Efficacy of vacuum ultraviolet photolysis for bromate and chlorate removal
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ABSTRACT
We introduce vacuum ultraviolet (VUV) photolysis at 172 nm as a more efficient process for bromate and chlorate removal than conventional ultraviolet (UV) photolysis at 254 nm. We discuss the effects of pH and coexisting salts on VUV photolysis. In experiments at various pH levels, the VUV photolysis performance decreased in the alkaline region for pH above 7. Furthermore, nitrate and inorganic carbon compromised the performance, probably owing to the generation of active oxidant species (such as hydroxyl radicals and carbonate radicals) during the photolysis. However, photochemical experiments conducted in pure water revealed that VUV photolysis is 4.1-fold more energy efficient than UV photolysis using a low-pressure mercury lamp. Although the performance of VUV photolysis in tap water was about 40% less efficient than that in pure water, mainly owing to the presence of bicarbonate ions, the performance was still higher than that of UV photolysis in pure water. However, VUV photolysis may not be feasible in tap water with a high concentration of nitrate ions, because nitrate produces a stronger inhibition effect than other salts.

Key words | bromate, chlorate, disinfection byproduct, photolysis, vacuum ultraviolet

INTRODUCTION
Bromate (\(\text{BrO}_3^-\)) and chlorate (\(\text{ClO}_3^-\)) ions are regulated disinfection byproducts in water supplies. Bromate is a possible carcinogen to humans (Group 2B by International Agency for Research on Cancer 1999), and \(\text{ClO}_3^-\) can lead to the oxidative damage of red blood cells and can interfere with the thyroid function (World Health Organization 2011). These halogenated oxyanions are produced by the reactions between disinfectants and precursor compounds. Hypochlorite in a feedstock solution can oxidize the bromide ion (\(\text{Br}^-\)) as a contaminant into \(\text{BrO}_3^-\), and \(\text{ClO}_3^-\) is known as a decomposition product of hypochlorite (Weinberg et al. 2003). Chlorine dioxide in tap water also generates \(\text{ClO}_3^-\) as a decomposition product (Korn et al. 2002). Accordingly, disinfectants usually contain a certain amount of \(\text{BrO}_3^-\) and \(\text{ClO}_3^-\) as contaminants (Boyard & Fair 1992; Weinberg et al. 2003). Furthermore, introduction of advanced water purification technologies such as ozonation and advanced oxidation into water purification processes also accelerates \(\text{BrO}_3^-\) and \(\text{ClO}_3^-\) formation via oxidation of \(\text{Br}^-\) and chloride (\(\text{Cl}^-\)) ions (von Gunten 2003). Thus, \(\text{BrO}_3^-\) and \(\text{ClO}_3^-\) contamination of potable water is a serious threat to human health.

Various technologies for \(\text{BrO}_3^-\) and \(\text{ClO}_3^-\) removal, such as chemical reduction (Westerhoff 2003), electrochemical reduction (Kishimoto et al. 2012), biological remediation (Hijnen et al. 1999; Nerenberg & Rittmann 2004), activated carbon techniques (Gonce & Voudrias 1994; Asami et al. 1999; Huang & Cheng 2008), and ultraviolet (UV) photolysis (Phillip et al. 2006) have been discussed. Rapid removal of these oxyanions was demonstrated by using chemical reduction and electrochemical reduction methods. However, chemical reduction requires additional chemical inputs, and electrochemical reduction has technical difficulties related to scaling up the method. Biological remediation also requires the addition of chemicals such as hydrogen gas (Nerenberg & Rittmann 2004) and/or organic compounds (Hijnen et al. 1999) to serve as electron donors. In the activated carbon
techniques, catalytic reduction by activated carbon is responsible for \( \text{BrO}_3^- \) removal (Huang & Cheng 2008), but no catalytic reduction of \( \text{ClO}_3^- \) has been observed (Gonce & Voudrias 1994). Furthermore, Asami et al. (1999) reported that the transition of granular activated carbon to biological activated carbon apparently reduced the \( \text{BrO}_3^- \) removal rate. Phillip et al. (2006) reported that UV photolysis successfully reduced \( \text{BrO}_3^- \) to \( \text{Br}^- \), which was enhanced by vacuum ultraviolet (VUV) light at 185 nm, emitted from a low-pressure mercury lamp. Because UV photolysis does not require the addition of any chemicals and has already been used for the disinfection of potable water, it may be a promising technology for \( \text{BrO}_3^- \) and \( \text{ClO}_3^- \) removal.

