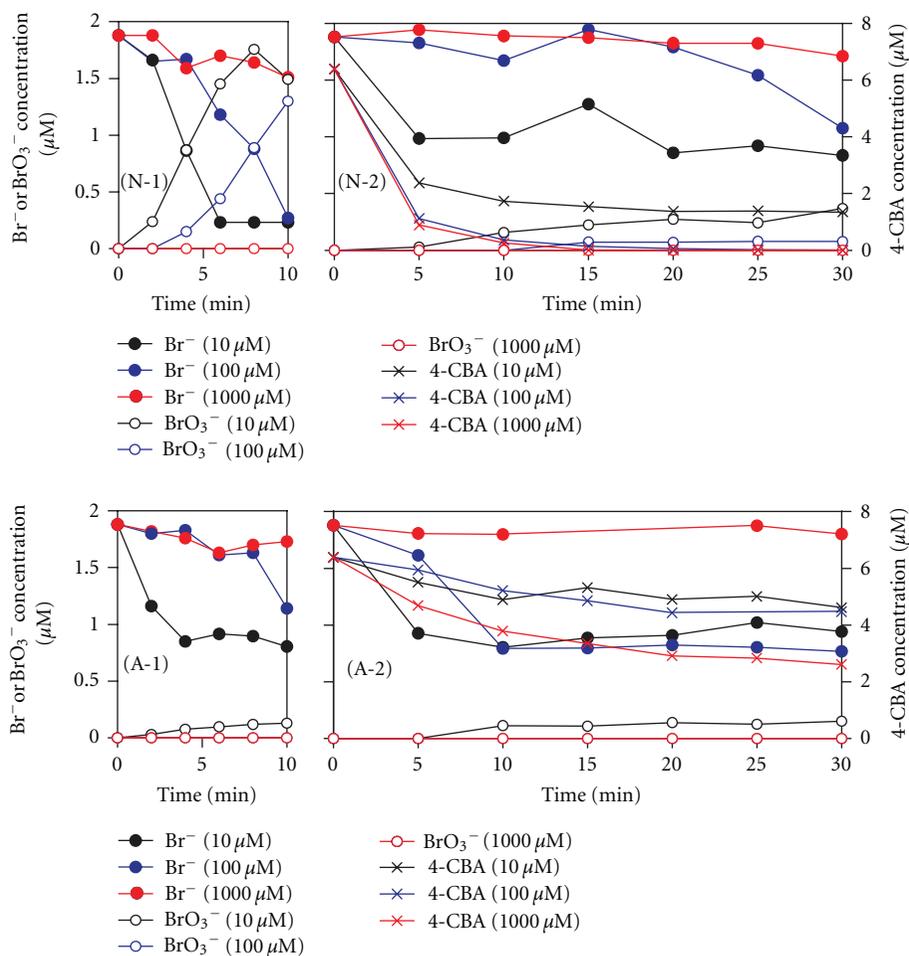


FIGURE 5: Changes in concentrations of Br⁻, BrO₃⁻, and 4-CBA during O₃/H₂O₂ at various H₂O₂ doses. The concentrations in the legend mean the H₂O₂ dose. The symbols in the bracket mean O₃/H₂O₂ at neutral pH without 4-CBA (N-1), O₃/H₂O₂ at neutral pH with 4-CBA (N-2), O₃/H₂O₂ at acidic pH without 4-CBA (A-1), and O₃/H₂O₂ at acidic pH with 4-CBA (A-2).

is inapplicable to advanced water treatment, because it is not effective to degrade refractory organic matters like 4-CBA. Ozonation is also difficult to apply to the organic contaminants removal, because it has higher BrO₃⁻ formation potential at the neutral pH than at the acidic pH as shown in Figure 4. Although the acidification successfully decreases the BrO₃⁻ formation potential of ozonation, it decreases the removal rate of organic contaminants too.

Contrary to H₂O₂ addition and ozonation, UV-based processes and O₃/H₂O₂ are potentially applicable to advanced water treatment with inhibiting BrO₃⁻ formation. The UV irradiation and UV/H₂O₂ successfully decompose organic contaminants without BrO₃⁻ formation. But their degradation rate of organic contaminants is not high, and H₂O₂ dose of 10 μM is too low to enhance the degradation rate of UV irradiation. The O₃/H₂O₂ is characterized by rapid degradation of organic contaminants and low BrO₃⁻ formation rate at high H₂O₂ dose. Although the acidification effectuates further decrease in BrO₃⁻ formation, it spoils the degradation of organic contaminants. Therefore, the acidification should not apply to O₃/H₂O₂. The feature of

