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The bromamine acid removal from aqueous solution using electro-Fenton and Fenton systems

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ABSTRACT

The bromamine acid (BA) removal is investigated in the electro-Fenton and Fenton systems. The BA is an important dye intermediate with difficult biodegradation. So removing BA with advanced oxidation processes may provide common information on anthraquinone dye wastewater treatment. BA has a typical quinonoid structure. It means that the degradation of BA may be coupled with a series of quinone–hydroquinone conversion reactions in these two systems. As a result, two distinct degradation processes for BA are shown in the electro-Fenton and Fenton systems. For a Fenton system, the BA degradation is divided into two phases: the BA quickly transforms into a hydroquinone structure (BAH) in the first few minutes probably due to the formation of a ternary HQ–Fe–H_2O_2 complex, and then the BAH is oxidized by the $^{\bullet}OH$; While, in the electro-Fenton system, the BAH is not accumulated during its degradation. Fenton reaction is the main reaction in the electro-Fenton system.

Keywords: Electro-Fenton; Fenton; Bromamine acid; Degradation

1. Introduction

Advanced oxidation processes (AOPs) have been widely used to treat organic pollutants in an aqueous solution based on the hydroxyl radical ($^{\bullet}OH$) [1–3]. Recently, there has been renewed interest in the use of Fenton-type AOPs, which generate the $^{\bullet}OH$ from hydrogen peroxide and iron compounds (Reaction 1) [3,4].

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\cdot}OH + Fe^{3+} + OH^- \qquad \text{(Reaction 1)}$$

Bromamine acid (BA) is an important dye intermediate with difficult biodegradation, so its degradation may provide common information on anthraquinone dye wastewater treatment with AOPs. The more interesting fact is that the BA has a typical quinonoid structure (Fig. 1), which means that the degradation of BA may couple with a series of electrochemical or chemical reactions in the electro-Fenton or Fenton systems.

In the electro-Fenton system, hydrogen peroxide (H_2O_2) can form in suit by the two-electron of oxygen reduction, while Fe^{2+} can also be regenerated on the cathode. Thereby, many cathode materials have been attempted to be used to enhance the electrogeneration of H_2O_2, such as gas diffusion electrode [5,6], activated carbon fiber [7], and traditional carbon electrode modified with a catalytic quinonoid compound [8]. In our previous research, the graphite electrode modified

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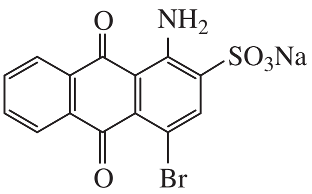


Fig. 1. Molecular structure of BA.

with polypyrrole/anthraquinonedisulfonate (PPy/AQ DS) composite film had shown an improved electrocatalytic performance for electrogenerated H_2O_2 in an electro-Fenton system [8,9].

On the other hand, Fe ion is proved to be efficient to promote the formation of $^{\bullet}OH$; however, $^{\bullet}OH$ will be consumed by the competitive Reaction 2:

$$^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad \text{(Reaction 2)}$$

It has been observed that enhancing Fe ion concentration may contrarily decrease the efficiency of the electro-Fenton system. Meanwhile, a high Fe ion concentration would result in the formation of an iron sludge ($Fe(OH)_3$) during the electro-Fenton oxidation process. Thus, Fe^{2+} regeneration by the reduction of Fe^{3+} species on the cathode to a small extent can availably solve the conflict in an Fe ion concentration [4,10].

The aminoanthraquinone polymer modified electrode is used as the cathode in the electro-Fenton system in the present work. Poly-1,5-diaminoanthraquinone (P15DAAQ) has shown an excellent electrocatalytic activity for oxygen reduction owing to of its high surface concentration of the reactive sites and the π–π stacked structure [11]. Besides the H_2O_2 generation, Fe^{3+} reduction was also investigated on the P15DAAQ modified Pt electrode.

