

Rapid removal of bromate ion from water streams with an electrolytic flow cell

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ABSTRACT

To control bromate (BrO_3^-) contamination in the water supply, it is necessary to develop a rapid BrO_3^- removal technology without a post-treatment. In this study, rapid removal of BrO_3^- from water streams was examined using an electrolytic flow cell. Copper was selected as a working electrode for BrO_3^- reduction by cyclic voltammetry. The electrolytic flow cell with a layered copper mesh cathode successfully reduced BrO_3^- to Br^- at around neutral pH. BrO_3^- removal followed the pseudo-first order reaction of BrO_3^- concentration, and the reaction rate constant based on common logarithm was evaluated to be 0.00224 s^{-1} . Only 3.6 min of contact time was required to decrease BrO_3^- concentration in tap water from 30 to $10 \mu\text{g/L}$ without pH control. Thus, the electrochemical process is feasible for rapid removal of BrO_3^- without post-treatment.

Key words | bromate, copper cathode, disinfection byproduct, electrochemical reduction, electrolysis, flow reactor

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INTRODUCTION

The bromate ion (BrO_3^-) is a disinfection byproduct in water supplies. Butler *et al.* (2005) summarized the toxicity of BrO_3^- . Its carcinogenicity to humans has not yet been confirmed. However, the International Agency for Research on Cancer has classified it as a Group 2B substance (possibly carcinogenic to humans) and the World Health Organization recommends a provisional guideline value of 0.01 mg/L for drinking water (WHO 2011).

BrO_3^- is formed by ozonation of water containing the bromide ion (Br^-). First, ozone and/or the hydroxyl radical oxidizes Br^- into hypobromous acid (HOBr) and/or the hypobromite radical ($\text{BrO}\cdot$). HOBr and $\text{BrO}\cdot$ are then further oxidized into BrO_3^- by ozone and/or the hydroxyl radical (Haag & Hoigné 1983; von Gunten & Hoigné 1994; Mizuno *et al.* 2004, 2007).

There are two approaches to controlling BrO_3^- contamination that occurs through ozonation: prevention of BrO_3^- formation and removal of BrO_3^- after formation (Xie & Shang 2006). The most popular method to prevent BrO_3^- formation involves optimizing the operating

conditions during ozonation. For instance, pH depression during ozonation reduces hydroxyl radical generation and limits BrO_3^- formation via the hydroxyl radical pathway (Elovitz *et al.* 2000). Precise ozone dose control is also effective in minimizing BrO_3^- formation (Kim *et al.* 2007). However, a low ozone dose and few hydroxyl radicals result in a slower degradation rate of micropollutants. In addition, pH depression enhances the formation of HOBr and brominated organic compounds (Xie & Shang 2006). Addition of ammonia is an alternative technology to minimize BrO_3^- formation during ozonation (von Gunten 2003; Xie & Shang 2006). Although ammonia addition is effective in reducing HOBr, which is an intermediate of BrO_3^- formation, it requires the post-treatment of residual ammonia (Wert *et al.* 2008) as ammonia increases the chlorine demand.

Various technologies for BrO_3^- removal after formation such as filtration, UV irradiation, photocatalytic decomposition, arc discharge, coagulation, chemical reduction, activated carbon techniques and biological remediation, have been considered (Butler *et al.* 2005).

In relation to these technologies, Butler *et al.* (2005) pointed out that iron-based chemical reduction and biological activated carbon (BAC) treatment had been well discussed. Ferrous ion and/or zero valent iron are used as reducing agents for BrO_3^- in iron-based chemical reduction (Butler *et al.* 2005; Xie & Shang 2006). As iron stains laundry and plumbing fixtures at levels above 0.3 mg/L (WHO 2011), a cost-effective removal technology for residual iron must be developed (Butler *et al.* 2005). In BAC treatment, catalytic reduction by activated carbon and biological remediation are responsible for BrO_3^- removal. The catalytic removal of BrO_3^- by granulated activated carbon (GAC) has been thoroughly discussed by many researchers. It has been reported that virgin GAC successfully reduces BrO_3^- to Br^- (Siddiqui *et al.* 1996; Asami *et al.* 1999; Bao *et al.* 1999; Kirisits *et al.* 2000; Huang & Chen 2004). However, Asami *et al.* (1999) and Huang & Chen (2004) reported that the transition of GAC to BAC apparently decreased the BrO_3^- removal rate. Although biological remediation of BrO_3^- was successfully demonstrated in some studies, it required addition of electron donors and/or depletion of dissolved oxygen before biological treatment (Hijnen *et al.* 1999; Kirisits *et al.* 2001; Butler *et al.* 2006). Therefore, Hijnen *et al.* (1999) concluded that biological remediation would not be feasible in water treatment because of extended reaction time and requirement for post-treatment to remove residual biomass and dissolved organic matter.

