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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.

A R T I C L E I N F O

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GRAPHICAL ABSTRACT

Schematic diagram of BrO₃⁻ reduction during pitting corrosion at the Ti anode surface.



ABSTRACT

Bromate (BrO₃⁻) is a carcinogenic disinfection by-product of drinking water. The conventional electrochemical reduction of BrO₃⁻ generally occured at the cathode. In this study, we investigated the reduction process of BrO₃⁻ via electrochemically induced pitting corrosion of titanium (Ti) anode in a twocompartment electrolytic cell. Ti electrode was oxidized to produce reactive Ti ions, e.g., Ti²⁺ and Ti³⁺, led by electrochemically induced pitting corrosion. These multivalent Ti species effectively reduced BrO₃⁻ 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 BrO₃⁻ 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⁻, NO₃, and SO₄²⁻), BrO₃⁻ 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 NO₃⁻ were reduced simultaneously. BrO₃⁻ 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.

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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 BrO₃ minimization before formation and BrO3 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 BrO₃⁻ 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 BrO₃. Mao et al. [15] investigated the electrochemical reduction of BrO₃ by a Pd modified carbon fiber (Pd/C) electrode, and the removal efficiency of $BrO_{\overline{3}}$ reached to 87.2% when the cathode potential was -2.0 V. Paschoal et al. [18] used the Ti/TiO₂ 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 Ti²⁺ and/or Ti³⁺ 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 TiO₂ 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 TiO₂ nanostructure on water disinfection processes. Kanki et al. [25] used TiO₂-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. NaBrO₃ (purity > 99%), NaBr (purity > 98%), NaNO₃ (purity > 99%), NaOH (purity > 98%) and H₂SO₄ (purity > 98%) were purchased from Kermel Chemical Reagent Co. Ltd. (Tianjin, China). Stock solution of BrO₃⁻, Br⁻, NO₃⁻, Cl⁻, and SO₄²⁻ was prepared by dissolving a certain amount of NaBrO₃, NaBr, NaNO₃, NaCl, and Na₂SO₄ in ultrapure water (specific conductivity of 18.2 MΩ·cm⁻¹), respectively.

The experimental Ti electrode (purity > 99.4%, \emptyset 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 BrO₃ concentration on BrO₃

| Table 1 | |
|-------------------------|------------------|
| Chemical composition of | of Ti electrode. |

| Element | Ti | Al | Zr | V | Fe | Nb | С | Н | 0 | Ν |
|--------------------|-------|------|------|------|------|------|------|------|------|------|
| Composition (wt.%) | 99.40 | 0.28 | <0.1 | <0.1 | 0.15 | <0.1 | <0.1 | <0.1 | 0.15 | <0.1 |

reduction. The synthetic solution was prepared by diluting the stock solution with ultrapure water and 0.5 M Na₂SO₄ was added into the solution to maintain higher current. The initial pH of the solution was adjusted by addition of $1.0 \text{ M} \text{ H}_2\text{SO}_4$ or 1.0 M NaOH.

In order to study the pitting corrosion of Ti electrode in a practical application, a trace level of BrO_3^- was added to the local tap water (run O), and detailed experimental conditions were presented in Table 3. All the experiments were performed at least in triplicate.

2.4. Analysis

A 5-mL sample was taken at a constant time interval and filtered using a syringe filter with 0.22-µm micropore filter membrane (LC + PVDF membrane, ANPEL Laboratory Technologies Inc., China). Each sample was stored in a refrigerator without any disposition before analysis. The concentrations of Cl⁻, Br⁻, BrO₃, NO₃⁻ and SO₄²⁻ were analyzed by a Dionex ion chromatography (IC) with an IonPac AS19 analytical column and an IonPac AG19 precolumn. Mobile phase eluent (flow rate 1.0 mL/min) for the IC was 9.4×10^{-3} mol/L Na₂CO₃ and 1.8×10^{-3} mol/L NaHCO₃. The pH was monitored using a standard glass electrode and pH meter (pHS-3C model, Leici, China).