Although the electro-Fenton system has shown much advantage for soluble pollutants' degradation, the Fenton system is easier to be created with low equipment cost [12]. The present work studies the BA removal from an aqueous solution using the electro-Fenton and Fenton systems. The different reaction processes was analyzed with electrochemical methods, spectrophotometry, and TOC detection.

2. Methods

2.1. Chemicals

BA (>99.5% purity) was purchased from the Shanghai Chemical Reagents Company. Other chemicals, such as Na_2SO_4, H_2SO_4, $Fe_2(SO_4)_3$, $TiOSO_4$, and H_2O_2, were either of reagent or analytic grade and used as received. The concentration of H_2O_2 was freshly determined with $KMnO_4$ solution (5.0125 mM) before use each time. The N_2, O_2-saturated 0.1 M H_2SO_4 solutions were obtained through bubbling N_2 and O_2 for 15 min, respectively. H_2SO_4 (0.1M) was diluted by 0.1 M Na_2SO_4 to obtain the required pH with a similar ion concentration. The value of pH was measured with a pB-10 pH-meter (Sartorius AG, Germany).

2.2. Electrochemical experiments

Electrochemical measurements were performed by a Potentiostat/Galvanostat Model 263A and a frequency response detector FRD 100 of Princeton Applied Research. A Pt electrode of 0.8 cm^2 was used for cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. The EIS was obtained at the frequencies between 0.01 Hz and 100 kHz, with an AC-amplitude of 10 mV_{rms}. All the potential values were reported against the SCE.

The Electrochemical deposition of P15DAAQ on the Pt electrodes was carried out by potential cycling between −0.3 and +1.8 V in an electrolyte of propylene carbonate with 10 mM 1,5-diamino-9,10-anthraquinone +0.1 M tetrabutylammonium perchlorate +0.45 M CF_3COOH at a scan rate of 20 mV/s at 10 ± 0.2°C. Other details on the preparation condition were described in our previous report [11]. P15DAAQ of different thickness was obtained by setting the number of cycles during the CV. The surface concentration of P15DAAQ electropolymerized by six cycles is 5×10^{-8} mol/cm^2 evaluated by Q/nFA, where $n = 2$, Q is the charge of cathodic peak of the last cycle during the electropolymerization and A is the surface area of the work electrode.

2.3. Electro-Fenton system

The potentiostatic electrolysis was conducted in an undivided cell of 2.3 cm in diameter and 25 ml solutions. The electro-Fenton system was performed with a 3 cm^2 Pt/P15DAAQ electrode as the cathode and a 4 cm^2 one as a counterelectrode. Pure oxygen was insufflated into the cell regulated with a flowmeter through a porous pipe diffuser placed exactly under the cathode. The experiments were also controlled with a Potentiostat/Galvanostat Model 263A.

2.4. Fenton system

The degradation of BA in a Fenton system was carried out in a 50 ml glass reactor with 4 mM H_2O_2, 80 mg/L BA solution (pH = 2.2), and 2 mM Fe^{3+}. Both the electro-Fenton and Fenton systems were stirred with a Teflon-coated magnetic stir bar and measured at an ambient temperature.

2.5. Analytical methods

The BA was analyzed with spectrophotometry (pPharmaspec, V-1700, Japan), and its residual concentration was measured at $\lambda = 485$ nm. The TOC analyses were carried out using a Shimadzu 5050 TOC-V_{CPH} analyzer. All samples extracted from the treated solutions were filtered through a 25 μm pore size filter paper before the analysis.

3. Results and discussion

3.1. Electrochemical behavior for BA

The BA is a typical quinonoid compound, so its electrochemical behavior should be considered in the electro-Fenton system. In fact, BA has shown an electrochemical reduction reaction in the CV research on an electrolysis system similar to a electro-Fenton system (Fig. 2). As can be seen, the BA showed its reduction current at the potential range of −0.2 to 0.5 V at the Pt/P15DAAQ electrode.