Thus, a versatile prevention technology for BrO_3^- contamination has not been established yet, and a rapid BrO_3^- removal technology without post-treatment remains a desirable goal. One of the possible candidates for rapid removal of BrO_3^- is electrochemical reduction, in which BrO_3^- is reduced to Br^- at the cathode (Kishimoto & Matsuda 2009). However, electrochemical reduction using an activated carbon cathode did not satisfy the above requirement. It was able to remove BrO_3^- contamination within a few minutes but required acidic conditions (Kishimoto & Matsuda 2009). In the present research, an effective cathode material for BrO_3^- reduction using cyclic voltammetry and feasibility of electrochemical treatment for BrO_3^- removal in water purification processes is investigated.

MATERIAL AND METHODS

Experimental procedure for the selection of electrode material

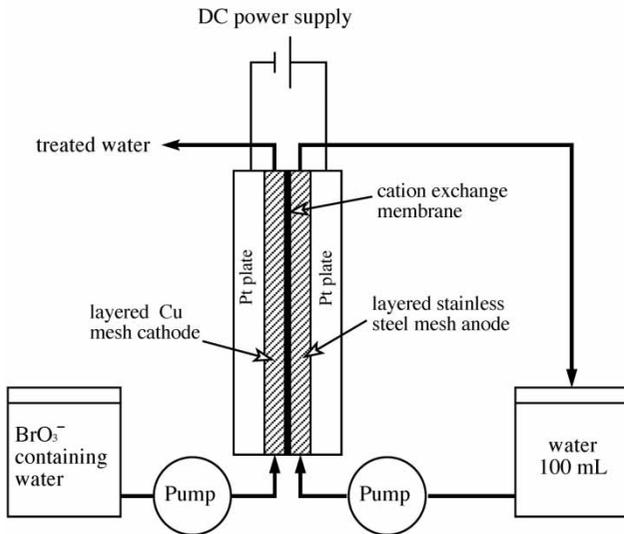
The optimal cathode material for BrO_3^- reduction was explored by cyclic voltammetry. The aqueous test solution comprised of 1/300 M potassium bromate (KBrO_3) with 0.1 M potassium sulfate (K_2SO_4) as a supporting electrolyte. In addition, 0.1 M of K_2SO_4 solution was used as a control. The pH was 5.8 for both solutions. The water temperature was not controlled but was 24 °C in all experiments.

The aqueous test solution was poured into a beaker and a working electrode, a counter electrode, and a reference electrode were inserted into the solution. The potential was swept at 50 mV/s using a potentiostat (HSV-100, Hokuto Denko, Japan). A cyclic potential sweep was repeated at least five times and stopped when the cyclic voltammogram was stable. Nickel (Ni), copper (Cu), aluminum (Al), titanium (Ti), iron (Fe), lead (Pb), zinc (Zn), platinum-coated titanium (Ti/Pt), brass (JIS C2600), stainless steel (ANSI304), and boron-doped diamond (BDD, Sumitomo Electric Hardmetal, Japan) were considered as the working electrode. The effective area of the working electrode was 27 cm². The electrode without Ti/Pt and BDD was ground with alumina abrasive before cyclic voltammetry. The counter electrode was a platinum wire. The reference electrode was composed of saturated silver-silver chloride (Ag/AgCl, standard potential 0.199 V at 25 °C).

