Bromate removal by electrochemical reduction at boron-doped diamond electrode

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ABSTRACT

The electrochemical removal of bromate ions was performed with BDD electrodes in a two-compartment electrolytic reactor. Bromate ions removal and the production of Br⁻ were observed and determined. The removal of bromate ions occurred at an applied bias potential of −0.45 V (vs. SCE). And, the removal rate increased with the applied bias potential. Within 2 h, nearly 90% of bromate ions were removed with the applied bias potential of −1.0 V (vs. SCE). Effect of pH on bromate ions removal was slight. SO_4^{2-} and Cl^- ions inhibit the electrochemical reduction of bromate ions, which can be explained by the competitive adsorption of coexisting anions at the electrode surface with the bromate ions. In comparison, the graphite and carbon paper electrode exhibit low catalytic activities toward reduction removal of bromate ions under the same experimental conditions. A possible reason was proposed.

1. Introduction

Bromide (Br^-) is naturally present in most water bodies, with concentrations varying from a few micrograms per liter to several milligrams per liter. It can be oxidized to form bromate ions (BrO_3^-) in drinking water through disinfection processes such as ozonation, hypochlorination, chloramination, or a combination of ozonation and hypochlorination [1]. Although evidence of carcinogenicity in humans is inadequate, the International Agency for Research on Cancer has classified it as a Group 2B substance. The world Health Organization recommends a provisional guideline value of 0.01 mg/L for drinking water [2].

Different approaches have been taken to reduce BrO_3^- concentrations in drinking water. The majority of studies have focused on optimizing ozonation processes to minimize bromate formation [3]. In addition, removal of BrO_3^- after its formation has also been investigated [4,5]. Various technologies for BrO_3^- removal have been discussed, such as photocatalytic reduction [6], activated carbon adsorption [7], zero iron reduction [8], and biological remediation. Bromate removal by ferrous iron and biologically activated carbon was popular. However, the issue of cost-effectively removing residual iron from the water stream must be resolved prior to development of a viable full-scale technique, because the WHO guidelines for drinking-water quality recommends iron concentrations less than 300 μg/L.

Consequently, it is meaningful to provide a new option to remove BrO_3^- from the water stream. Mussini and Longhi summarized the standard potential of BrO_3^- and HOBr as follows [9]:

$$BrO_3^- + 5H^+ + 4e^- \rightleftarrows HOBr + 2H_2O \qquad 1.447\ V\ vs\ SHE$$

$$HOBr + H^+ + 2e^- \rightleftarrows Br^- + H_2O \qquad 1.341\ V\ vs\ SHE$$

These potentials clearly show BrO_3^- and HOBr act as oxidants and electrochemical reduction of BrO_3^- may proceed at the cathode in an electrochemical system. Several electrode materials catalyzing BrO_3^- reduction were reported such as molybdenum oxide, tungsten oxide, and polyoxometalate. These metallic oxides were applied to amperometric detection of BrO_3^- [10–12]. However, application of the metallic oxides for water treatment is limited because of their instability as a cathode. A stability of an electrode is an important factor in water treatment. Accordingly, BrO_3^- reduction by a stable electrode is desired for water treatment.

Boron-doped diamond (BDD) films have been largely used as electrode material in electrochemical studies since BDD films posses an extraordinary chemical stability and low capacitive currents in an extended range of potential [13]. The recent use of BDD thin-film in anodic oxidation of organic pollutants has been largely investigated [14–18]. It is known that carbon materials such as vitreous carbon [19], carbon felt [20], and carbon nanotube [21] can be used as cathode materials to reduce organic contaminants or

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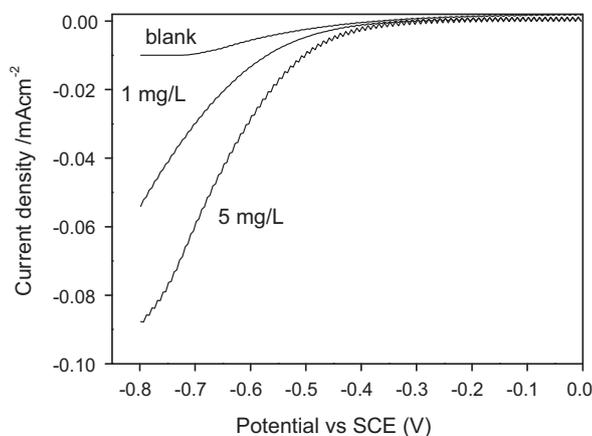*E-mail address:* hjliu@rcees.ac.cn (H. Liu).