Fig. 1. A schematic view of two-compartment electrolytic cell for BrO_3^- reduction. (a) The component of the main reactor, and (b) the structure of the sheltered zones.

| Table 2 | | | | |
|--------------|---------|-----------|------------|-------------|
| A summary of | initial | reduction | experiment | conditions. |

| Run | Sample | Terminal voltage (V) | Current (mA) | Initial pH | Initial BrO ₃ (µg/L) |
|-------------|--------------------|------------------------------|-----------------|--|------------------------------------|
| A B C | Synthetic water | 0 1.0 ± 0.1 10.0 ± 0.1 | 50 50 50 | $\begin{array}{c} 4.7 \pm 0.2 \\ 4.7 \pm 0.2 \\ 4.7 \pm 0.2 \end{array}$ | 800 ± 07 800 ± 10 800 ± 08 |

The chemical composition of solid samples collected from the Ti electrode surface was analyzed by field scanning electron microscopy coupled/energy- dispersive X-ray spectrometry (FSEM/ EDX) and X-ray photoelectron spectroscopy (XPS). FSEM/EDX was carried out on a Quanta 200 scanning electron microscope (FEI. USA). XPS was performed on an Escalab 250Xi Electron Energy Spectrometer (Thermo Scientific. USA). The images of Ti electrode before and after pitting corrosion were observed by a TM3000 microscope (Hitachi Limited, Japan).

3. Results and discussion

3.1. Pitting corrosion of Ti electrode

Pitting corrosion behavior of Ti electrode in BrO₃ solution was first investigated by potentiodynamic polarization (PP) technique. Fig. 2 shows the potentiodynamic polarization (PP) curves of the Ti electrode at solution pH 2.8, 4.7, 7.0 and 9.8, respectively. The values of corrosion potential (E_{Corr}), pitting potential (E_{Pit}), and corrosion current density (j_{Corr}) obtained from the PP curves are listed in Table 4. As showed in Table 4, when the potential screened from -2000 mV to E_{corr} , the E_{corr} gradually increased from -665 mV to -402 mV with the increasing pH values, implying that the corrosion resistance of Ti electrode is enhanced. The j_{Corr} is calculated by extrapolation of the cathodic branch of polarization curves to the E_{corr} , but it was changed irregular at the different pH (2.8– 9.8). The corrosion current density is normally proportional to the metal corrosion rate [26-28]. At the pH of 7.0, the lowest current density $(1.08 \pm 0.2 \,\mu\text{A} \cdot \text{cm}^{-2})$ was observed, which implies a lowest corrosion rate in the neutral condition.

With the potential increasing towards the positive direction, the potential finally reached the E_{Pit} , where the current density increased suddenly due to the dissolution of zero-valent titanium into activated Ti ions, such as Ti²⁺ or/and Ti³⁺. A similar corrosion behavior has been reported by Sherif et al. [29], when the pitting corrosion occurred on nanocrystalline aluminum alloys in natural seawater, the current increased rapidly in the anodic reaction due to the dissolution of zero-valent aluminum into Al(III) with the release of electrons. A higher pitting potential of zero-valent titanium was reported by Basame and White [30] that the pitting potentials were 9.61 ± 0.43 V to 100 mM chloride, and 1.61 ± 0.28 V for 100 mM bromide, respectively.

To get further sense about the pitting corrosion of Ti electrode during BrO₃⁻ reduction, the Ti electrode surface before and after pitting corrosion was observed by a TM3000 microscope. The image in Fig. 3a shows that the raw Ti electrode surface is smooth and the color is metal gray before electrochemical experiments. Also, there are many filamentous gaps distributed all over the surface of Ti electrode. After the electrochemical reduction (see in Fig. 3b), a large number of irregular deep pits formed all over the

 Table 3

 A summary of electrochemical experiment results.