BrO_3^- removal experiment

Rapid BrO_3^- removal by the optimal cathode material, Cu, was examined using an electrolytic flow cell (Figure 1). The electrolytic flow cell had two compartments, an anodic and a cathodic. The empty volume of each compartment was 25 cm³ and the compartments were divided by a cation-exchange membrane (Nafion N117, DuPont, USA). The anode was layered with stainless steel mesh (#150) and the cathode with Cu mesh (#40/36). These layered mesh electrodes fully filled each compartment. The cathode area was 1.7 × 10³ cm². The feed water to the cathodic

(a) Experimental setup



(b) Structure of layered Cu mesh cathode

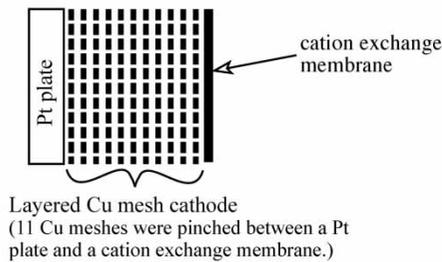


Figure 1 | Experimental setup and the structure of the cathodic compartment.

compartment was 7.5 mg-BrO₃⁻/L of KBrO₃ solution (pH 6.1 ± 0.3) or KBrO₃-spiked tap water (98 µg-BrO₃⁻/L, pH 7.0, Table 1), and the feed solution to the anodic compartment was distilled and ion-exchanged water. The feed water was circulated between the anodic compartment and a reservoir tank but was not circulated in the cathodic compartment. The water flow rate for both compartments was set at 1.54 mL/s. The hydraulic retention time of the cathodic compartment was 9.7 s. A DC power supply (AD8735D, A&D, Japan) operated in galvanostatic mode. Electrolytic current ranged from 0 to 0.40 A for the KBrO₃ solution and 0.03 A for the KBrO₃-spiked tap water.

The half reaction of the electrochemical reduction of BrO₃⁻ is expressed as follows:

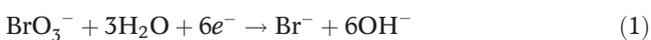


Table 1 | Water quality of KBrO₃-spiked tap water

Item	value
Cations	
Na ⁺	9.8 mg/L
K ⁺	1.6 mg/L
Ca ²⁺	11.8 mg/L
Mg ²⁺	2.3 mg/L
NH ₄ ⁺ -N	ND ^a
Anions	
F ⁻	0.09 mg/L
Cl ⁻	15.7 mg/L
Br ⁻	0.3 mg/L
NO ₃ ⁻ -N	0.29 mg/L
NO ₂ ⁻ -N	ND ^a
SO ₄ ²⁻	12.3 mg/L
PO ₄ -P	0.01 mg/L
BrO ₃ ⁻	0.098 mg/L
ClO ₃ ⁻	0.04 mg/L
pH	7.0
Electric conductivity	159 µS/cm
Free chlorine	0.16 mg/L
Combined chlorine	0.09 mg/L

^aND: not detected.

Therefore, current efficiency of BrO₃⁻ reduction (CE) was calculated from the following equation:

$$\text{CE} = \frac{6F\Delta CQ}{I} \times 100(\%) \quad (2)$$

where, ΔC is the decrement of BrO₃⁻ concentration (µM) or the increment of Br⁻ concentration (µM), Q is the flow rate of the feed solution (=0.00154 L/s), I is the electrolytic current (A), and F is the Faraday constant (=96,485 × 10⁻⁶ C/µmol).

Chemical analysis

Anions and cations were analyzed using an ion chromatography system (DX-500, Dionex, USA). Analytical conditions were as follows. Column: Dionex IonPac AS12A with a suppressor (Dionex ASRC-ULTRA 4 mm);

mobile phase: aqueous solution with 2.7 mM Na_2CO_3 and 0.3 mM NaHCO_3 ; flow rate: 1.0 mL/min; sample injection volume: 100 μL ; oven temperature: 40 °C. The BrO_3^- concentration was determined by ion chromatography coupled with a post-column system (Dionex BRS-500). Reaction conditions in the post-column were as follows. Reactant A: 1.5 M KBr and 1.0 M H_2SO_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 solution pH and electrical conductivity (EC) were measured with a pH meter (Twin pH B-212, Horiba, Japan) and an EC meter (Twin Cond B-173, Horiba, Japan), respectively. The residual chlorine was determined by the *N,N*-diethyl-*p*-phenylenediamine colorimetric method using a chlorine checker (HI95711, Hanna Instruments, USA).