Fig. 1. Cyclic voltammograms of BrO_3^- ions with various concentrations at BDD electrode (pH 7.5, 0.1 mM Na_2SO_4 solution).

metal ions. However, there have been very few investigations of BDD electrodes employed as cathodes. Bouamrane et al. studied the effectiveness of BDD for reducing nitrate to ammonia [22]. Several studies have investigated metal deposition, including mercury, silver, copper, and cadmium [23,24]. Reduction of trichloroethene at BDD electrodes was also reported and production of acetate and chloride ions with no detectable intermediates was observed [25].

Herein, the effectiveness of a BDD cathode for reductive destruction of BrO_3^- ions was examined. Effects of pH and applied bias potential on the removal of BrO_3^- ions were investigated. Reduction of BrO_3^- ions at the graphite and carbon paper electrode was also checked.

2. Experimental

BrO_3^- solution with given concentration was prepared by the dilution of potassium bromate solution ($KBrO_3$, analytical grade) with distilled water. The solution pH was adjusted by addition of sulfuric acid (H_2SO_4, guaranteed grade) and potassium hydroxide (KOH, guaranteed grade).

Electrochemical experiments were performed in a two-compartment electrolytic cell divided by a cation exchange membrane (Nafion N-117, DuPont, Willmington, DE). Each cell was a rectangular glass block measuring 10 cm in height, 5.2 cm in width, and 5.0 cm in length. Electrolyte in both compartments of the cell was mixed by a stir bar and magnetic stir plate. BDD electrode (Adamant Technologies SA, 4 cm × 5 cm) was used as the cathode; a Pt wire was used as the anode; the saturated KCl electrode was used as the reference electrode. Each cell is left unsealed and exposed to room air. The electrochemical reaction employed a basic electrochemical system (Basic electrochemical system, Princeton Applied Research Co., U.S.A).

The concentrations of bromate and bromide ions were determined by ion chromatography (Dionex, ICS-1000) with an IonPac AG15 guard column and an IonPac AS15 analytical column. All the experiments were performed at least in duplicate. The reported values are within the experimental error of ±2.0%.

3. Results and discussion

3.1. Electrochemical behavior of BrO_3^- at BDD electrode

As shown in Fig. 1, the linear sweep voltammetry of the BDD electrode in 0.1 mM Na_2SO_4 with various BrO_3^- ion concentrations (10 mV/s) shows a cathodic current starting at −0.45 V (vs.
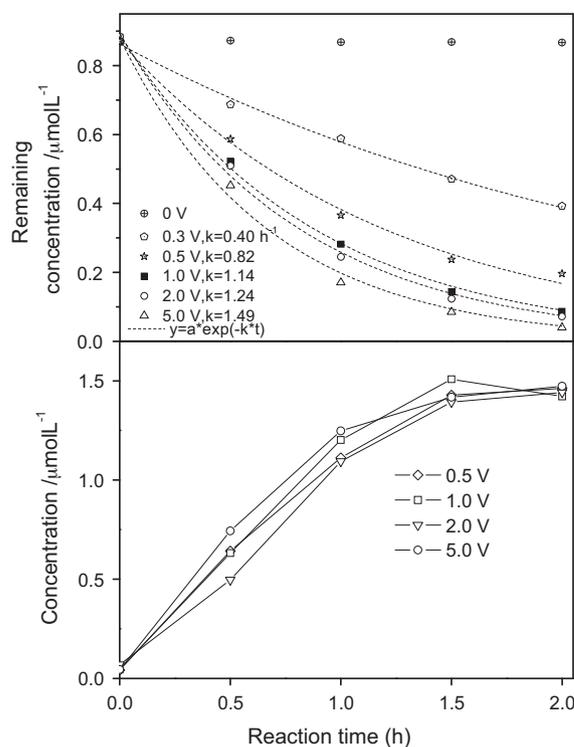

Fig. 2. Effect of applied bias potential on BrO_3^- removal and Br^- formation at BDD electrode (0.1 mM Na_2SO_4 solution).

