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Electrochemically induced pitting corrosion of Ti anode: Application to the indirect reduction of bromate

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HIGHLIGHTS

- A two-compartment electrolytic cell was designed to reduce bromate.
- Ti electrode was oxidized during electrochemically induced pitting corrosion.
- Bromate was effectively reduced to bromide by reactive Ti species.
- Pseudo-first-order model described the experimental data well.
- The electrochemical mechanism of bromate reduction was proposed.

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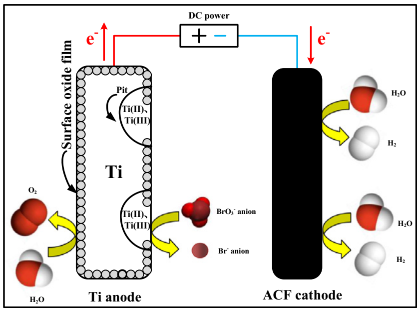
GRAPHICAL ABSTRACT

Schematic diagram of BrO_3^- reduction during pitting corrosion at the Ti anode surface.



ABSTRACT

Bromate (BrO_3^-) is a carcinogenic disinfection by-product of drinking water. The conventional electrochemical reduction of BrO_3^- generally occured at the cathode. In this study, we investigated the reduction process of BrO_3^- via electrochemically induced pitting corrosion of titanium (Ti) anode in a two-compartment electrolytic cell. Ti electrode was oxidized to produce reactive Ti ions, e.g., Ti^{2+} and Ti^{3+}, led by electrochemically induced pitting corrosion. These multivalent Ti species effectively reduced BrO_3^- to Br^-. The pitting potential (E_{Pit}) of Ti electrode was 1501 mV (SHE) at pH 7.0. However, the product analysis showed that the amount of reduced BrO_3^- was not in accordance with that of generated Br^-, and a 19.8% loss of bromine mass should contribute to the formation of solid by-products. With the presence of coexisting anions (Cl^-, NO_3^-, and SO_4^{2-}), BrO_3^- at initial concentration of 100 μg/L also could be reduced to below the maximum contaminant level (MCL) of 10 μg/L, as well as the Cl^- and NO_3^- were reduced simultaneously. BrO_3^- reduction by electrochemically induced corrosion of Ti electrode is feasible, but its practical application is limited by the high energy costs and unwanted Ti dissolution.

1. Introduction

Bromate (BrO_3^-) is a disinfection by-product frequently detected in drinking water when raw water containing bromide was disinfected by ozonation or advanced oxidation. It has been experimen-

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tally confirmed that BrO_3^- can cause renal cell tumors in rats and mice [1,2]. Although evidence of carcinogenic potential in humans is inadequate, the International Agency for Research on Cancer (IARC) has classified BrO_3^- as a potential carcinogen in humans [3]. This classification has led authorities, including those in the European Union (EU), United States and China, to establish the enforceable maximum contaminant level (MCL) of BrO_3^- in drinking water at 10 μg/L (0.078 μmol/L) [4].

BrO_3^- is a stable anion with high solubility and low reactivity. Once formed in water, it is difficult to be naturally degraded. Recently, the majority of researchers have focused on BrO_3^- minimization before formation and BrO_3^- removal after formation. Ammonia addition and pH depression are considered as alternative technology to control BrO_3^- formation during ozonation [5,6]. For another, continuous efforts have been devoted into the research and development of appropriate methods for effectively removing BrO_3^- after formation, including coagulation [7], adsorption process [8,9], chemical or electrochemical reduction [3], and biological remediation [10]. Butler et al. [11] pointed out that iron-based chemical reduction and biological activated carbon (BAC) treatment maybe the most developed technologies. Although these two methods can efficiently reduce BrO_3^- to Br^-, the issue of cost-effectively removing residual iron or biomass from the water must be resolved before these technology were extensively applied in water treatment [12,13]. In the last few years, electrochemical technology has aroused increasing interest in environmental applications due to its ecological compatibility and selectivity, for example, the elimination of oxo-anions from water [14–16]. Electrochemical reduction is considered as a promising method to eliminate BrO_3^- due to no second pollution companied. Li et al. [17] prepared a silver nanoparticles modified electrode and used it as a working electrode for electrocatalytic reduction of BrO_3^-. Mao et al. [15] investigated the electrochemical reduction of BrO_3^- by a Pd modified carbon fiber (Pd/C) electrode, and the removal efficiency of BrO_3^- reached to 87.2% when the cathode potential was −2.0 V. Paschoal et al. [18] used the Ti/TiO_2 material as a photocathode for BrO_3^- removal, and 70% of BrO_3^- could be reduced to Br^- at neutral pH under an applied potential of −0.20 V versus saturated calomel electrode (SCE). As evidenced by many researchers, these electrochemical processes could occur through both direct and indirect reduction mechanisms [19], and BrO_3^- can be transformed to Br^- by electrochemical reduction at the cathode.