RESULTS AND DISCUSSION

Selection of electrode material

Some examples of cyclic voltammograms obtained are shown in Figure 2. When an electrode material has catalytic

activity for BrO_3^- reduction, an increment in the reduction current is expected when BrO_3^- is added. Furthermore, it is favorable for BrO_3^- removal to enhance the reduction current at higher potential, because the electrolysis of water takes place at lower potential and leads to deterioration of current efficiency. Accordingly, an electrode material, which more strongly enhances the reduction current at higher potential, is desired for the electrochemical removal of BrO_3^- .

Pt is widely used as a catalyst for hydrogen evolution (Logan 2010), but it did not show any catalytic activity for BrO_3^- reduction. The cyclic voltammograms of Ti, Al, and Pb also did not change, with or without the addition of KBrO_3 (data not shown). The reduction current using the Fe electrode increased with the addition of KBrO_3 , but the increment was relatively small. Similar behavior was observed for the Ni electrode. BDD is known to have a wide potential window (Fujishima *et al.* 2000). Therefore, it was expected to be effective in BrO_3^- reduction. However, a distinguishable increase in the reduction current was not observed. Consequently, these electrode materials (Pt, Ti, Al, Pb, Fe, Ni, BDD) were not effective in BrO_3^- reduction.

Cu, Zn, brass, and stainless steel incremented the reduction current with the addition of KBrO_3 . The

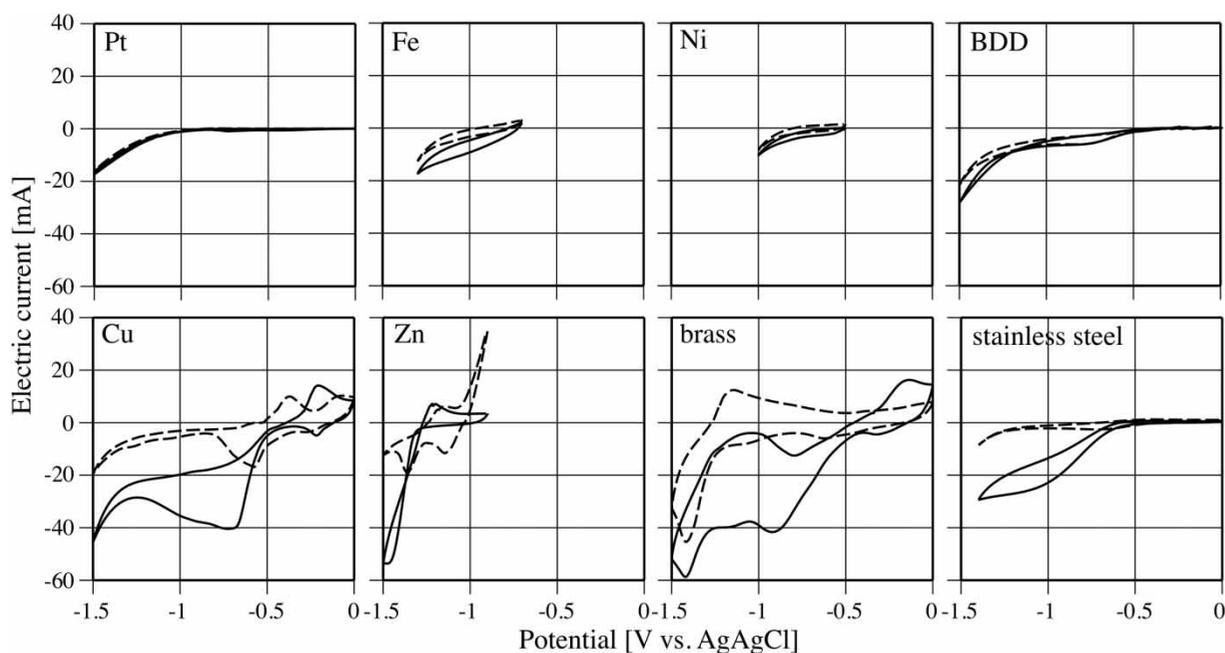


Figure 2 | Cyclic voltammograms (solid line: 0.1 M K_2SO_4 + 1/300 M KBrO_3 , dotted line: 0.1 M K_2SO_4).

augmentation of the reduction current observed in the potential was <-1.4 V vs. Ag/AgCl for Zn and <-0.6 V vs. Ag/AgCl for Cu, brass, and stainless steel. Cyclic voltammograms of Cu and Zn were complicated due to the high ionization tendency of Zn and the high reactivity of Cu with oxygen. Brass is an alloy of Cu and Zn. Therefore, the cyclic voltammogram of brass seemed like a composite of the voltammograms of Cu and Zn. A relatively smooth voltammogram was observed using a stainless steel electrode. Stainless steel (ANSI304) is an alloy of Fe, Ni, and chromium (Cr). As Fe and Ni did not show a distinguishable reduction current increment, Cr might contribute to the enhancement of the reduction current.