A constant potential experiment was carried out in a H_2SO_4/Na_2SO_4 solution with 77 mg/L BA (pH = 2.2, oxygen free) with cathodic potential at −0.2 V for 30 min. As the UV–Vis spectrum in Fig. 3 shows, the absorption peaks at 485, 230, and 250 nm decreased, while the side peak at 280 nm increased. This side peak corresponds to a hydro-quinonoid structure, implying a change in the BA structure. The BA concentration after electrolysis is 59 mg/L as calculated by the absorption peaks at 485 nm. Provided the reduction reaction for the BA is Reaction 3 in Table 1, the calculated charge for Q/HQ reaction is 0.28 C according to Eq. (1).

$$Q_r = n_{BA}(C_0 - C_t)VF/M_{BA} \tag{1}$$

where the n_{BA} ($n_{BA} = 2$) is the transferred electron for reaction 3, C_0, C_t are, respectively, the BA concentrations before and after the electrolyte, V is the volume of BA solution, and the M_{BA} is the molecular weight of BA. Meantime, the recorded charge is 0.39 C during the constant potential experiment, which is close to the calculated charge (0.28 C). Thus, the charge transferred during the BA reduction accorded with the 2-electron reduction reaction. This confirms the proposed reaction 3 during the BA reduction. Meanwhile, the constant potential experiment with an applied potential at 0.7 V proves the reversibility of a possible Reaction 3.

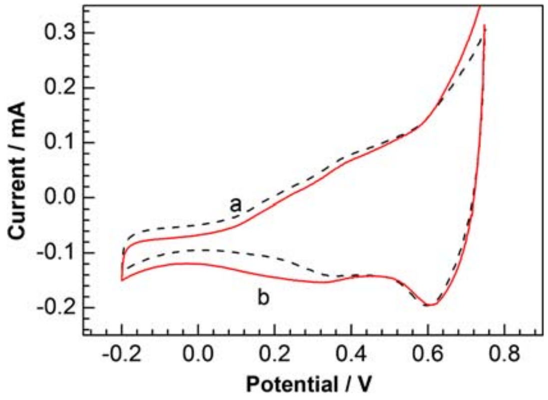


Fig. 2. Cyclic voltammograms of Pt/P15DAAQ electrode (3 cm^2) in H_2SO_4/Na_2SO_4 (pH = 2.2) solution (a), with 80 mg/L BA (b) (oxygen free), scan rate: 20 mV/s.

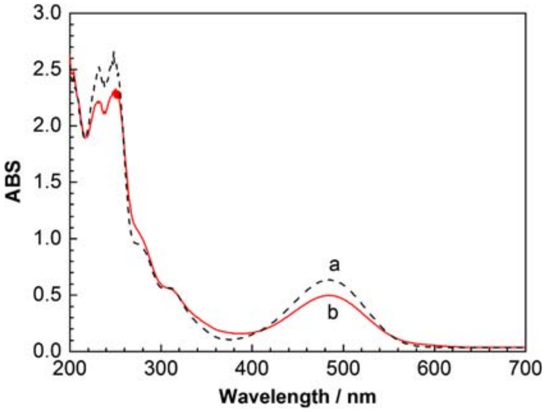
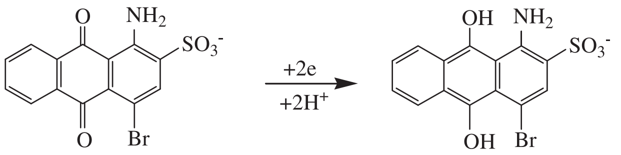


Fig. 3. UV–Vis spectrum of 80 mg/L BA solution (pH = 2.2, oxygen free) before (a) and after (b) electrolysis with the Pt/P1,5-DAAQ electrode at −0.2 V for 30 min.

