

Short Communication

Indirect Electrochemical Synthesis of 2-nitro-4-methylsulfonyl Benzoic Acid Mediated by $\text{Cr}^{3+}/\text{Cr}^{6+}$

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A new indirect electrolytic synthesis of 2-nitro-4-methylsulfonylbenzoic acid was adopted in this study. The influence factors related to the processes of liquid phase oxidation of 2-nitro-4-methylsulfonylbenzoic acid and electrochemical oxidation of Cr^{3+} were investigated, and indirect electrochemical synthesis of 2-nitro-4-methylsulfonylbenzoic acid was also conducted. The experimental results showed that concentrations of H_2SO_4 , feed ratio and solution temperature had significant influence on oxidative ability and electrochemical reactivity of chromium ions. The highest yield of 2-nitro-4-methylsulfonyl benzoic acid (49.4%) could be obtained during liquid phase oxidation with feed ratio of 1:4 in 7.0 mol/L H_2SO_4 at 95°C. The current efficiency of electrochemical oxidation of Cr^{3+} could reach up to 99% with current density of 5 A/dm² at 35°C. The tests were cycled for eight times at the optimal conditions, and the average yield of 2-nitro-4-methylsulfonyl benzoic acid and current efficiency of electrochemical oxidation of Cr^{3+} were 47.9% and 85.2% respectively. These indicated that the system has good stability and this technology could have a good prospect of commercialization.

Keywords: 2-nitro-4-methylsulfonyl toluene, 2-nitro-4-methylsulfonyl benzoic acid, chromium sulfate, chromium trioxide, indirect electrochemical oxidation.

1. INTRODUCTION

2-nitro-4-methylsulfonyl benzoic acid (BA) is an important intermediate for the preparation of mesotrione which is a high efficiency herbicides. There are a lot of reports relating to the synthesis of BA, in which the oxidation method was usually adopted, such as method of sodium dichromate oxidation, potassium permanganate oxidation and nitric acid oxidation. However, those methods have

been gradually abandoned due to the large amount of waste generated in producing process which was difficult to deal with. Thus, we need to find a new synthetic method to overcome these deficiencies.

The synthesis of organics with electrochemical technology is one of the simplest, cheapest and efficiency methods. It uses electrons as the oxidant or reductant instead of chemical oxidant or reductant, which is favourable to separation of the target product. Electrochemical synthesis method can normally be divided into direct electrochemical and indirect electrochemical synthesis. 2-nitro-4-methylsulfonyl toluene (NMST), which is the raw material of BA used in this paper, is slightly soluble in water. Thus, it may need supporting electrolyte by using the direct electrochemical, which makes the product difficult to separate. Besides, NMST and other aromatic compounds are easy to form tar-like polymer on the electrode which led to the passivation of the electrode[1]. This indicated that the ideal way for BA is the indirect electrochemical synthesis method. There were already lots of literatures about the use of indirect electrochemical synthesis mediated by $\text{Cr}^{3+}/\text{Cr}^{6+}$, $\text{Mn}^{2+}/\text{Mn}^{3+}$, $\text{Ce}^{3+}/\text{Ce}^{4+}$ and other ions [2-9]. Based on the literatures, we knew that the indirect electrochemical oxidation by using $\text{Ce}^{3+}/\text{Ce}^{4+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ as the mediator was mainly used to synthesize quinones and aldehyde, while indirect electrochemical oxidation by using $\text{Cr}^{3+}/\text{Cr}^{6+}$ as the mediator was mainly used to synthesize acid. BA is an acid which has several electron-withdrawing groups, and the oxidizability of Mn^{3+} and Ce^{4+} cannot meet the demand of oxidation, while the oxidizability of Cr^{6+} may be enough. In the present work, for the electrosynthesis of BA, $\text{Cr}^{3+}/\text{Cr}^{6+}$ has been used as the mediator following the ex-cell method (Figure 1). The indirect electrochemical synthesis process can be operated in a closed loop which consisted of the electrogeneration of a Cr^{6+} solution and the oxidation of NMST. After work up, the BA and a Cr^{3+} solution were obtained. The Cr^{6+} solution can be reused for the electrogeneration of the initial Cr^{3+} solution. Thus, there were no problems with effluents contaminated by chromium salts. In this paper, the influence factors related to the process of liquid oxidation of NMST and electrochemical oxidation of were investigated, and the indirect electrochemical synthesis of BA with cyclic tests was also conducted.