| Run | Sample | pН | Current (mA) | Initial BrO $_3^-$ (µg/L) | Residual BrO ₃ (µg/L) | $K_1^{a}(\min^{-1})$ | \mathbb{R}^2 for K_1 |
|-----|-----------------|---------------|--------------|---------------------------|----------------------------------|----------------------|--------------------------|
| D | Synthetic water | 4.7 ± 0.1 | 10 | 800 | 421.5 ± 20.2 | 0.004 ± 0.0002 | 0.966 |
| E | | | 25 | 800 | 234.2 ± 12.6 | 0.006 ± 0.0003 | 0.983 |
| F | | | 50 | 800 | 195.6 ± 15.6 | 0.008 ± 0.0002 | 0.988 |
| G | | | 100 | 800 | 114.2 ± 8.9 | 0.011 ± 0.0002 | 0.984 |
| Н | Synthetic water | 2.8 ± 0.2 | 50 | 800 | 86.6 ± 7.7 | 0.012 ± 0.0005 | 0.985 |
| I | | 4.7 ± 0.1 | 50 | 800 | 195.6 ± 15.6 | 0.008 ± 0.0002 | 0.988 |
| J | | 7.0 ± 0.1 | 50 | 800 | 212.2 ± 6.7 | 0.007 ± 0.0006 | 0.989 |
| К | | 9.8 ± 0.2 | 50 | 800 | 252.2 ± 6.7 | 0.006 ± 0.0002 | 0.991 |
| L | Synthetic water | 4.7 ± 0.1 | 50 | 100 | 9.2 ± 0.2 | 0.012 ± 0.0003 | 0.913 |
| Μ | | | 50 | 200 | 35.23 ± 6.1 | 0.008 ± 0.0001 | 0.979 |
| Ν | | | 50 | 400 | 89.5 ± 5.8 | 0.007 ± 0.0005 | 0.956 |
| 0 | Tap water | 7.0 ± 0.1 | 10 | 97.5 ± 2.0 | 9.4 ± 0.4 | - | - |

^a K_1 is the pseudo-first-order kinetics rate constant.



Fig. 2. Potentiodynamic polarization curves of Ti electrode in solutions with neutral 0.5 M Na₂SO₄ solution at different pH. Reaction conditions: initial BrO₃⁻⁻ concentration 800 µg/L, temperature 25 °C.

Table 4Corrosion parameters obtained from polarization curves at different pH.

| | E _{corr} /mV | E _{Pit} /mV | E_v/mV | $j_{Corr}/(\mu A \cdot cm^{-2})$ |
|----------|-----------------------|----------------------|----------|----------------------------------|
| pH = 2.8 | -665 | 1041 | 1706 | 12.82 ± 0.5 |
| pH = 4.7 | -601 | 1191 | 1792 | 7.91 ± 0.4 |
| pH = 7.0 | -499 | 1501 | 2000 | 1.08 ± 0.2 |
| pH = 9.8 | -402 | 1390 | 1792 | 6.32 ± 0.2 |

Ti electrode surface, and the chromaticity of Ti electrode surface became dark and straw yellow. Meanwhile, few solid products were split away from the Ti electrode surface, and the surface atomic structure and chemical composition of these solid byproducts was discussed later.

The corrosion behavior of Ti electrode before and after the reduction was investigated by using cyclic voltammetry. As showed in Fig. S1 (see Supporting information), oxidation peak A and peak B were observed at -0.27 V and -0.16 V for the Ti electrode before and after the reduction, respectively. After the electrochemical reduction, Ti electrode was easy to suffer from oxidation due to the breakdown of the passive film. Meanwhile, the cathodic current of Ti electrode after reduction was larger than that of fresh Ti electrode, indicating that the reduction of BrO₃ was favorable when the pitting corrosion of Ti electrode occurred [31]. However, there was no reduction peak found in the positive and negative scans, which suggested that the pitting corrosion of Ti electrode was an irreversible process.

3.2. Effect of terminal potential on BrO_3^- reduction

To evaluate the influence of potential on BrO_3^- reduction induced by electrochemically pitting corrosion, three terminal potential, 0, 1.0, 10.0 V was applied across the Ti electrode. Fig. 4 shows the reduction of BrO_3^- at different terminal potential. Apparently, no decrease in BrO_3^- occured and no Br^- was detected during the treatment without terminal potential application (run A). When the potential was imposed at 1.0 V (run B), there was still no reduction for BrO_3^- . Pitting corrosion on the Ti electrode can't be induced in this case due to the terminal potential lower than the required pitting potential. But tiny bubbles were observed at both the Ti anode and the ACF cathode. Tiny bubbles at the surface of two electrodes were regarded as oxygen (O₂) and hydrogen gas (H₂) respectively, which forms for the electrolytic reaction of water [3].