Here, we focus on the VUV photolysis technique for \( \text{BrO}_3^- \) and \( \text{ClO}_3^- \) removal. Although the VUV light is less effective for microorganism disinfection than the UV light at 254 nm (Wang et al. 2010), the photolysis of \( \text{BrO}_3^- \) and \( \text{ClO}_3^- \) is expected to be enhanced by the VUV light’s high photon energy, as has been reported by Phillip et al. (2006). We also discuss the effects of pH and coexisting substances on VUV photolysis. Furthermore, conventional UV photolysis using a low-pressure mercury lamp has also been conducted for comparison, because low-pressure mercury lamps are conventionally used for the disinfection of potable water.

**MATERIAL AND METHODS**

**Photochemical reactor**

The photochemical reactor was composed of a glass beaker with a volume of 3 L and an UV lamp with a length of 120 mm, which was installed at the center of the beaker. Two UV lamp types were used. One was an excited xenon dimer lamp (excimer lamp; 172/120Z, Heraeus, Germany), which consumed 20 W of electric power and mainly emitted VUV light at the wavelength of 172 nm. The total irradiance at 172 nm, measured by using a VUV sensor (VUV-S172, Ushio, Japan), was 5.7 W. The second type was a low-pressure mercury UV lamp (UVL20PH-6, SEN Lights, Japan), which consumed 20 W of electric power and mainly emitted 254 nm of UV light. The VUV light at 185 nm was cut off by a water jacket around the UV lamp. The total irradiance at 254 nm measured by using a UV sensor (UVD-S254, Ushio, Japan) was 4.3 W. Two liters of \( \text{BrO}_3^- \) or \( \text{ClO}_3^- \) contaminated water was treated in this reactor for 60 minutes. The contaminated water was continuously mixed by using a magnetic stirrer (CT-3, As One, Japan) during the photolysis.

**Contaminated water**

Potassium salts and deionized water were used for preparing \( \text{BrO}_3^- \) or \( \text{ClO}_3^- \) contaminated water. The initial concentration was 1.00 mg/L. The solution pH was adjusted by adding sulfuric acid or sodium hydroxide. The effects of sulfate, phosphate, ammonium, bicarbonate, and nitrate were determined by adding the corresponding sodium or sulfate salts at the final concentration of 0.500 mM. VUV photolysis was also applied to tap water by adding potassium bromate at the final concentration of 100 \( \mu \text{g} \cdot \text{L}^{-1} \).

**Chemical analysis**

The concentrations of \( \text{BrO}_3^- \) and other anions were determined by using ion chromatography coupled with a post-column system (DX-500 with BRS-500, Dionex, USA), but the post-column system was not used when the \( \text{BrO}_3^- \) concentration was above 100 \( \mu \text{g} \cdot \text{L}^{-1} \). 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 Na\(_2\)CO\(_3\) and 0.3 mM NaHCO\(_3\); flow rate: 1.0 mL/min; sample injection volume: 100 \( \mu \text{L} \); oven temperature: 40 °C. The reaction conditions in the post-column were as follows. Reactant A: 1.5 M KBr and 1.0 M \( \text{H}_2\text{SO}_4 \); reactant B: 1.2 mM NaNO\(_2\); 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 concentrations of \( \text{ClO}_3^- \) and other anions were also determined by using ion chromatography under the same conditions as those for determining \( \text{BrO}_3^- \). A pH meter (B-212, Horiba, Japan) was used for measuring pH. Bicarbonate concentration was determined in pursuance of 4500-CO\(_2\) D in *Standard Methods* (2012).
RESULTS AND DISCUSSION