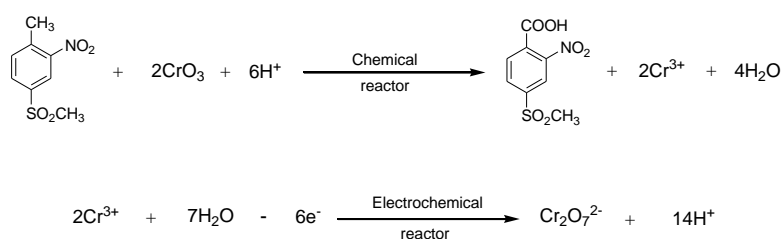


Figure 1. Electrochemical indirect synthesis of the BA using the $\text{Cr}^{3+}/\text{Cr}^{6+}$ system

2. EXPERIMENTAL

2.1. Chemicals and Instruments

The reagents used in this study included CrO_3 , 99%, $\text{Cr}_2(\text{SO}_4)_3$, 99%, 2-nitro-4-methylsulfonyl toluene (NMST), 99%, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, NaOH , NaCO_3 , H_2SO_4 , H_3PO_4 , N-phenyl anthranilic acid and Petroleum ether. All reagents were of analytical grade reagents.

RST5200E electrochemical workstation was purchased from Suzhou Risetest. RXN-605D regulated DC power was purchased from ShenZhen Zhaoxin. JJ-1 constant speed digital mechanical stirrer and DK-S24 constant temperature water bath were purchased from Jintan Universal Scientific Instrument.

2.2. Experimental Procedure

2.2.1. Liquid-phase oxidation

A 250ml four-necked flask was prepared by adding a certain amount of aqueous H₂SO₄ solution of CrO₃. We added 4.3g of NMST after the solution was heated to the desired temperature. And then, the reaction was stopped after 6 h. After cooling to the room temperature, the product could be easily obtained because of the precipitation of BA in the reactive solution.

2.2.2. Electrochemical oxidation of Cr³⁺

The electrochemical oxidation of Cr³⁺ carried out in a homemade electrochemical cell with a homogeneous cation exchange membrane. The self-made PbO₂/Pb and Pb electrodes were used as the anode and cathode respectively[10,11]. The H₂SO₄ solution and H₂SO₄ solution with Cr₂(SO₄)₃ were used as the catholyte and anolyte, respectively.

The Cr⁶⁺ content in the solution was determined by titration with ammonium ferrous sulfate. The N-phenyl anthranilic acid was used as the indicator. When the color of the solution changed from red to yellowish green, the titration was arrived at the end point. The current efficiency can be calculated by the equation

$$\eta = \frac{c2 - c1}{It} VF \times 100\% \quad (1)$$

Where *c1* and *c2* represent the concentration of Cr⁶⁺ before and after the electrochemical oxidation respectively, *V* is the volume of electrolyte, *F* is the Faraday constant, *I* is electrochemical current and *t* is the electrolysis time.

3. RESULTS AND DISCUSSION

3.1. Liquid-phase oxidation of BA

The process of indirect electrochemical synthesis of BA by using Cr³⁺/Cr⁶⁺ as mediator including two aspects: liquid-phase oxidation reaction between Cr⁶⁺ and NMST and electrochemical oxidation of Cr³⁺. Before exploring the factor of regeneration of Cr³⁺/Cr⁶⁺, the effect of reaction temperature, H₂SO₄ concentration, and feed ratio (*n*(NMST) : *n*(Cr⁶⁺)) on liquid-phase oxidation reaction was investigated.

3.1.1. The effect of feed ratio

Figure 2 showed the effect of feed ratio on yield of BA in the 7 mol/L H₂SO₄ solution. As shown in Figure 2, the yield of BA increased from 29.6% to 49.4% with increase of the feed ratio from 1:2 to 1:4. Thus, it was obtained that the increase of the feed ratio may be beneficial to the yield of BA. However, with the further increasing of the feed ratio, the yield of BA remained about the same. This indicated that 1:4 is the optimal feed ratio. We also found that the reaction solution was green after the reaction finished, when the feed ratio was between 1:2 and 1:4. This was indicated that all the Cr⁶⁺ has been reduced into Cr³⁺, and the NMST has not been fully oxidized by the Cr⁶⁺. However, when the feed ratio exceeded 1:4, the color of the solution was brownish green. This phenomenon could be explained that the amount of Cr⁶⁺ was enough and the NMST was totally oxidized.