O₃/UV is rapid degradation of organic contaminants, low dissolved ozone concentration, and much H₂O₂ accumulation. As the BrO₃⁻ formation in O₃/UV is restrained under the coexistence of organic contaminants, the O₃/UV is applicable, if water contains sufficient quantity of organic contaminants. Figure 10 shows the relationship between BrO₃⁻ concentration and cumulative ozone consumption. Figure 10 demonstrates that O₃/UV and O₃/H₂O₂ at the H₂O₂ doses of 100 and 1,000 μM were significantly decreased BrO₃⁻ formation per ozone consumption in comparison with ozonation and O₃/H₂O₂ at the H₂O₂ dose of 10 μM. Kim et al. [17] reported that BrO₃⁻ concentration in O₃/H₂O₂ remained less than 10 μg/L, when the molar ratio of H₂O₂ to ozone was above 0.5. In our study of O₃/H₂O₂ at the H₂O₂ dose of 100 μM, BrO₃⁻ was not produced at ozone consumption less than 250 μM. Thus, our result approximately accorded with the research by Kim et al. [17].

Consequently, if the concentration of organic contaminants is low, the UV irradiation and/or UV/H₂O₂ are applicable to organic contaminants removal without BrO₃⁻ formation, though it is necessary to beware nitrite formation

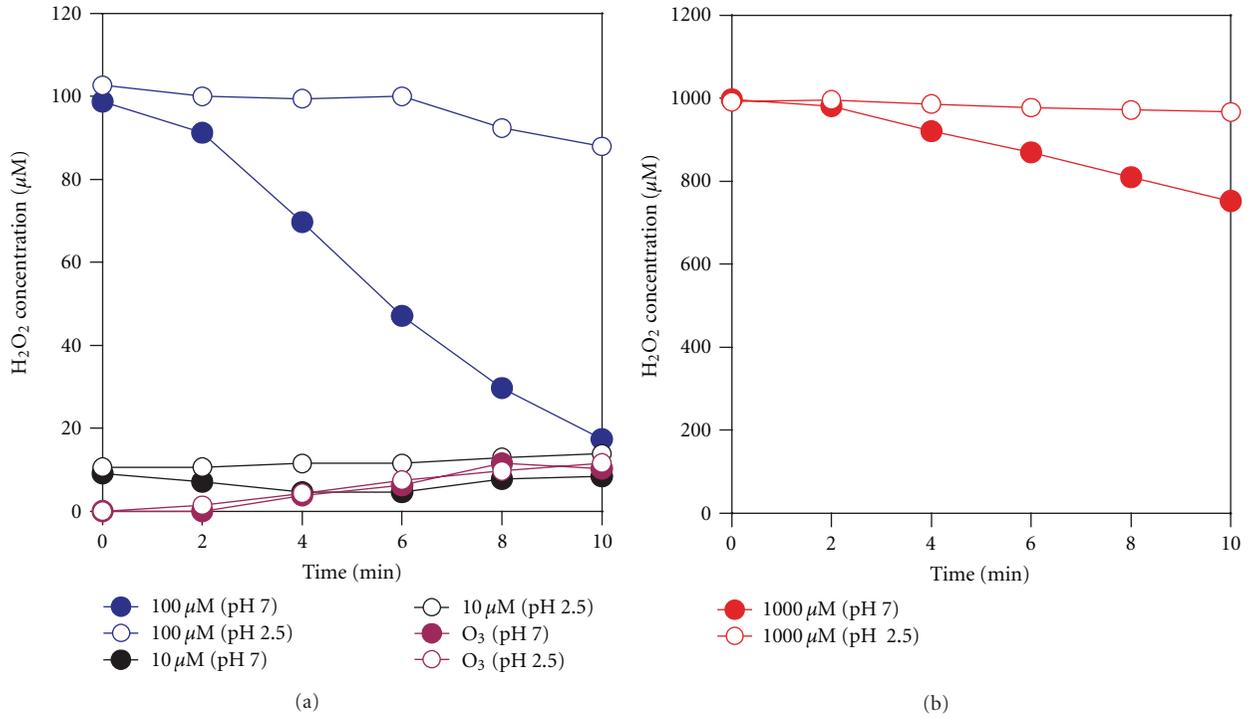


FIGURE 6: Changes in H_2O_2 concentrations during O_3/H_2O_2 and ozonation without 4-CBA. The concentrations in the legend mean the H_2O_2 dose in O_3/H_2O_2 .