SCE). The peak intensity increases with the concentration of BrO_3^- ions, which indicates that the BrO_3^- ions can be reduced by BDD electrode.

3.2. Effect of applied bias potential on bromate removal

As shown in Fig. 2, no decrease in BrO_3^- ions occurred without electrolysis. Thus, the BDD electrode used in this study exerted no catalytic activity on BrO_3^- without electrochemical bias application and adsorption of BrO_3^- on the BDD electrode was negligible. By contrast, BrO_3^- removal was observed when the applied bias potential was applied. Corresponding Br^- ions were also detected. The sum of molar concentration of BrO_3^- and Br^- reached over 70% of the initial BrO_3^- concentration, indicating that most of the BrO_3^- removed was electrochemically reduced to Br^-. The bromous or hypobromous will be generated in the electrochemical reduction of bromate, which is unstable and the disproportionation reaction will occur as described by Lee and Lister [26].

The bromate reduction rate constants (k_1), obtained using a first-order reaction rate to simulate the data in Fig. 2, are 0.40, 0.82, 1.14, 1.24, and 1.49 h^{-1} for 0.3, 0.5, 1.0.2.0.and 5.0 V, respectively. All of the R^2 values were larger than 0.99. Such apparent bromate reduction rates provide a relative comparison of the effectiveness of bromate reduction with various applied bias potential. It is observed that removal efficiency of BrO_3^- increases with the applied bias potentials. And, the increase is slight when the applied bias potential is higher than 1.0 V. The reduction removal of organic or inorganic compounds at cathode was mainly via direct electron reduction or indirect hydrogen atoms reduction [27]. The cathodic reduction of BrO_3^- is thermodynamically superior to hydrogen evolution. Therefore, at an applied bias potential less than −1.0 V, BrO_3^- may be electrochemically reduced without hydrogen evolution.
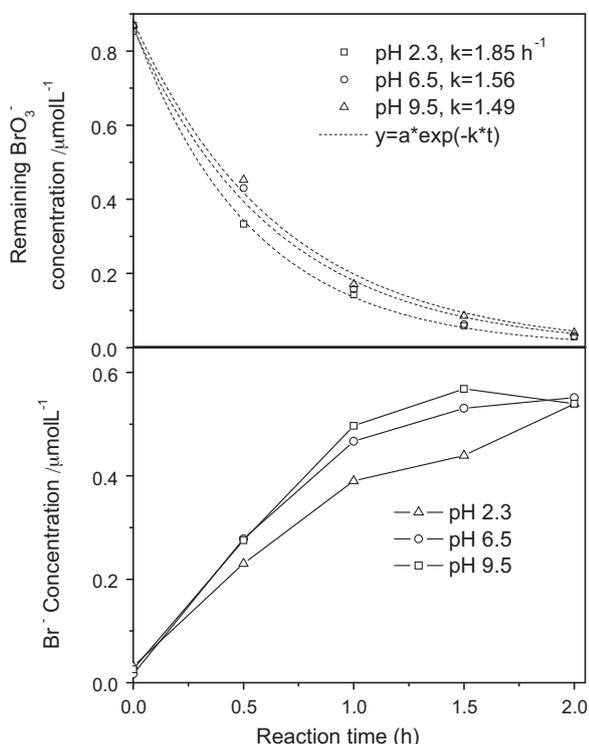
Fig. 3. Effect of pH values on bromate removal and Br⁻ formation at BDD electrode (0.1 mM Na₂SO₄ solution).

3.3. Effect of pH on bromate removal

The electroreduction process produces hydroxide ions at the surface of cathode so the pH near the surface is most probably higher than that in the bulk solution and the pH of an unbuffered electrolysis medium increases as the electrolysis proceeds. Removal of bromate ions under various pH conditions with a constant applied bias potential of −2.0 V was investigated. As shown in Fig. 3, the removal rate of bromate ions increase slightly with the decrease of solution pH. It has been reported that the removal of bromate ions strongly depended on solution pH, with low pH accelerating the removal rate. The similar dependency on pH in GAC treatment was observed by Kishimoto and Matsuda [4]. Bromic acid (HBrO₃) may be more reactive than BrO₃⁻ because anions are generally difficult to approach the cathode because of electrostatic repulsive force [28].