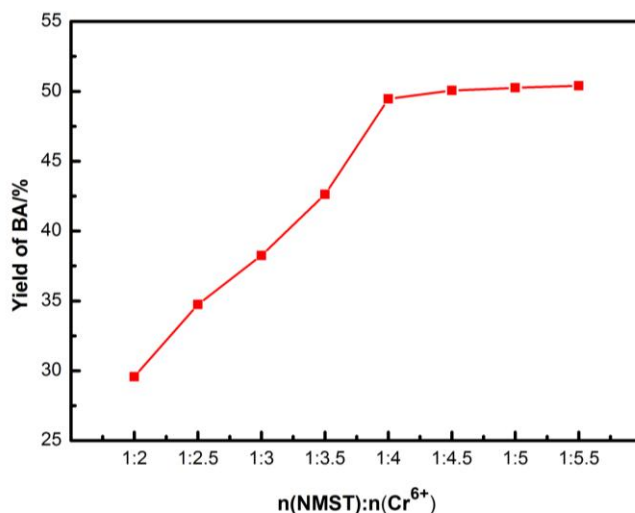


Figure 2. Effect of feed ratio on yield of BA c (H₂SO₄)=7 mol/L, T=95°C

3.1.2. The effect of temperature

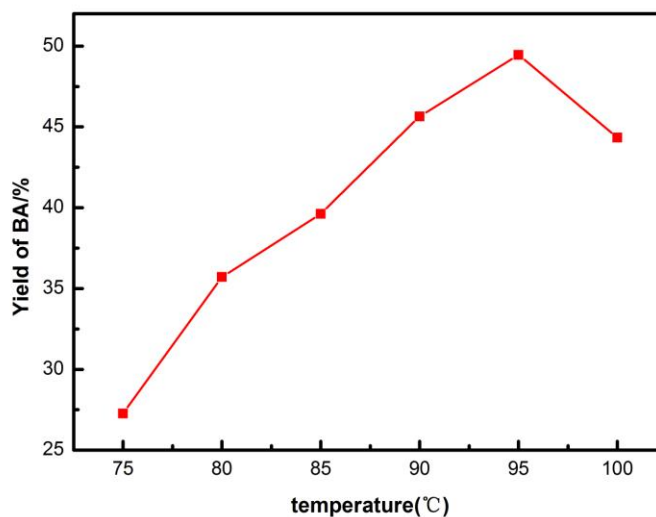


Figure 3. Yields of BA at various reaction temperature n (NMST) : n (Cr⁶⁺)=1:4, c (H₂SO₄)=7 mol/L

Figure 3 showed the evolution of yield of BA and the reaction temperature in 7.0 mol/L H₂SO₄. As shown in Figure 3, the yield of BA increased from 27.3% to 49.4%, when the initial temperature increased from 75 °C to 95 °C. However, as the reaction temperature raised to above 95 °C, the yield of BA decreased. This indicated that increasing the temperature during the liquid phase oxidation process was beneficial to the reaction. But when the temperature was above 95 °C, the yields of the byproducts increased. This led to the decreasing of the yield of BA. In view of the above experimental results, the actual reaction temperature was limited to 95 °C. Compared to the traditionally nitric acid oxidation method, the operating temperature of our work was mild.

3.1.3. The effect of sulfuric acid concentration

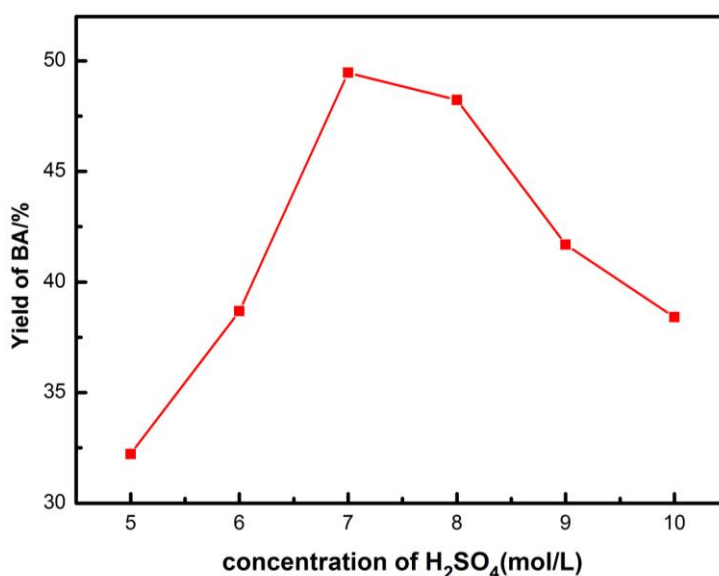


Figure 4. Effect of concentration of H₂SO₄ on yield of BA n (NMST) : n (Cr⁶⁺)=1:4, $T=95^{\circ}\text{C}$