Effect of pH on VUV photolysis

Figure 1 shows the temporal changes in $\text{BrO}_3^-$ and $\text{Br}^-$ concentrations during VUV photolysis at pH 7. The $\text{BrO}_3^-$ concentration decreased with time, and the corresponding increase in $\text{Br}^-$ was observed. Thus, $\text{BrO}_3^-$ was successfully reduced into $\text{Br}^-$ by VUV photolysis. Because $\text{BrO}_3^-$ exhibits a strong absorption spectrum in the VUV range (Peldszus et al. 2004), direct photolysis was concluded to be the dominant mechanism for VUV photolysis, as has been pointed out by Jung et al. (2014). Figure 2 shows the $\text{BrO}_3^-$ and $\text{ClO}_3^-$ degradation curves during VUV photolysis for various pH levels on a semilogarithmic axis. The data clearly demonstrate that VUV photolysis of both oxyanions followed the pseudo-first-order reaction kinetics, because the following linear relation was established under the pseudo-first-order reaction kinetics:

$$\ln C = \ln C_0 - kt$$

where $C$ is the contaminant concentration, $C_0$ is the initial concentration of the contaminant, $t$ is the elapsed time [min], and $k$ is the rate constant of degradation [min$^{-1}$]. These kinetics were similar to the $\text{BrO}_3^-$ decomposition kinetics under UV light from low-pressure mercury lamps (Phillip et al. 2006). Figure 3 summarizes the pseudo-first-order degradation rate constants of $\text{BrO}_3^-$ and $\text{ClO}_3^-$ at various pH levels, estimated from the slopes of the corresponding degradation curves plotted using a semilogarithmic axis. The degradation rate constants decreased for pH values above 7. This tendency was observed for both $\text{BrO}_3^-$ and $\text{ClO}_3^-$, although the degradation rate of $\text{BrO}_3^-$ was higher than that of $\text{ClO}_3^-$. The acid dissociation
constant of bromic acid (HBrO₃) was reported to be 73.9 ± 3.0 mol/L (Kamble & Nandibewoor 1996). Accordingly, the main chemical species for all pH values in this research was BrO₃⁻. Therefore, the reduced degradation rate constant of BrO₃⁻ at alkaline pH was not owing to the different reactivity associated with different chemical species. Although the acid dissociation constant of chloric acid (HClO₃) has not been reported, the above discussion will apply to HClO₃, owing to the similar chemical characteristics of HBrO₃ and HClO₃.

Hayon & McGarvey (1967) reported that hydroxyl radicals (•OH) were produced by VUV photolysis of hydroxide ions (OH⁻). The •OH can oxidize Br⁻ and Cl⁻ and their oxyanions, and finally produce BrO₃⁻ and ClO₃⁻ (von Gunten & Oliveras 1998; von Gunten 2005). Therefore, the regeneration of BrO₃⁻ and ClO₃⁻ by •OH from the photolysis of OH⁻ was inferred to be responsible for inhibiting the BrO₃⁻ and ClO₃⁻ removal under alkaline pH.

**Effect of coexisting salts on VUV photolysis**

Figure 4 shows the degradation rate constants obtained when various salts coexisted with the BrO₃⁻ and ClO₃⁻ ions.
at pH 7. Figure 4 clearly shows that sodium ions, sulfates, and phosphates did not affect the degradation rates of BrO$_3^-$ and ClO$_3^-$, because the degradation rate constant in the presence of sodium sulfate (Na$_2$SO$_4$) or sodium dihydrogen phosphate (NaH$_2$PO$_4$) did not differ from that obtained in the control experiment. Consequently, the inhibition of photolysis in alkaline pH was not caused by sodium ions that were used for pH control.

Contrary to Na$_2$SO$_4$ and NaH$_2$PO$_4$, the presence of sodium nitrate (NaNO$_3$) and sodium bicarbonate (NaHCO$_3$) significantly inhibited the photolysis of BrO$_3^-$ and ClO$_3^-$. It is known that photolysis of nitrates yields ·OH (Mark et al. 1996; Mack & Bolton 1999), which can oxidize Br$^-$ and Cl$^-$ and their oxyanions into BrO$_3^-$ and ClO$_3^-$. Therefore, the regeneration of BrO$_3^-$ and ClO$_3^-$ by ·OH from the photolysis of nitrate ions was inferred to contribute to inhibiting the BrO$_3^-$ and ClO$_3^-$ removal in the presence of nitrate. Photolysis of carbonate and bicarbonate ions yields carbonate radicals (Hayon & McGarvey 1967; Behar et al. 1970), which can enhance BrO$_3^-$ formation by accelerating the oxidation of hypobromite ions into hypobromite radicals (von Gunten 2003). Therefore, carbonate radicals produced by the VUV photolysis of bicarbonate ions were inferred to cause the decrease in the BrO$_3^-$ degradation rate. It was also inferred that the carbonate radicals inhibited ClO$_3^-$ removal in a similar manner.