3.2. Degradation of BA in the electro-Fenton system

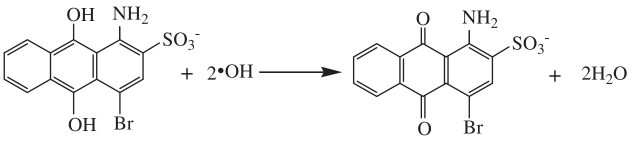
The reduction characteristic of BA means that it would contend for electrons with Fe^{3+} and oxygen on the cathode during the electro-Fenton reaction process. So, the standard rate constants for BA, Fe^{3+} and oxygen reduction [11] on Pt/P15DAAQ electrode were compared in Table 1. The standard rate constants for BA and Fe^{3+} reduction were calculated with the EIS using a equivalent circuit model (detailed data are not shown) [11]. Though these standard rate constants were obtained in the existence of a single reduction reagent, they were measured in the same solution and under the same cathodic potential. They also reflected the competition for the three reagents in the real electro-Fenton system to a certain extent. Comparatively, BA reduction is much slower than Fe^{3+} and oxygen

Table 1
Standard rate constant for the reaction on the cathode in a electro-Fenton system

No.	Reaction	Standard rate constant ($\times 10^{-5}$ cm/s)
3		1.16
4	$Fe^{3+} + e \rightarrow Fe^{2+}$	12.6
5[11]	$O_2 + 2H^+ + 2e \rightarrow H_2O_2$	34.2

reduction, and oxygen reduction reaction is the main reduction reaction. This means that the Fenton reaction would be the main reaction in this electro-Fenton system.

Furthermore, the UV–Vis spectra in Fig. 4 obtained during electro-Fenton degradation of BA show a strong decrease in the absorption peaks at 485, 230, and 250 nm, without the emergence the side peak at 280 nm as shown. This reflects that the BA with a hydro-quinonoid structure (BAH) did not accumulate during the electro-Fenton process. According to previous reports on the degradation of anthraquinone and benzoquinone dye in the Fenton system [4,13–20], $^{\bullet}OH$ could not only oxidize the C–C bonds beside the carbonyl in the anthraquinone structure, but it could also attack the C–C bonds beside the hydroxyl group in the hydroquinone structure. So the possible oxidant reaction of $^{\bullet}OH$ may bifurcate into two parts: (I) BAH could be oxidized and further converted into phthalic acid by $^{\bullet}OH$ directly [16,17]; (II) BAH could also be oxidized back to BA by $^{\bullet}OH$ (Reaction 6) and then degrade.



(Reaction 6)

3.3. Chemical behavior of BA

Though, BA has shown an active electrochemical redox behavior, its chemical characteristic is relatively stable. We have studied the oxidant action of H_2O_2 to BA. As shown in Fig. 5, BA did not show a change in structure when 1 mM H_2O_2 was added to the BA solution and stirred for 1 h. The change in absorbance at 200–250 nm should be the result of having added the H_2O_2. This phenomenon reflects the fact that H_2O_2 cannot oxidize the BA; meanwhile, it can also prove that the degradation of BA in the electro-Fenton system is due to the attack of $^{\bullet}OH$.

3.4. Degradation of BA in Fenton system

The Fenton reagent was also used to degrade the BA. In this reaction process, the degradation of BA was completely different from the situation in the electro-Fenton system. The color of BA could fade away within 15 min. Spectrophotometry was frequently used to analyze this process. As Fig. 6 shows, the absorbance peak at 485 nm had almost disappeared at about the seventh min. Meanwhile, an absorbance peak emerged at 280 nm, which was proposed to correspond to the BAH according to the result of electro-Fenton research (Fig. 3). Then this absorbance peak gradually weakened as the Fenton reaction went.

From the spectrophotometric analysis, degradation of BA in the Fenton system can be divided into two steps: in the first step, the BA was reduced to BAH quickly; in the following step, the formed BAH began to degrade gradually.