The previous research indicated that the concentration of H₂SO₄ had a great influence on the experimental result. Therefore, it was worthy to study the relationship between the yield of BA and H₂SO₄ concentration. As shown in Figure 4, it was found that the yield of BA increased firstly with the increase of the H₂SO₄ concentration which was under 7 mol/L. At the further increasing of H₂SO₄ concentration, we found that the yield of BA was decreased. This was indicated that the optimal H₂SO₄ concentration was 7 mol/L. Under conditions of low acid concentration, the yield of BA increased with the increase of the concentration of H₂SO₄, which may resulted from the incidentally of Cr⁶⁺ under the low acid concentration. The increase of acid concentration restrained the hydrolysis, which was conducive to the reaction of liquid-phase oxidation. But when the H₂SO₄ concentration was higher than 7 mol/L, the yield decreased obviously, which was due to the excessive acid concentration generating more side reactions at the same time[12]. In summary, 7 mol/L was the favorable concentration in the reaction of liquid-phase oxidation.

3.2. Electrochemical oxidation of Cr^{3+}

Electrochemical oxidation of Cr^{3+} is an important step in the process of indirect electrochemical synthesis, which directly determines industrial application of the indirect electrochemical synthesis system. Thus, we have investigated the influencing factors, such as temperature, current density and concentration of H_2SO_4 , which were concerning of the current efficiency.

3.2.1. The effect of temperature

As we known, the increase of the reaction temperature usually makes the acceleration of the electrochemical reaction and promotion of the electrolyte conductivity, which could affect the current efficiency. Figure 5 showed the current efficiency of electrochemical oxidation of Cr^{3+} changing with temperature. As shown in Figure 5, the current efficiency increased from 75.6% to 99%, when the temperature increased from 20 °C to 35 °C. However, the anode current efficiency decreased when the temperature was more than 35°C. This phenomenon can be explained by the so that acceleration of the hydrolysis reaction of chromium ion by elevating the operating temperature [13]. Therefore, according to the experimental results, the electrolysis temperature was controlled at 35 °C in the following work.

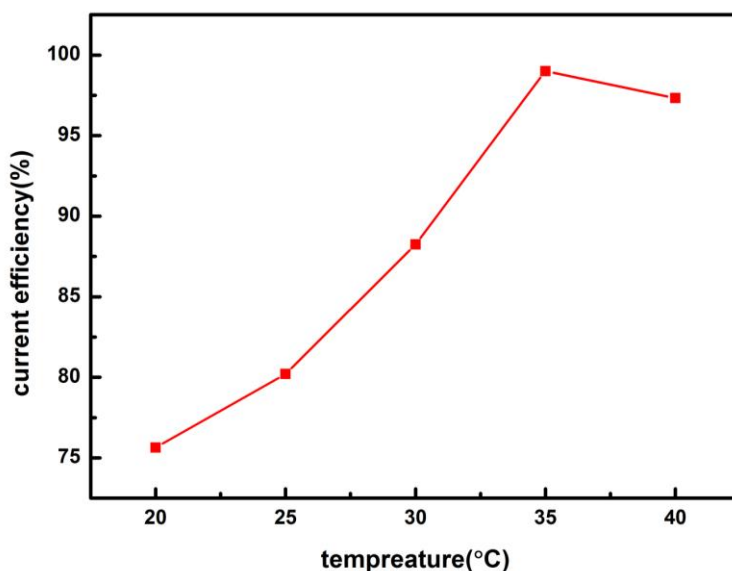
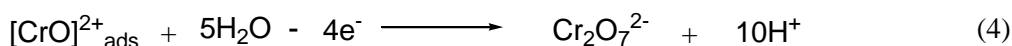
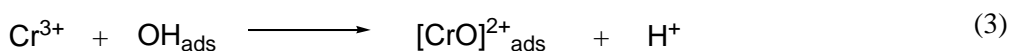


Figure 5. Effect of temperature on current efficiency $j=5 \text{ A/dm}^2$, $c(\text{H}_2\text{SO}_4)=4 \text{ mol/L}$

