The influencing factors and mechanism of degradation of hypersaline tobias acid in electro-catalytic oxidation

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Keywords: tobias acid; electro-catalytic oxidation; COD removal efficiency; current efficiency.

Abstract. Naphthalene organic compounds are produced and consumed widely in China recently, which has brought about great pressure to the local environment. How to cope with naphthalene organic intermediate wastewater (NOIW) effectively becomes an urgent task in the coming years. Electro-catalysts oxidation (ECO), a kind of efficient and convenient technology without secondary pollution, has been broadly applied in biorefractory wastewater treatment. In this paper, Tobias acid was selected as a typical naphthalene organic compound to be treated through ECO, during which sodium chloride was invoked as the electrolyte. The degradation law was investigated under various electrolysis conditions including concentration of tobias acid, current density, concentration of supporting electrolyte sodium chloride, initial pH of the solution. The optimal conditions were as follows: the current density was 150 mA/cm^2, concentration of supporting electrolyte sodium chloride was 5000 mg/L and initial pH was 10.0. In addition, the experiment was carried out to explore the mechanisms of electro-catalytic oxidation in which the electrolyte was changed to sodium sulfate. Results showed that indirect oxidation contributed more to the electrochemical reaction in the tobias acid degradation compared with direct oxidation. Furthermore, some active oxidants such as chlorine, hypochlorous acid and hypochlorite generated by electrolysis of chlorine ions played decisive roles in the indirect oxidation as well as the whole electrolysis process.

1.Introduction

As environmental pollution the naphthalene organic compound caused becomes more and more serious, the way to solve NOIW has received tremendous attentions. However, NOIW not only has the general characteristics of benzene wastewater, but also has the following features [1][2]:1)high water-solubility, high concentration, complicated composition; 2)strong acid(alkali); 3)dark color; 4)great toxicity; 5)low bio-degradability.

As a new method of wastewater treatment, ECO has the unique features which are not possessed by the traditional methods. Different types of ECO for refractory wastewater have attracted a great deal of attention[3][4]. Tobias acid, a typical naphthalene organic compound, was selected to be degraded through ECO. And its degradation law with the changes of various electrolysis conditions was investigated in this paper. On the base of it, the mechanisms of degradation had been analyzed by changing the electrolyte to sodium sulfate from sodium chloride.

2.Experimental Methods

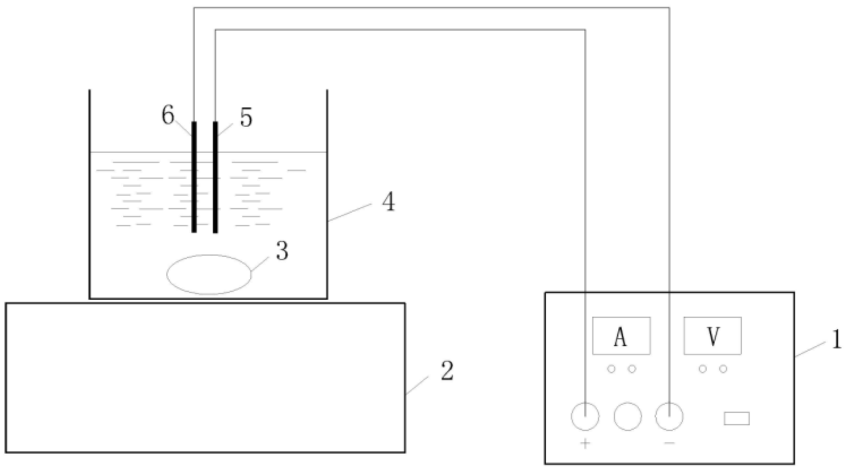
2.1 Experimental instruments and materials

Main experimental materials: tobia acid; sodium chloride; sodium sulfate; sodium hydroxide; potassium dichromate; pH buffer; silver nitrate

Main experimental instruments:LB-901 COD constant temperature heater; precise pH instrument ; HJ-3 thermostatic magnetic agitator; BS 224 S electronic balance

2.2 Experimental device

The two-dimensional flat-plate electrochemical instrument is shown in figure 1. The specification of electrolytic cell which is made of pmma is 180*60*150mm. Titanium and graphite used for anode and cathode respectively are paralleled in electrolytic cell which are put in the magnetic stirrer. In addition, there is 5mm between titanium plate and graphite plate whose specification is 60*50*20mm and 50*50*1mm. Circuit consists of outside sources and wire. At last, voltage and current can be adjusted directly.