Based on the cyclic voltammetry results of the 11 materials tested, Cu appeared to be most suitable because the reduction current sharply increased at relatively higher potential around -0.7 V vs. Ag/AgCl.

Performance of the electrolytic flow cell

Figure 3 shows the increment of Br^- concentration and the decrement of BrO_3^- concentration after the electrochemical treatment of the KBrO_3 solution. The decrement of BrO_3^- concentration was almost the same as or slightly higher than the increment, although in two cases it was smaller. This means that some intermediates, such as bromite ions and hypobromite ions, were generated. Both the increment and decrement were enhanced by the increase in the

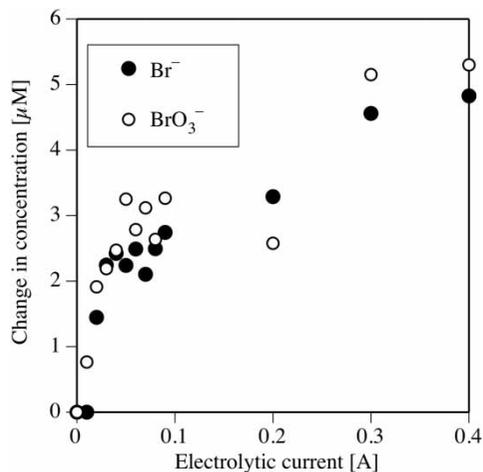


Figure 3 | Increment of Br^- concentration and decrement of BrO_3^- concentration after the electrochemical treatment of KBrO_3 solution.

electrolytic current. However, the enhancement effect seems to reach a plateau with a higher electrolytic current. This enhancement effect is believed to be the rate-determining step transitioned from an electron-transfer process to a mass-transfer process on the electrode surface. Another possible cause is the enhancement of the electrolysis of water at a higher electrolytic current because the standard potential of BrO_3^- (reaction [1]) is 0.584 V vs. SHE (standard hydrogen electrode), which is higher than that of hydrogen evolution from water (-0.828 V vs. SHE) (Mussini & Longhi 1985). Figure 4 shows the observed current efficiencies estimated from changes in Br^- or BrO_3^- concentrations. The maximum current efficiency was 6.7% with Br^- and 8.5% with BrO_3^- . These values are similar to the results achieved in the previous study using an activated carbon felt electrode (current efficiency: 8.7%, electrolytic current: 0.20 A, initial BrO_3^- concentration: 100 μM , pH 2.0; Kishimoto & Matsuda 2009). However, it should be noted that the experiments in this study were performed at around neutral pH. When an activated carbon felt cathode was used, the current efficiency was $<0.5\%$ at pH over 5 (Kishimoto & Matsuda 2009). Thus, the Cu cathode is superior to the activated carbon felt cathode at around neutral pH.

Further, treatment of KBrO_3 -spiked tap water was performed using the Cu mesh cathode. The influent to and the effluent from the electrolytic flow cell were sampled for chemical analysis and then the effluent was resupplied

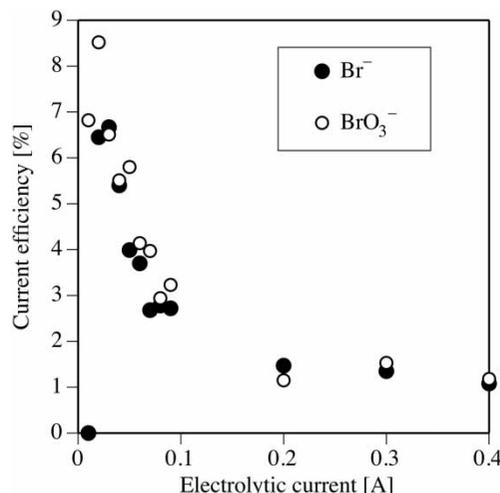


Figure 4 | Current efficiencies of BrO_3^- reduction.

to the electrolytic flow cell to model the cascade involved in actual water treatment.