In contrast to runs A and B, BrO_3^- removal was realized when the potential was imposed at 10.0 V (run C in Fig. 4), which was higher than the corresponding pitting potential. It can be found that $BrO_3^$ concentration was gradually decreased from 801.5 µg/L to 197.6 µg/L, and nearly 75% of removal efficiency were achieved. The end product of Br⁻ was detected in solution and its concentration increased from 0 μ g/L to 278.4 μ g/L. One interesting discovery was the mass imbalance of bromine in solution at run C. Supposing that the total bromine mass balance was achieved and Br⁻ was the only end product from BrO₃⁻ reduction, the sum of normalized concentration of Br⁻ (6.25 μ M) and residual BrO₃⁻ will be equal to initial concentration of BrO₃. However, the sum value was found to decline and only 80.2% of total bromine weight mass was achieved. The bromine lost in the reduction process should contribute to the formation of solid by-products. A similar result has also been observed by previous researchers that the NO_3^- and ClO_4^- could be reduced simultaneously at the surface of the Ti electrode, but only 81% of the total nitrogen weight mass and 86% of the total chlorine weight mass were achieved [20].

In order to confirm that BrO_3^- was reduced just owing to the pitting corrosion of Ti electrode, the Ti electrode was replaced with an activated carbon electrode, and the terminal potential of 0 V and 10 V was imposed in the experiment. As showed in Fig. S2 (see Supporting information), the concentration of BrO_3^- did not change over time at 0 V and 10 V, respectively. The results revealed that BrO_3^- reduction indeed was induced by the pitting corrosion of Ti electrode in two-compartment electrolytic cell.

3.3. Effect of electric current on BrO_3^- reduction

The DC power was applied to supply constant currents of different values, and residual concentrations of BrO_3^- were measured



Fig. 3. The SEM images of Ti electrode (a) before, and (b) after pitting corrosion.



Fig. 4. Transitions of BrO₃⁻ and Br⁻ concentration for runs A (0 mV), B ($1.0 \pm 0.1 \text{ mV}$) and C ($10.0 \pm 0.1 \text{ mV}$). Reaction conditions: initial BrO₃⁻ concentration 800 µg/L, pH 4.7 ± 0.2, current 50 mA.

over 24 h. All experiments were carried out until the DC power supply could not provide the desired stability current. Fig. 5a shows that the residual concentration of BrO₃ decreases with the current increasing. When the current raised from 10 mA to 100 mA, the residual concentrations of BrO₃ decreased from 421.5 μ g/L to 114.2 μ g/L. It suggested that higher currents accelerated the pitting corrosion which resulted in the increasing of pitting sites. Thus, an increasing amount of reactive sites leaded to a faster rate of BrO₃ reduction.

A pseudo-first-order kinetic model was used to describe the BrO_3^- transformation with the reaction time and the expression was presented as follows:

$$\ln(C_t/C_0) = -K_1t + b \tag{1}$$

where C_0 is the initial concentration of BrO_3^- , C_t is the concentration of BrO_3^- at time *t*, K_1 is the pseudo-first-order model rate constant (min⁻¹) and *t* is the contact time. The kinetic analysis of data in Fig. 5b showed that the correlation coefficients (R^2) were in the range from 0.966 to 0.984 (Table 3), indicating the suitability of the pseudo-first-order reaction kinetics to describe BrO_3^- removal. As showed in Table 3, the value of K_1 kept a low level until the current is 10 mA. When the current was over 10 mA, it began to rise with the current increasing, and then reaches a plateau of 0.011 min⁻¹ after the current of 100 mA. Within the range of 10 mA to 100 mA, the rate constant showed a linear correlation with the current ($R^2 = 0.947$, inset in Fig. 5b). There may be two electrochemical conversions for this correlation, namely direct pitting corrosion and indirect electrochemical reduction. In the initial 20 min, the removal rate of BrO₃⁻ was slow and the chromaticity of Ti electrode surface gradually from metal gray to straw yellow. It suggested that this primary process was direct pitting corrosion which destroyed the passive film on the Ti electrode surface to produce activated Ti ions, e.g., Ti²⁺ or/and Ti³⁺ [21]. Then, most of BrO₃⁻



Fig. 5. (a) Effect of current on BrO_3^- reduction, and (b) the pseudo first-order kinetic model for BrO_3^- reduction. The inset is linear plot of the rate constants (K_1) with current. Reaction conditions: initial BrO_3^- concentration 800 µg/L, pH 4.7 ± 0.2.