1.DC regulated power supply(including digital display) ; 2.Magnetic stirrer; 3.Magnetic rotor ;
4.Electrolytic cell; 5.Titanium electrode 6.Graphite electrode
Fig 1 The diagrammatic sketch of electrochemical oxidation

2.3Experimental procedures

Firstly, 1L tobias acid sample of certain concentration was compounded. Then 550ml sample was added into the electrolytic cell. The current reached at set value under the reaction conditions through regulating the voltage. Finally, certain water samples were removed at regular intervals then the parameters like current, voltage values, COD removal rate and current efficiency were registered[5][6].

3. Results And Discussion

3.1 Effect of current density

Experiments were performed under selected experimental conditions: the concentration of tobias acid was set at 300mg/L, sodium chloride concentration was 3000mg/L, current density was set at 50, 100, 150, 200 mA/cm^2 respectively.

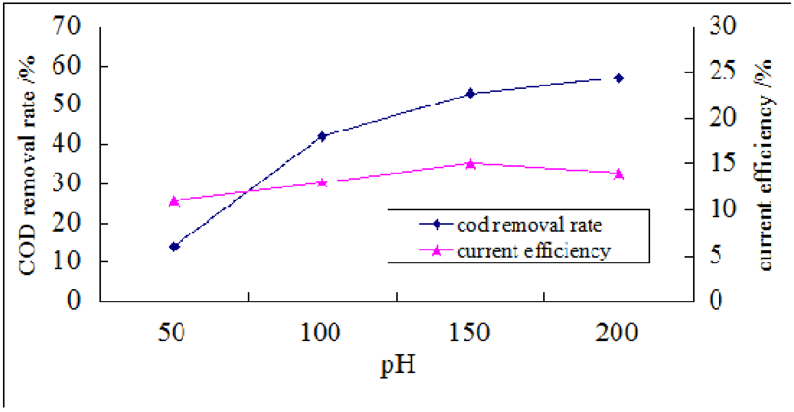


Fig 2 Effect of current density on
COD removal efficiency and current efficiency

From figure 2, it's obvious that the removal rate of COD was proportional to current density of 50~200 mA/cm^2. In details, the removal rate of COD grew sharply as the current density increased from 50 to 100 mA/cm^2 while current density changed from 100 to 200 mA/cm^2, the growth of COD removal rate slowed. As for current efficiency, it rose steadily first to the maximum value at current density 150 mA/cm^2 then fell when current density continued to increase. In a word, with the raising of current density, the degree of the oxidation came up as well as the speed of the reaction and COD removal rate.

When current density was under 100 mA/cm^2, as current density ascended, the concentration of hydroxyl radical which was formed in the reaction increased. The organics were degraded rapidly through quick oxidation and free radical chain process, under the reaction of hydroxyl radical. At that time, electrobath voltage was still lower than the overpotential for oxygen evolution with no remarkable side effects[7][8]. Therefore, COD removal rate increased as well as current efficiency. In higher current density condition(above100 mA/cm^2), with the ascension of the current density, electrobath voltage rose to exceed overpotential for oxygen evolution of anodic, which strengthened side effects. Meanwhile, the mass transfer process of organic matter was deterred by a large number of bubbles on the surface of the anode. As a result, current efficiency began to decline and the increasing tendency of COD removal rate became gentle.

3.2Effect of sodium chloride concentration

Experiments were conducted under the conditions that the concentration of tobias acid was 300mg/L, current density was 150mA/cm^2, sodium chloride concentration was set at 2000mg/L, 3000mg/L, 5000mg/L, 7000mg/L. Then the solution was tested when electrolysis time was 120min.

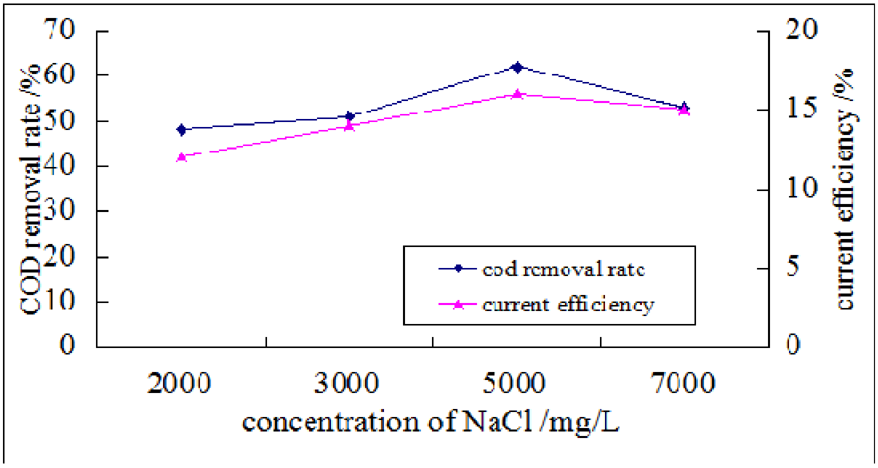


Fig 3 Effects of concentration of sodium chloride on COD removal efficiency and current efficiency