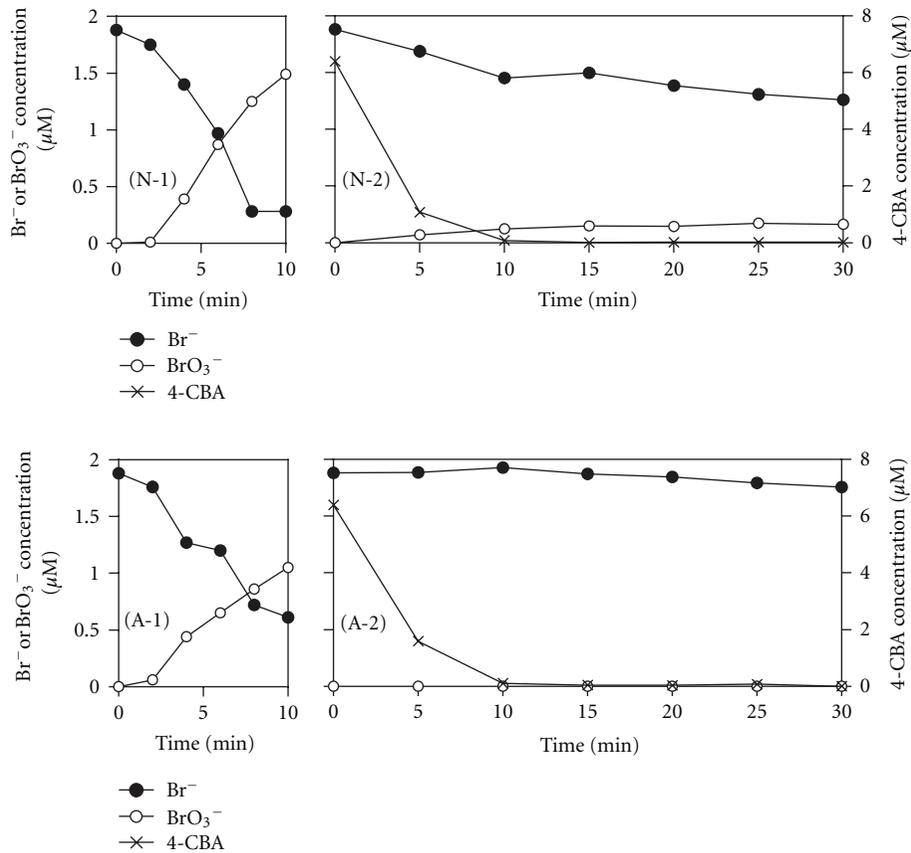


FIGURE 7: Changes in concentrations of Br^- , BrO_3^- , and 4-CBA during O_3/UV at neutral pH without 4-CBA (N-1), O_3/UV at neutral pH with 4-CBA (N-2), O_3/UV at acidic pH without 4-CBA (A-1), and O_3/UV at acidic pH with 4-CBA (A-2).

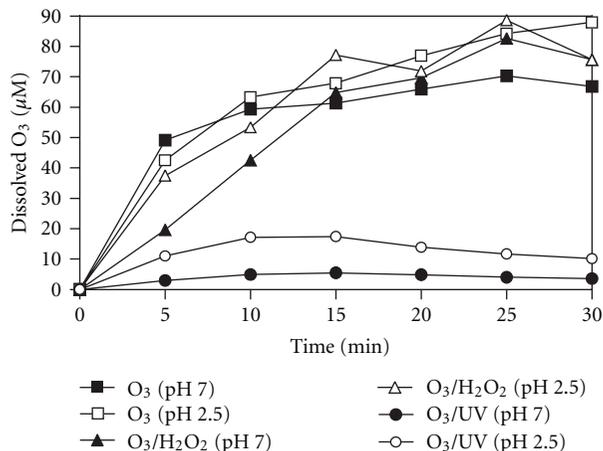


FIGURE 8: Changes in dissolved ozone concentrations during ozonation, O_3/H_2O_2 (the H_2O_2 dose of $100 \mu M$), and O_3/UV with the addition of 4-CBA.