Fig. 6. Effect of solution pH on BrO_3^- reduction and the pseudo first-order model for BrO_3^- reduction. Reaction conditions: initial BrO_3^- concentration 800 μ g/L, current 50 mA.



Fig. 7. Effect of initial BrO_3^- concentration on BrO_3^- reduction. Reaction conditions: pH 4.7 ± 0.2, current 50 mA.

was rapidly reduced via electrochemical reaction with the active reductants (Ti^{2+} or/and Ti^{3+}). After this stage, the dominant end product of the indirect electrochemical reduction was Br^- .

3.4. Effect of initial pH on BrO_3^- reduction

Reduction of BrO_3^- under various pH conditions were investigated with a constant current of 50.0 mA. As showed in Fig. 6, the kinetic rate constants of BrO_3^- increase slightly with the decrease of solution pH. The rate constants raise from 0.006 to 0.012 min⁻¹ when the pH decreases from 9.8 to 2.8 (Table 3). It notes that the reaction rate of pH 2.8 is nearly twice as that of pH 9.8. A lower solution pH has a tendency to produce more strongly acidic conditions inside pits which promote BrO_3^- reduction [32]. A similar tendency was observed in bromate removal using an activated carbon felt electrode by Kishimoto and Matsuda [3]. The removal rate of BrO_3^- strongly depends on solution pH and the overall reaction of BrO_3^- reduction to Br^- is expressed by:

$$BrO_{3}^{-} + 6H^{+} + 6e^{-} \leftrightarrow Br^{-} + 3H_{2}O$$
 (2)



Fig. 8. Electrochemical reduction of BrO_3^- in local tap water. Reaction conditions: initial BrO_3^- concentration 800 µg/L, pH 7.0 ± 0.1, current 50 mA.

The H⁺ concentration on the electrode surface played an important role in the chemical equilibrium of the BrO₃⁻ reductive reaction as showed in Eq. (2). Pecsok and Fletcher [33] also found that when the β -alanine was used to enhance the Ti³⁺ reduction of ClO₄⁻, a large amount of black precipitate (Ti(OH)₃) was quickly formed with pH increasing from 2.3 to 6.2. The transient formation of Ti³⁺ precipitation resulted in a significant decrease in soluble Ti³⁺, then inhibited Ti³⁺ reduction of ClO₄⁻.

3.5. Effect of initial BrO_3^- concentration on BrO_3^- reduction

The electrochemical reduction of BrO_3^- at different initial BrO_3^- concentration was investigated and the results are presented in Fig. 7. The reduction rate of BrO_3^- decreased slightly with initial BrO_3^- concentration increasing from100 to 800 µg/L. When the initial BrO_3^- concentration is 100 µg/L, the rate constant is 0.012 min⁻¹ and the residual BrO_3^- is lower than the enforceable MCL of 10 µg/L. However, the rate constant at initial BrO_3^- concentration of 800 µg/L decreases to 0.008 min⁻¹ (run F) and the residual BrO_3^- raises to 195.6 µg/L, which is much larger than the enforceable MCL. Correspondingly, removal efficiency of BrO_3^- decreases from 90.11% to 75.55%. The reason could be explained that the electrochemically induced pitting corrosion can't provide enough activated multivalent Ti species to reduce BrO_3^- .

3.6. Reduction of BrO_3^- in tap water

The Cl⁻, NO_3^- and SO_4^{2-} was ubiquitous anions present in tap water systems [31,34]. Meanwhile, BrO₃ concentration has been detected in tap water and drinking water, generally at trace levels, i.e. the concentration less than 100 μ g/L [35]. In our laboratory, tap water contains $40 \pm 5 \text{ mg/L}$ of Cl⁻, $10 \pm 1 \text{ mg/L}$ of NO₃⁻, and $35 \pm 2 \text{ mg/L of } SO_4^{2-}$. $100 \mu \text{g/L of } BrO_3^{-}$ was added in tap water to investigate the influences of coexistence anions on BrO₃⁻ reduction during the electrochemical process and the results exhibited in Fig. 8. As showed in Fig. 8, the reduction of BrO_{3}^{-} maintains high efficiency in the presence of coexisting anions (Cl⁻, NO₃⁻, and SO_4^{2-}). However, the concentrations of Cl^- and NO_3^- also show decreasing trends. The decrease in chloride concentration should be attributed to the oxidation of Cl⁻ to Cl₂ [36]. Other researchers have also speculated that chloride oxidation reaction could be taken at the Ti-water interface with the formation of hypochlorite or volatile chlorite [20].