Considering that the BA is stable to H_2O_2, the added Fe^{3+} is suggested to assist in the electron transport between H_2O_2 and Fe^{3+}. So the quick formation of BAH is supposed to have been due to the generation of a ternary HQ–Fe–H_2O_2 complex [1]. Then, the degradation of BA took place in the next step. Otherwise, the TOC analysis proved that the TOC removal mainly took place in the second step.

4. Conclusion

Electrochemical experiments prove that BA reduction reaction could happen on the cathode to form BAH. However, the formed BAH does not accumulate and could be oxidized by the $^{\bullet}OH$ directly during its

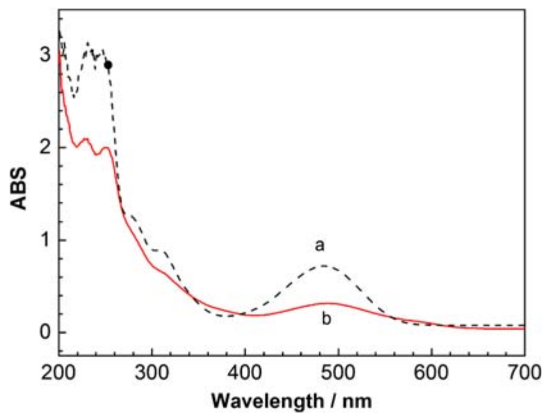


Fig. 4. UV–Vis spectrum of a BA solution before (a) and after (b) electrolysis at −0.2 V for 30 min in an electro-Fenton system.

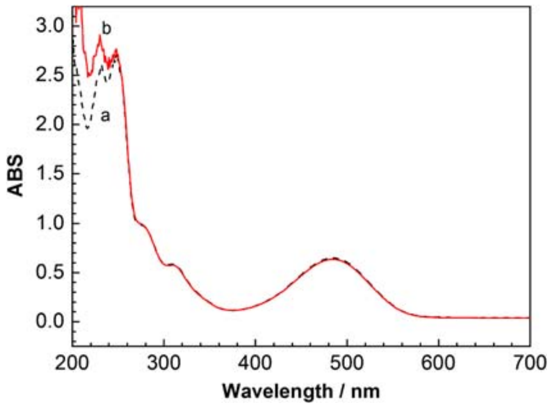


Fig. 5. UV–Vis spectrum of BA solution (pH = 2.2) (a) and after stirring with 1 mM H_2O_2 for 60 min (b).

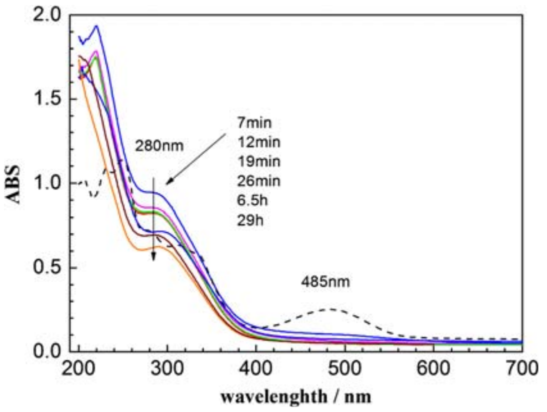


Fig. 6. UV–Vis spectrum of a BA solution (pH = 2.2) (----) and after stirring with 4 mM H_2O_2 and 2 mM Fe^{3+} at different reaction time. All the solutions have been diluted with water of the same volume before the measurement.

degradation process in the electro-Fenton system. The degradation of BA in the Fenton reaction process could be divided into two steps: the BA transfers into BAH quickly probably for the formation of a HQ–Fe–H_2O_2 complex; then the formed BAH happens to degrade. Comparatively, an electro-Fenton system avoids wasting H_2O_2 or charge for the formation of BAH, so it shows the superiority to Fenton system for removing the BA.

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