The CV curve of BDD electrode with and without BrO₃⁻ ions under basic, neutral and acid conditions were given in Fig. 4. It can be seen that the current variation under various pH conditions was slight. By contrast, the obvious differences of current values were observed in the presence of BrO₃⁻ ions. The cathodic current at pH 4.2 was larger than that at pH 6.8. And, the cathodic current was low in the pH of 8.5. The above results indicated that the reduction of BrO₃⁻ ions was favorable in the acid conditions. Additionally, in the presence of bromate, the evolution of H₂ will be inhibited and the current in the CV with bromate was smaller than that without bromate ions. In an alkaline medium, hydroxide ions occupy active sites and hindered the adsorption of bromate ions, which may be responsible for the enhanced reduction rate of BrO₃⁻ ions.

3.4. Effect of coexisting ions on bromate removal

Cl⁻, SO₄²⁻, SiO₃²⁻, and CO₃²⁻ were ubiquitous present in drinking water, which were selected to assess the impact of coexisting anions on the bromate reduction. Catalytic bromate reduction in
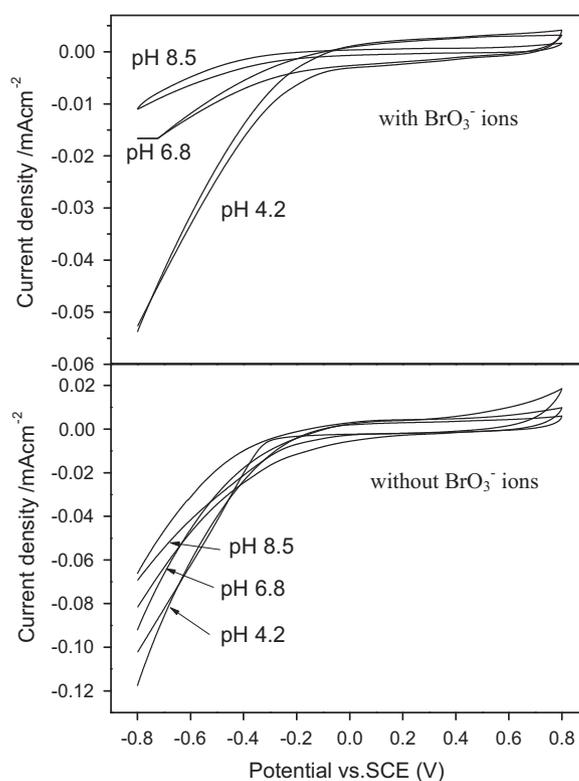

Fig. 4. Cyclic voltammograms of BDD electrode with and without BrO₃⁻ ions (0.1 mM Na₂SO₄ solution, 20 mg/L BrO₃⁻ ions).

the presence of Cl⁻, SO₄²⁻, SiO₃²⁻, and CO₃²⁻ with various concentrations is compared. As shown in Fig. 5, a consistent trend is observed that the presence of coexisting anions led to suppress bromate reduction and the inhibition effect was promoted with the increase of anion concentration. And, SO₄²⁻ exhibits the most prominent inhibition effect on the bromate reduction among all anions tested. The reduction of bromate at very negative potentials (−2.0 V vs. SCE) takes place far from the electrode surface, possibly at the outer Helmholtz plane (oHp), because they are repelled from the likely charged electrode. Therefore, the direct adsorption of bromate on the electrode surface under these conditions is not possible. The inhibition may be related with the ability of bromate to approach the oHp [29]. The adsorption affinity to anion-exchange resins is ordered as follows: SO₄²⁻ > Cl⁻ > SiO₃²⁻ ≈ CO₃²⁻ [30]. The
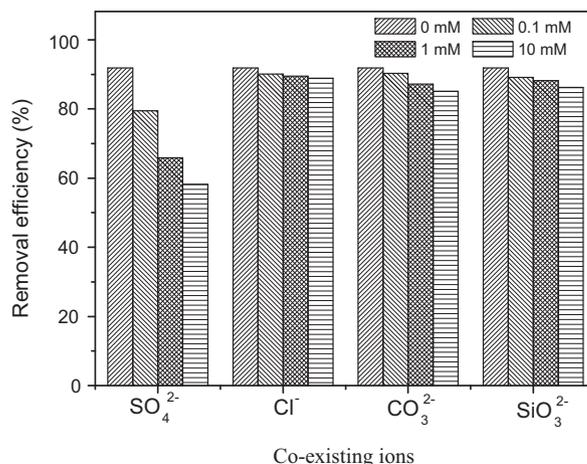