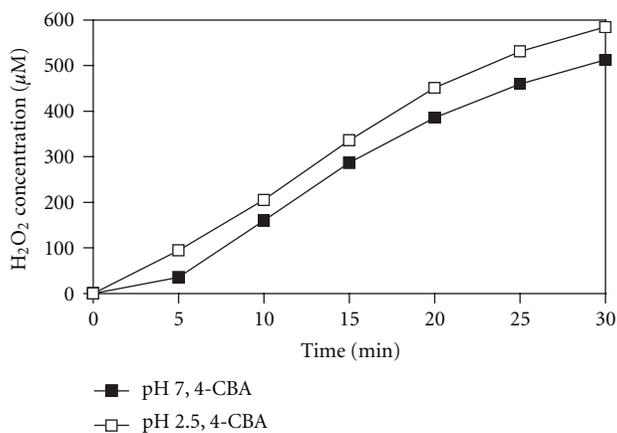


FIGURE 9: Changes in H_2O_2 concentrations during O_3/UV with 4-CBA.

during the treatment [34]. However, if the concentration of organic contaminants is high, O_3/H_2O_2 and O_3/UV should be discussed as advanced oxidation processes. When O_3/H_2O_2 is applied, the H_2O_2 dose should be more than the half of ozone consumption, because low H_2O_2 dose is ineffective for BrO_3^- control. When O_3/UV is applied, the reaction time should be optimized, because extended reaction time increases the BrO_3^- formation potential. The real-time monitoring of UV absorbance of organic contaminants in water [35] may be effective in the optimum control of the reaction time of O_3/UV without BrO_3^- formation.

4. Conclusion

In this research, BrO_3^- formation potential of UV irradiation, H_2O_2 addition, ozonation, UV/H_2O_2 , O_3/H_2O_2 , and O_3/UV treatment were discussed for organic contaminants

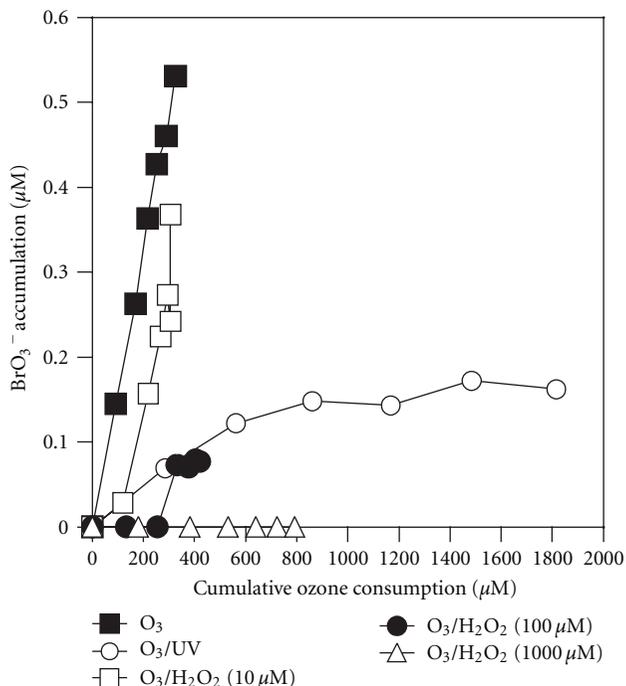


FIGURE 10: Relationship between cumulative ozone consumption and BrO_3^- accumulation during each treatment with 4-CBA addition at neutral pH. Each treatment continued 30 minutes.

removal with restraining BrO_3^- formation using KBr solution with 4-CBA as a model refractory organic contaminant.

The UV irradiation, H_2O_2 addition, and UV/H_2O_2 prevented BrO_3^- formation completely. However, H_2O_2 addition was inapplicable as advanced water treatment because of its weak oxidation ability. The UV irradiation and UV/H_2O_2 could decompose the organic contaminant moderately. Ozonation produced the most BrO_3^- at neutral pH. Although acidification could decrease the BrO_3^- formation, it also deteriorated the oxidation ability of ozonation. Therefore, it was thought to be difficult to apply ozonation to organic contaminants removal with restraining BrO_3^- formation. The O_3/H_2O_2 successfully decreased BrO_3^- formation at the H_2O_2 doses of $100 \mu M$ or higher. The degradation rate of 4-CBA was larger than the UV irradiation and UV/H_2O_2 . However, the behavior of BrO_3^- formation in the O_3/H_2O_2 at the H_2O_2 dose of $10 \mu M$ was similar to that in ozonation because of a deficiency of H_2O_2 . The O_3/UV also showed rapid degradation of 4-CBA. Although it produced much BrO_3^- under the absence of 4-CBA, the BrO_3^- formation was strongly inhibited by the coexistence of 4-CBA. Consequently, if the concentration of organic contaminants is low, the UV irradiation and/or UV/H_2O_2 are applicable to organic contaminants removal without BrO_3^- formation. However, if the concentration of organic contaminants is high, O_3/H_2O_2 and O_3/UV should be discussed as advanced oxidation processes because of their higher organic removal efficiency.

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