Figure 5 shows the logarithmic plot of the BrO_3^- residual rate during the treatment of KBrO_3 -spiked tap water at the electrolytic current of 0.03 A (the current density of 0.018 mA cm^{-2}). The BrO_3^- concentration steadily decreased with time. However, the current efficiency remained low with values of 0.11%. In the BrO_3^- removal experiment with KBrO_3 -spiked tap water, the initial BrO_3^- concentration was $0.77 \text{ }\mu\text{M}$ ($98 \text{ }\mu\text{g-BrO}_3^-/\text{L}$) whereas in the KBrO_3 solution was $59 \text{ }\mu\text{M}$ ($7.5 \text{ mg-BrO}_3^-/\text{L}$). Therefore, mass transfer to the Cu cathode was believed to limit the BrO_3^- reduction rate. The mass transfer by diffusion follows Fick's law:

$$F = D \frac{C - C_s}{\Delta x} \quad (3)$$

where, F is diffusion flux ($\mu\text{mol cm}^{-2} \text{ s}^{-1}$), D is a diffusion coefficient ($\text{L cm}^{-1} \text{ s}^{-1}$), C is BrO_3^- concentration in the bulk solution (μM), C_s is BrO_3^- concentration at the cathode surface (μM), and Δx is the thickness of the diffusion layer (cm). When diffusion limits the overall reaction rate, C_s is nearly equal to zero. Accordingly, the overall reaction rate should be proportional to C . Furthermore, the cathodic compartment was fully filled with Cu mesh electrodes in this study. Therefore, the BrO_3^- reduction in the cathodic

compartment was macroscopically regarded as a heterogeneous system. Consequently, the pseudo-first order reaction was assumed to analyze the BrO_3^- reduction rate in the cathodic compartment as follows:

$$\frac{dC}{dt} = -kAC \quad (4)$$

where, k is the BrO_3^- reduction rate constant at the current density of 0.018 mA cm^{-2} (cm s^{-1}), A is the specific cathode area per the compartment volume ($=68 \text{ cm}^2 \text{ cm}^{-3}$), and t is contact time (s).

The solution of the Equation (4) was as follows:

$$\log \frac{C}{C_0} = -k'At \quad (5)$$

where, C_0 is initial BrO_3^- concentration (μM), and k' is common logarithm-based k (cm s^{-1}). The relationship between $\log(C/C_0)$ and t shown in Figure 5 demonstrates that the $\log(C/C_0)$ is proportional to t . Thus, BrO_3^- reduction followed the pseudo-first order reaction with the slope of $k'A$, which was estimated to be 0.00224 s^{-1} . The $\log(C/C_0)$ in the BrO_3^- removal experiment using the KBrO_3 solution with an electrolytic current of 0.03 A (the current density of 0.018 mA cm^{-2}) is also plotted in Figure 5. The plot is slightly lower than that for the KBrO_3 -spiked tap water. This means that the BrO_3^- reduction rate constant decreased slightly when using KBrO_3 -spiked tap water. The KBrO_3 -spiked tap water contained residual chlorine (Table 1). Therefore, it was believed that residual chlorine reduction on the cathode competed with BrO_3^- reduction and resulted in decrease in the current efficiency.

The necessary contact time to satisfy the BrO_3^- criterion for drinking water ($10 \text{ }\mu\text{g/L}$: WHO 2011) can be calculated using the estimated rate constant ($k'A = 0.00224 \text{ s}^{-1}$). The calculation results are summarized in Figure 6. For instance, when raw water has a concentration of $30 \text{ }\mu\text{g-BrO}_3^-/\text{L}$, 214 s (3.6 min) of contact time is required to satisfy the criterion. Kirisits *et al.* (2001) reported that 40% BrO_3^- removal from an influent containing $20 \text{ }\mu\text{g/L}$ BrO_3^- concentration was obtained by the biological activation of a carbon filter with 20 min empty bed contact time. In our electrochemical process, the same BrO_3^- removal (40%) is estimated to be achieved with only 1.7 min contact time. Accordingly,