However, some researchers discovered that the indirect electrochemical reduction of oxo-anions could occur at the anode rather than the traditional cathode [20,21]. Wang et al. [20] investigated the removal of perchlorate (ClO_4^-) and nitrate (NO_3^-) at the Ti anode by indirect electrochemical reduction process. When an anodic current was applied at the Ti electrode, Ti species such as Ti(III) or Ti(II) were generated. Both Ti(II) and Ti(III) species were potent reductant that could reduce ClO_4^- and NO_3^- ions. Lee et al. [21] reported that ClO_4^- could be effectively reduced to chloride by soluble Ti species such as Ti^{2+} and/or Ti^{3+} during electrochemically induced pitting corrosion of zero-valent titanium. Pitting corrosion is a form of localized corrosion leading to the formation of holes or pits in passivated metals surface, and an anodic potential applied in the metal-electrolyte system is found to have the capability of accelerating pitting corrosion [22]. In practice, Ti metal is the fourth most abundant metal and can be available at a popular price. So Ti metal and porous Ti are widely applied in the fabrication of fuel cells, redox flow batteries and other electrochemical reactors [23]. Furthermore, its oxide TiO_2 is also commonly used in water separation and purification system due to its photocatalysis capability. For example, Sun et al. [24] discussed the effects of TiO_2 nanostructure on water disinfection processes. Kanki et al. [25] used TiO_2-coated ceramic particles in a fluidized bed photocatalytic reactor for water purification. However, to our knowledge, there is no information available concerning indirect electrochemical reduction of BrO_3^- using Ti metal material.

In the present study, the Ti electrode served as an anode was examined to evaluate its ability of reducing BrO_3^- during the electrochemical process. The main aim of this work were (1) to investigate the terminal potential of pitting corrosion of Ti electrode, (2) to study the effect of currents, initial pH, initial BrO_3^- concentration, and co-reduction of Cl^-, NO_3^-, and SO_4^{2-} in tap water, (3) to gain insight into the electrochemical mechanism in the reduction of BrO_3^-.

2. Materials and methods

2.1. Chemicals

All the chemicals used in this study were of analytical reagent grade. $NaBrO_3$ (purity > 99%), NaBr (purity > 98%), $NaNO_3$ (purity > 99%), NaOH (purity > 98%) and H_2SO_4 (purity > 98%) were purchased from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Stock solution of BrO_3^-, Br^-, NO_3^-, Cl^-, and SO_4^{2-} was prepared by dissolving a certain amount of $NaBrO_3$, NaBr, $NaNO_3$, NaCl, and Na_2SO_4 in ultrapure water (specific conductivity of 18.2 MΩ·cm^{-1}), respectively.

The experimental Ti electrode (purity > 99.4%, ∅5 × 150 mm) was cut from commercially pure Ti rod (HuaTai Company, China), and its chemical composition is showed in Table 1.

Activated carbon fiber served as the cathode (purity > 98.5%, 80 mm, 80 mm, 5 mm) was purchased from Nantong environmental protection technology Co., LTD (Jiangsu, China). This activated carbon fiber (ACF) was primarily washed with ethanol to remove organic impurities and cleaned several times by using an ultrasonic cleaner (KQ-500E, China). Afterwards, it was dried at room temperature and stored in desiccator for further use.

2.2. Pitting potential of Ti electrode

Pitting potential of Ti electrode was measured by the potentiodynamic polarization method. All the tests were carried out on a CHI660B electrochemical workstation (Chenhua Instrument, Shanghai, China), consisting of a three-electrode system with Ti electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum sheet as the counter electrode. The polarization curves were recorded from −2000 to 2000 mV (SCE) with a scan rate of 10 mV·s^{-1} at different pH (2.8–9.8). The cyclic voltammetric (CV) measurements were carried out on the same workstation with the potential scan rate of 10 mV·s^{-1} in the range of −1.8 V to 1.8 V. All the work was conducted at room temperature (25 °C).

2.3. Experimental set-up and reduction experiments

A two-compartment electrolytic cell was designed for experiments (shown in Fig. 1). Constituents included a DC power, magnetic stirrer, anode chamber (600 mL), and cathode chamber (600 mL), in which the structure of the two chamber was divided by a cation exchange membrane (Nafion 117, DuPont, USA). Both anode (Ti) and cathode (ACF) were submerged in a solution at a depth of 8 cm and constant potential or/and current was supplied by a DC power supply (Rek PS-303D, China).

The initial experiments (run A through run C) were carried out to study the terminal potential induce pitting corrosion of Ti electrode, and the experimental conditions in Table 2 were based on results of potentiodynamic polarization tests. Subsequent experiments (run D through run N) were conducted to investigate the effects of current, initial pH, and initial BrO_3^- concentration on BrO_3^-