3.2.2. The effect of current density

The current density in the electrochemical oxidation is a crucial parameter, which directly affects the current efficiency [14]. As shown in Figure 6, with the increase of the current density, the current efficiency increased firstly with current densities when it was less 5 A/dm^2 . And with further

increasing of the current density, the current efficiency decreased. This was indicated that the optimal current density was 5 A/dm². In theory, the consumption of OH_{ads} has two kinds of ways at the PbO₂ electrode surface, which are as follows [15,16]: (1) OH_{ads} gradually oxidized Cr³⁺ into Cr₂O₇²⁻; (2) two OH_{ads} combine to produce the O₂ and H₂O, which led to the oxygen evolution. These processes are represented by the equations shown below.



With the increase of the current density, the concentration of the OH_{ads} around the electrode will increase. Meanwhile, the rate constant of Cr³⁺ oxidation increase which leads to the reduction of the activation energy. However, with the further increasing of the current density, the intensification of electrode polarization make the oxygen evolution reaction occur easily. Thus, the current efficiency of the oxidation medium regeneration will decrease. In this frame, the current density with 5 A/dm² was appropriate in our work.

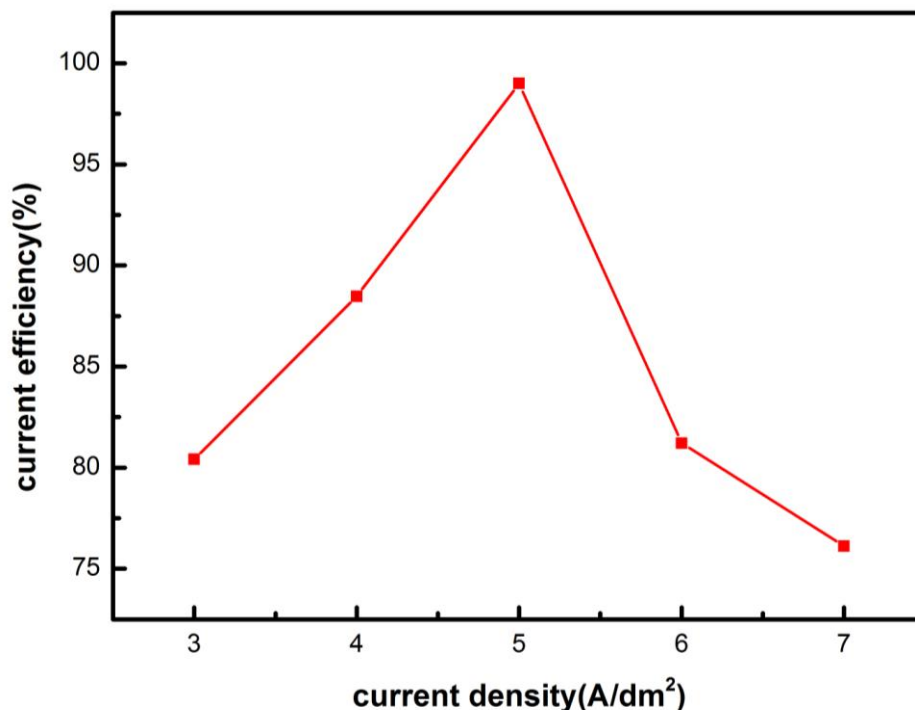


Figure 6. Effect of current density on current efficiency $T=35\text{ }^{\circ}\text{C}$, $c(\text{H}_2\text{SO}_4)=4\text{ mol/L}$

3.2.3. The effect of sulfuric acid concentration

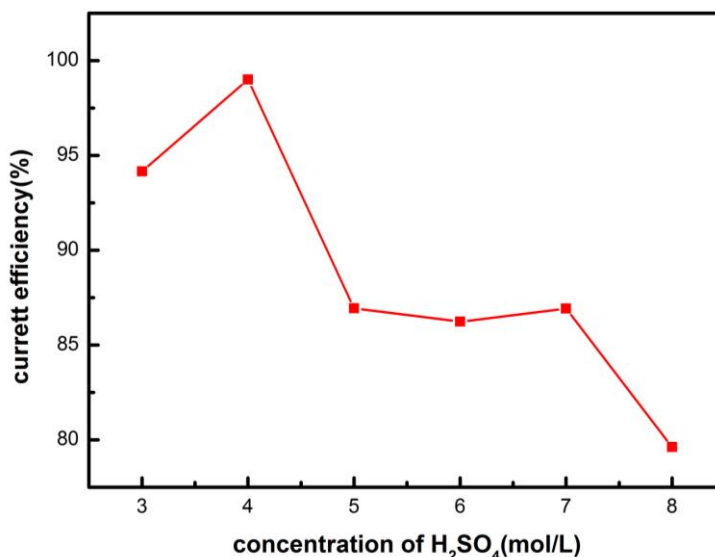


Figure 7. Effect of H₂SO₄ concentration on current efficiency $T=35\text{ }^{\circ}\text{C}$, $j=5\text{ A/dm}^2$