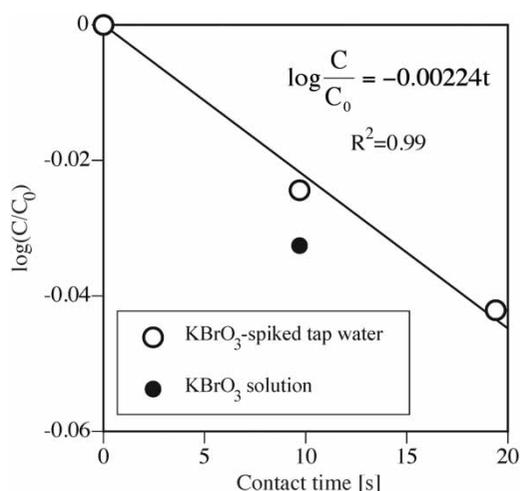


Figure 5 | Logarithmic plot of BrO_3^- residual rate (C/C_0) against contact time. Open plots indicate the treatment result of KBrO_3 -spiked tap water and solid plot indicates that of KBrO_3 solution. Electrolytic current was set at 0.03 A in both cases.

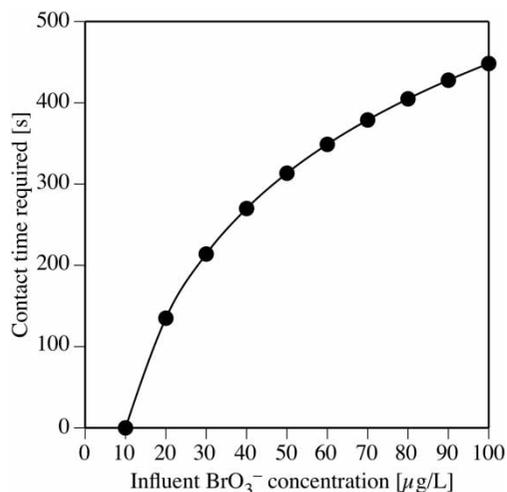


Figure 6 | Contact time required to satisfy the criterion for drinking water (10 μg-BrO₃⁻/L).

it is reasonable to conclude that the electrochemical process is a promising technology to achieve rapid removal of BrO₃⁻ from the water streams.

CONCLUSIONS

To control BrO₃⁻ contamination in the water supply, the development of a rapid BrO₃⁻ removal technology without a post-treatment is desirable. In this research, rapid removal of BrO₃⁻ from water streams was examined using an electrolytic flow cell. The conclusions are summarized as follows:

1. The optimal electrode material for electrochemical removal of BrO₃⁻ was explored by cyclic voltammetry. Eleven electrode materials, Ni, Cu, Al, Ti, Fe, Pb, Zn, Ti/Pt, brass, stainless steel, and BDD, were examined. Cu, Zn, brass, and stainless steel showed distinguishable increments of reduction current with the addition of KBrO₃ to the electrolyte. Finally, Cu was selected as the most suitable material of the 11 because the reduction current was sharply increased at the potential around -0.7 V vs. Ag/AgCl.
2. An electrolytic flow cell with a layered Cu mesh cathode was manufactured and tested for BrO₃⁻ removal from 7.5 mg-BrO₃⁻/L KBrO₃ solution (pH 6.1 ± 0.3). The BrO₃⁻ reduction to Br⁻ was observed in the electrolytic flow cell. The maximum current efficiency for BrO₃⁻ removal reached 8.5% without pH control.

3. BrO₃⁻ removal from KBrO₃-spiked tap water (98 μg-BrO₃⁻/L, pH 7.0) was examined using the electrolytic flow cell with a specific cathode area of 68 cm² cm⁻³ and an applied current density of 0.018 mA cm⁻². BrO₃⁻ removal rate followed the pseudo-first order reaction of BrO₃⁻ concentration and the pseudo-first order reaction rate constant based on common logarithm was evaluated to be 0.00224 s⁻¹. Although the current efficiency remained low due to low initial BrO₃⁻ concentration, rapid removal of BrO₃⁻ was established. For instance, only 3.6 min of contact time was required to decrease the BrO₃⁻ concentration in tap water from 30 to 10 μg/L. Thus, it is feasible to use the electrochemical process for rapid removal of BrO₃⁻ from water streams.

ACKNOWLEDGEMENTS

This study was performed under the research project 'Research on removal of halogen oxide anions by electrochemical reduction (No. 20560512)', which was financially supported by Grants-in-Aid for Scientific Research, Japan Society for the Promotion of Science.

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First received 10 October 2011; accepted in revised form 13 January 2012