Figure 3 illustrates the effect of sodium chloride concentration on efficiency of COD removal and current. COD removal rate and current efficiency went up first and dropped later with the growth of the sodium chloride concentration. When the concentration of sodium chloride was 5000mg/L, COD removal rate and current efficiency reached its peak of 16.66% and 62.40% respectively.

It could be manifested that solution conductivity increased as the concentration of sodium chloride went up. In condition of a definite current density, the output voltage reduced which was beneficial for anode to work at lower overpotential for oxygen evolution and the extent of side reaction lessened subsequently. At the same time, an amount of indirect oxidation agent raise greatly, resulting in a rise of COD removal rate. But a number of chloride ions were adsorbed on the surface of anode when sodium chloride concentration was too high, which hindered the mass transmission and adsorption of organic pollutants on the surface of the anode, leading to a decline of COD removal rate.

3.3Effect of tobias acid concentration

Experiments were performed under the conditions that the concentration of sodium chloride was 300mg/L, current density was 150mA/cm^2, tobias acid concentration was set at 50mg/L, 100mg/L, 200mg/L, 300mg/L. Then the solution was tested when electrolysis time was 120min.

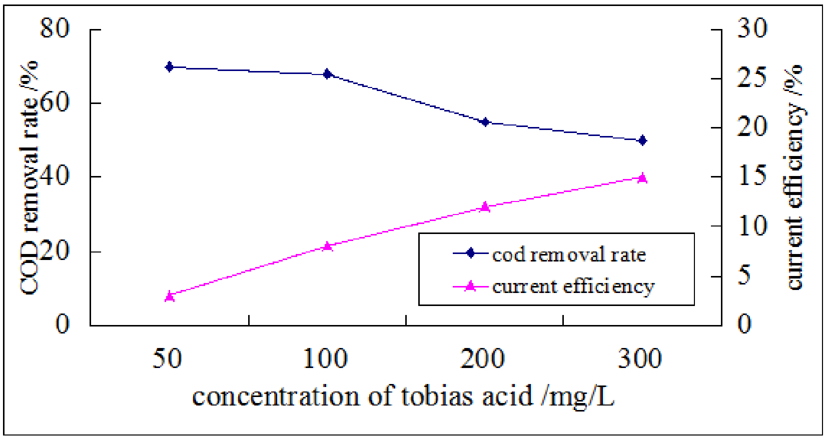


Fig 4 Effects of concentration of tobias acid on COD removal efficiency and current efficiency

It can be observed from figure 4 that the higher the concentration of tobias acid was, the higher current efficiency became when tobias acid concentration ranged from 50~200 mg/L. However, COD removal rate changed oppositely, which was inversely proportional to the concentration of tobias acid. Fundamentally, the higher the concentration of tobias acid was, the more molecules participated in during the reaction. As a result, the absolute values of removing COD increased although the increasing amplitude of it was still smaller than COD removal rate. Meanwhile, the rise of current efficiency was mainly contributed to the improved probability of collision and chain transfer reaction between organics and active intermediate materials produced in the electrolysis process.

3.4 Effect of sodium sulfate electrolyte

Indirect oxidation is a way in which a variety of oxidants produced during electrochemical reaction are used to degrade organic pollutants. Considering that Cl^- was widely distributed in practical wastewater, sodium sulfate was used in place of sodium chloride for investigating the function that Cl_2, ClO^- and HClO played in indirect oxidation.

The concentration of tobias acid was set at 50mg/L, sodium sulfate concentration was 5000mg/L, current density was 400mA/cm^2. Examine the solution when electrolysis time was 60min, 120min, 180min and 240min.