Figure 7 showed the effect of H₂SO₄ concentration on current efficiency. As shown in Figure 7, when the concentration of H₂SO₄ was 4.0 mol/L, the current efficiency was the best in this investigation, which was due to the inhibition of the hydrolysis reaction of Cr⁶⁺ in the 4.0 mol/L H₂SO₄. When the concentration of H₂SO₄ was higher than 4mol/L, the current efficiency decreased obviously, which was due to the effect of H⁺ and SO₄²⁻ on Cr³⁺, leading to the Cr³⁺ concentration decrease at the anode surface [17]. It was found that the better Cr concentration of H₂SO₄ was 4.0 mol/L and 7.0 mol/L in electrochemical oxidation process and liquid-phase synthesis process, respectively. However, as we known, the maintenance of the same concentration of H₂SO₄ between the electrochemical oxidation process and liquid-phase synthesis process is suitable for the indirect electrochemical synthesis in the successful recycling of the electrolyte. Furthermore, the current efficiency was about 87% when the H₂SO₄ concentration was 7 mol/L, which could be acceptable for the BA synthesizing. And, it would decrease the emission of the pollution.

3.3. Indirect electrochemical synthesis of BA

Based on the results mentioned above, the factors influencing the liquid phase oxidation of NMST and Cr³⁺ electrochemical oxidation step were discussed separately, and received a two-step optimum working conditions. But in the actual application process, liquid-phase oxidation and Cr³⁺ electrochemical oxidation were cyclically done continuously, after the liquid-phase oxidation reaction is complete, the aqueous phase residual trace organics may affect the current efficiency of recycling of the oxidation medium. In this frame, we have designed an ex-cell indirect electrochemical synthesis device, and have investigated the electrochemical properties of Cr³⁺/Cr⁶⁺ recycling during the indirect electrochemical synthesis for BA. The results were shown in Table 1. It was known that the reactive

solution may unavoidably contain small amount of organics, which would lead to the falling of current density as the number of recycles increased. However, compared to the unused electrolyte, the current efficiency of the electrochemical oxidation of Cr^{3+} obtained with the reactive solution was almost the same, as presented in Table 1. This indicated that the existence of the amount of organics had little effect in our system. In addition, the current efficiency of the electrochemical recycling of the oxidation medium was maintaining about 85% and the yield of BA in liquid-phase oxidation was maintaining about 48% during the cycling experiment, which indicated the good stability of this system.

Table 1. Results of indirect electrochemical synthesis of BA

Entry	Yield of BA/%	Current efficiency/%
1	49.4	86.3
2	47.2	85.4
3	48.1	85.8
4	47.5	85.2
5	47.2	84.5
6	48.2	84.8
7	47.3	85.3
8	48.6	84.6
average	47.9	85.2

4. CONCLUSIONS

The BA could be selectively synthesized in the H_2SO_4 solution during liquid-phase oxidation, and the highest yield of the BA could be obtained in 7mol/L H_2SO_4 at 70°C. The optimal electrochemical oxidation conditions of Cr^{3+} were as follows: current density 5A/dm², H_2SO_4 concentration 7 mol/L and reaction temperature 35 °C. Both heterogeneous electrolysis of Cr^{3+} and synthesis of BA by the oxidation of Cr^{6+} could be carried out separately in the same concentration of H_2SO_4 , which was beneficial to simplify the production process. The current efficiency of the electrochemical recycling of the oxidation medium and the yield of BA in liquid-phase oxidation was maintaining about 85% and 48% during eight times of cycling experiment, respectively. This was indicated that the technology of the indirect electrochemical synthesis of BA had good stability. And this technology of synthesizing BA with the oxidation mediator $\text{Cr}^{3+}/\text{Cr}^{6+}$ could have a good prospect of commercialization.

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