**Comparison of VUV photolysis with UV photolysis**

Figure 5 shows changes in BrO$_3^-$ concentrations during VUV and UV photolyses. Both lamps successfully degraded BrO$_3^-$. However, the degradation rate constant in VUV photolysis was 4.1 times higher than that in UV photolysis, although the electrical input to both lamps was the same. Consequently, VUV photolysis was potentially more energy efficient than the conventional UV photolysis, judged on the basis of both the electrical input and total irradiance.

**VUV photolysis in tap water**

VUV photolysis of BrO$_3^-$ in tap water is compared with that in pure water in Figure 6. The degradation rate constant of VUV photolysis in tap water was about 40% smaller than that in pure water. Tap water contained 0.52 mM of bicarbonate and only 0.011 mM of nitrate. When 0.500 mM of bicarbonate or nitrate was added, the degradation rate constant of BrO$_3^-$ decreased from 0.0241 to 0.0148 min$^{-1}$ or 0.0064 min$^{-1}$, respectively, as shown in Figure 4. Assuming that the reduction of the degradation rate is proportional to the concentrations of bicarbonate and nitrate, the
bicarbonate and nitrate ions in tap water were expected to slow the degradation rates by 0.0097 min\(^{-1}\) and 0.00059 min\(^{-1}\), respectively. Consequently, the degradation rate in tap water was estimated to be 0.140 min\(^{-1}\), which was nearly equal to the observed rate (0.141 min\(^{-1}\)). Thus, it was inferred that the reduction of the degradation rate in our experiments was mainly caused by the presence of bicarbonate ions in tap water, whereas nitrate ions made a weak contribution. However, if tap water contains higher concentrations of nitrate ions, BrO\(_3\) and ClO\(_3\) control by using VUV photolysis might not be feasible, because nitrate ions produce stronger inhibition effects than other salts.

### CONCLUSIONS

The efficacy of VUV photolysis at 172 nm for BrO\(_3\) and ClO\(_3\) removal was determined. VUV photolysis successfully degraded BrO\(_3\) and ClO\(_3\) into Br\(^-\) and Cl\(^-\), respectively. BrO\(_3\) and ClO\(_3\) removal followed the pseudo-first-order reaction kinetics on BrO\(_3\) and ClO\(_3\) concentrations, respectively. The degradation rate constant was nearly the same across the pH values in neutral and acidic ranges, although the rate was reduced at alkaline pH. The presence of nitrate and bicarbonate ions also yielded lower BrO\(_3\) and ClO\(_3\) degradation rates. The negative effects of pH and nitrate and bicarbonate ions on the degradation rates were attributed to the regeneration of BrO\(_3\) and ClO\(_3\) by active oxidant species produced via the photolysis of coexisting ions, namely OH that was produced by the photolysis of nitrate or OH\(^-\), and carbonate radicals that were produced by the photolysis of bicarbonate ions.

The comparison of VUV photolysis with the conventional UV photolysis at 254 nm revealed that the energy efficiency of VUV photolysis on the basis of electrical input to the lamp was 4.1 times higher than that of UV photolysis in pure water. Although the degradation rate constant in tap water obtained by using VUV photolysis was about 40% lower than that in pure water, mainly owing to the presence of bicarbonate ions and insignificantly owing to the presence of nitrate ions, the degradation rate constant observed in tap water was still higher than that obtained for UV photolysis in pure water. However, if tap water contains a high concentration of nitrate, the BrO\(_3\) and ClO\(_3\) control by using VUV photolysis might not be feasible, because nitrate ions produce stronger inhibition effects than other salts.

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