Fig. 9. Characterization of particulate by-products sloughed off from the Ti electrode. (a) FSEM of samples, (b) EDX of samples, (c) XPS spectra of Ti species, and (d) XPS spectra of Br species.

In addition, nearly 80% of NO_3^- was removed during electrochemical reduction process, which should be attributed to the conversion of NO_3^- to ammonia (NH₃), nitrogen (N₂) or nitrogen oxides. Wang et al. [20] discovered that the dominant end product of $NO_3^$ in indirect electrochemical reduction was nitrite, and the other intermediates would be formed simultaneously, such as NH₃ and nitrogen oxides. During the NO_3^- reduction, Li et al. [14] found that the reduction by-products could further efficiently be oxidized at the Ti/IrO₂-Pt anode. In contrast to the decreasing concentration of Cl⁻ and NO₃⁻, the concentration of SO₄²⁻ almost remained constant in the electrochemical process (Fig. 8). Despite the fact that Ti²⁺ and Ti³⁺ species are strong reducing agents, there was no report of SO₄²⁻ reduction by Ti²⁺ or Ti³⁺. U. Kölle and P. Kölle developed a method to produce Ti(II) by reductive dissolution of zero-valent titanium in the presence of H₂SO₄ and fluoride [37]. Park et al. [38] reported a method to degrade perchlorate using Ti(II) which produced from zero-valent titanium by using H₂SO₄ and fluoride. These results indi-



Fig. 10. Schematic diagram of BrO_3^- reduction mechanism induced by electrochemically pitting corrosion at the Ti electrode surface.

rectly suggested that the Ti^{2+} or Ti^{3+} was stable in sulfate solution. The slight decline of SO_4^{2-} in this study could be due to its adsorption onto TiO_2 generated in electrochemical oxidation. This is analogous to the observation that SO_4^{2-} could be adsorbed onto the TiO_2 powder [39].

3.7. Proposed mechanisms for electrochemical reduction

To explain the mechanism of BrO_3^- reduction at Ti electrode, the particulate by-products of electrochemical reduction sloughed off from the Ti electrode were collected and characterized by FSEM/ EDX and XPS. EDX analysis in Fig. 9b shows clearly several peaks, which represent Ti, O, S, Br and their weight mass is 40.36%, 49.35%, 3.27% and 0.55%, respectively. These analysis results demonstrate that the lost bromine is constructed into the particulate by-products structure and 3.27% of S was ascribed to the adsorptive SO_4^{2-} derived from acidity regulator H₂SO₄. The valence state of Ti and Br was further investigated by XPS technique (Fig. 9c-d). After the electrochemical reduction, the Ti electrode exhibited spin-orbit doublet, i.e. $Ti(2p_{1/2})$ at 458.99 eV and Ti $(2p_{3/2})$ at 464.69 eV (Fig. 9c), which were attributed to the presence of TiO₂. In general, Ti electrode is incapable of reducing halide ions, such as CIO_4^- , BrO_3^- and NO_3^- , since Ti electrode is usually protected by a gray thick (0.5-7.0 nm) oxide film which spontaneously forms in air. However, application of an anodic potential or low level current on Ti electrode can accelerate and generate pitting corrosion, which breaks down the passive film effectively and produces reactive Ti ions, e.g., Ti²⁺ and Ti³⁺ [21]. Activated Ti ions (Ti²⁺ and Ti³⁺) as strong reductants can availably stabilize oxygen atoms from oxo-anions. The solid compounds of TiO₂(s) would be finally formed on the Ti electrode surface. Based on the discussion above, pitting corrosion of Ti electrode may have occurred as following procedure:

$$Ti \xrightarrow{+e^{-}} Ti^{2+} \xrightarrow{+e^{-}}_{+H_20;0} Ti^{3+} \xrightarrow{+e^{-}}_{+H_20;0} Ti^{4+}(TiO_2)$$
(3)

Fig. 9d shows the binding energy of Br (3d) at 68.69 eV, which confirms the presence of Br⁻ in the solid TiO₂. The loss of total bromine as discussed in the previous section could be explained that the BrO₃⁻ was reduced to Br⁻ or a small number of intermediates such as BrO₂, HBrO₂, HBrO, and Br₂ [3], and then adsorbed into TiO₂ lattice.