Fig. 5. Effects of co-existing ions on the removal of bromate ions with the applied bias potential of −2.0 V and reaction time of 2 h.
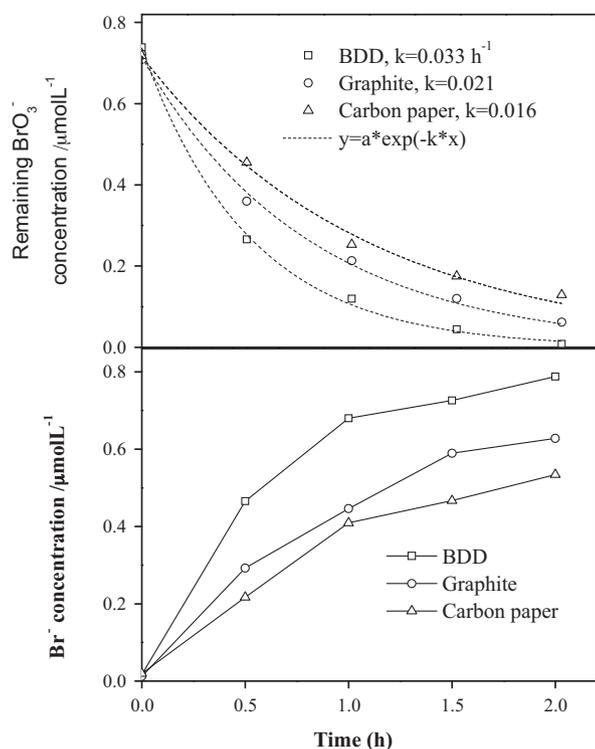
Fig. 6. Removal of bromate ions and formation of Br^- via electroreduction using various electrode materials with same experiment conditions (pH 6.5, applied bias potential −1.0 V).

observed sequence of inhibition effects of the tested anions on the bromate reduction was consistent with the above sequence. In general, an anion with high ionic charge and small ionic size invokes strong electrostatic interaction. Compared to Cl^-, SO_4^{2-} has higher ionic charge, resulting in stronger inhibition effect on the bromate reduction [31].

3.5. Comparison with other systems

BDD electrode, blank carbon paper electrode, and graphite electrodes are both composed of carbon atoms, terminated with oxygen or hydrogen atoms. Reduction of bromate ions at the above three kinds of electrodes with the same reaction area were investigated under same experimental conditions. It can be seen from Fig. 6 that the removal rates of bromate ions were 0.033, 0.021, and 0.016 h^{-1} for the BDD electrode, the carbon paper electrode, and the graphite electrode, respectively.

One possible reason for the difference in the electroreduction of bromate ions is that BDD surfaces are composed of sp^3 hybridized C atoms bound to either two or three other C atoms, whereas carbon paper and graphite surfaces contain sp^2-hybridized C atoms, bound to either one or two other C atoms. The specific functional groups on BDD electrodes play an important role in mediating reduction of inorganic compounds [32]. In addition, the oxygenated groups such as carboxyl, carbonyl, and hydroxyl groups at BDD electrodes are suspected to be involved in mediating electron transfer at BDD

electrodes and remain on the surface even after cathodic polarization [33].

4. Conclusions

The obtained results indicated that bromate ions can be efficiently removed via electroreduction using BDD electrode. And, most of bromate ions were converted into bromide ions. The removal rate of bromate ions increased with the applied bias potential. The removal rate increases slightly with the solution acid degree. SO_4^{2-} and Cl^- ions inhibit the electrochemical reduction of bromate ions, which can be explained by the competitive adsorption of coexisting anions with the bromate ions. And, the BDD electrode exhibit higher electrocatalytic activities in bromate ions reduction than graphite and carbon paper electrodes.

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