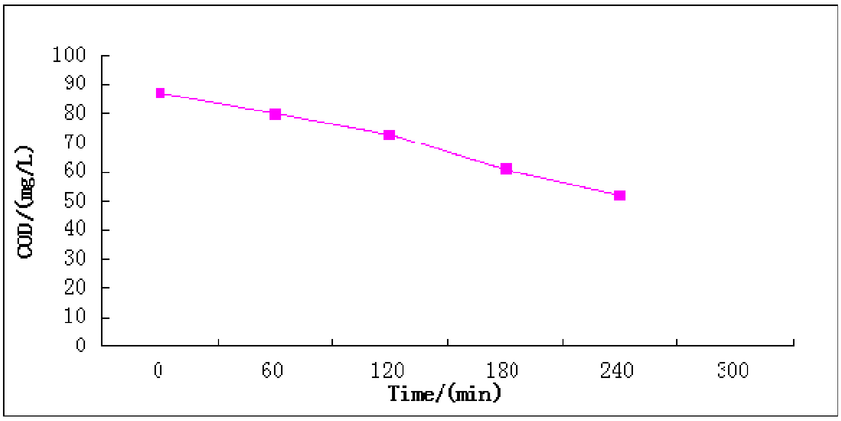


Fig 3-7 COD Changes of the solution when the electrolyte is Na_2SO_4

As can be seen from Fig 3-7, the COD of solution descended around 13.6 mg/L when electrolysis time reached 120min while COD was reduced by 35 mg/L and the removal rate of COD was 40.74%, when time came to 240min. However, COD removal rate reached 71.15% in condition that the electrolyte was NaCl, concentration of tobias acid was 50mg/L and current density was set at 150mA/cm^2.

3.5 Analysis of the electrolytic reaction mechanism

According to the Comninellis's theory of ECO [9], reactive oxygen on the surface of IrO_2 electrode was apt to selective oxidation for treating organics. That was to say, it would succeed in reacting with aromatic materials rather than fatty acid. Reaction in anode Ti/IrO_2 might take place when solution was electrolyzed: first of all, tobias acid would be got involved in the direct electrochemical reaction on the electrode[10-12](R represent tobias acid).

$$IrO_2 + H_2O \rightarrow IrO_2(HO\cdot) + H^+ + e^- \quad (1)$$

$$IrO_2(HO\cdot) \rightarrow IrO_3 + H^+ + e^- \quad (2)$$

$$R + IrO_3 \rightarrow RO + IrO_2 \quad (3)$$

Otherwise, it's generally recognized that tobias acid could be oxidized by some strong active oxidants produced on the electrode through indirect electrochemical process[13-17]. The intermediate active species generated during the reaction were largely composed of H_2O_2, HO_2 •, ClO^-, HO • [18-20].

Once Cl^- existed in the solution, the reactions would occur:

$$Cl^- + e^- \rightarrow Cl_2 \quad (4)$$

$$Cl_2 + H_2O \rightarrow 2H^+ + ClO^- + Cl^- \quad (5)$$

$$ClO^- + R \rightarrow RO + Cl^- \quad (6)$$

Furthermore, the side effects are described as follows which would have an impact on the current efficiency of anode IrO_2, especially the oxygen evolution reaction.

$$4OH^- - 4e^- \rightarrow O_2 + 2H_2O \quad (7)$$

$$H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad (8)$$

All in all, direct and indirect oxidations happened simultaneously during the reaction of electro-catalysis. On one hand, IrO_3 played the vital part of oxidation in direct oxidation as shown in equation (1-3). But the effect of direct oxidation was heavily undermined by the side reaction stemmed from the low potential of IrO_2 anode, which could be confirmed by the low current efficiency as shown in Fig(2-4). On the other hand, it could be inferred that Cl_2, ClO- and HClO during indirect oxidation played a principal part in the indirect oxidation as well as the whole electrolysis process when large numbers of chloride ions exiting in solution, which could be confirmed by the results in Fig 3-7. The sharp reduction of COD degradation ability was mainly due to a lack of intermediate active materials such as Cl_2, ClO- and HClO once NaCl was replaced by Na_2SO_4.

4 Conclusion

After studying on COD removal rate and current efficiency under different electrolytic conditions, the optimal conditions were turned out and the reaction mechanism on degradation of tobias acid was discussed.

1.Current efficiency increased with the rising tobias acid concentration. Nevertheless COD removal rate went down at the same time.

2.COD removal rate was well correlated with current density. However, current efficiency went up first to maximum value of 16% when current efficiency was 150mA/cm^2 and then dropped down.

3. When the concentration of sodium chloride came to 5000mg/L, COD removal rate and current density reached a peak at the same time.

4.Indirect oxidation contributes more to the electrochemical reaction in the tobias acid degradation compared with direct oxidation. Furthermore, some active oxidants such as chlorine, hypochlorous acid and hypochlorite generated by electrolysis of chlorine ions played decisive roles in the indirect oxidation as well as the whole electrolysis process.

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