Considering the adsorption behaviors of TiO_2 lattice, the experiments were supplemented to investigate the adsorption of BrO_3^-

(800 µg/L) and Br⁻ (800 µg/L) on commercially available P25 TiO₂ powder (AnWeiAn Lab Equipments CO., Ltd, Beijing, China). As showed in Fig. S3 (see Supporting information), Br⁻ exhibited more strong adsorption on TiO₂ powder than BrO₃⁻ when the dosage of TiO₂ powder was 1.0 g/L. At low pH 2.8, the residual concentration of BrO₃⁻ and Br⁻ was 650 µg/L and 583 µg/L after 180 min. With the initial pH increasing to 9.8, the removal efficiency of Br⁻ and BrO₃⁻ declined to only 10.1% and 5.2%, respectively. These adsorption behavior confirmed that the amount of Br⁻ and BrO₃⁻ adsorbed on TiO₂ was very little. Analogous results were observed by Kazarinov and co-workers that some anions have a relatively low adsorbability on TiO₂ [40].

Generally, the mechanism for BrO₃⁻ reduction can be proposed via two electrochemical conversions, direct pitting corrosion and indirect electrochemical reduction. A schematic view was referred to describe these two conversions (Fig. 10). Firstly, upon the application of an anodic current at the Ti electrode, the passive film of Ti electrode was electrochemically induced by pitting corrosion or direct oxidation to produce activated Ti ions, e.g., Ti²⁺, Ti³⁺, which were considered as strong reducing agents. Then, the BrO₃⁻ was transported from the solution to the pits of Ti electrode surface and simultaneously reduced to Br⁻ with Ti²⁺ or Ti³⁺ species. The Ti²⁺ or Ti³⁺ species was finally oxidized to stable TiO₂(s) while a part of Br⁻ was doped onto TiO₂ lattice. In addition, tiny bubbles were observed at both the surface of the electrode, which belonged to O₂ and H₂ at Ti anode and ACF cathode, respectively.

4. Conclusions

This study explored a novel technology to reduce BrO₃ base on electrochemically induced pitting corrosion of Ti electrode. The corrosion potential (E_{Corr}) was gradually increased from -665 mVto -402 mV with the pH values increasing from 2.8 to 9.8, and the pitting potential (E_{Pit}) of Ti electrode was 1501 mV (SHE) at pH of 7.0. Related experiments were also conducted to evaluate the effects of terminal potential, electric current, initial pH and initial BrO₃ concentration on BrO₃ reduction. Experimental results showed that it was beneficial to reduce BrO_3^- at lower pH and lower initial BrO_3^- concentration. The electrochemical treatment of bromate-contaminated tap water indicated that the reduction of BrO_3^- was still operative in the presence of coexisting anions $(Cl^{-}, NO_{3}^{-}, and SO_{4}^{2-})$. The mechanism of BrO₃ reduction was further investigated by surface analysis of the solid end products remaining on the Ti electrode using SEM/EDX and XPS. The $BrO_3^$ was firstly transported from the solution to the pits of Ti electrode surface and then indirect reduction with activated Ti ions (Ti²⁺ and Ti³⁺).

Although BrO_3^- is effectively reduced during electrochemically induced corrosion of Ti electrode, this process may not be immediately applicable to BrO_3^- treatment. There are three challenges to be overcome: (1) high energy costs, (2) generated by-product, and (3) unwanted Ti dissolution during treatment of trace levels of BrO_3^- . In our opinion, lowering the pitting potential of Ti electrode is critical to overcoming the high cost of the electrochemical process and production of by-product, and it will be more feasible in field application.

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Appendix A. Supplementary data

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