

Electrochemical degradation of tridecane dicarboxylic acid wastewater with tantalum-based diamond film electrode

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Abstract

Tantalum-based diamond film electrode is found having wider potential window and better catalyzing-oxidation efficiency by testing its electrochemical performance. By examining electrochemical degradation performance of tridecane dicarboxylic acid organic wastewater on these electrodes, the effect of various technique conditions on the COD removal, including potential, electrolysis time, the distance of two electrodes, pH value and with and without stirring, are investigated. The result shows that COD removal rate is 99% and meets the discharge standard of China. The specific electricity consumption is 6.4 kWh/kg COD. The proper technique conditions are 1.6 V potential, 7 h electrolysis, 20 mm distance of the two electrodes and pH value from 3 to 5.

Keywords: Tantalum-based diamond film electrode; Tridecane dicarboxylic acid organic wastewater; Electrocatalytic oxidation

1. Introduction

Tridecane dicarboxylic acid ferment residue is a high concentration organic wastewater. Generally, anaerobic biological treatment is used to treat this kind of wastewater. But, high concentration sulfate in wastewater can restrain the anaerobic biochemical reaction severely. So, the digest process is difficult to go on [1]. Moreover, biological treatment needs larger land, more complex management and emit bad smell.

At present, electrochemical oxidation for wastewater treatment is a general interest of researchers in advanced oxidation techniques. Organic can be directly degraded by anode reaction or been oxidized by hydroxide radical ($\cdot\text{OH}$) during the electrochemical oxidation process. This kind of method can decompose organic into carbon dioxide and water completely. So, it will not bring second pollution and produce poisonous intermediate products [2]. In addition, it has advantages for its simple equipment, less land demand and easy to be controlled automatically. But, because of lacking proper

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anode material, this technique has low current efficiency and high energy consumption and has not been applied in a long time.

In recent years, with the new electrode materials appearance, it is certain to be effective to treat wastewater using electrochemical oxidation. Some researchers [3,4] found that electrode with high oxygen evolution overpotential such as boron-doped diamond film electrode has higher current efficiency and COD removal rate when it is used to treat organic wastewater. Diamond film electrode has strong mechanical strength, high chemical stability and excellent electrochemical performance. Its surface will not have apparent changes even if operating at high current density. And also, it has very wide electrochemical window and higher oxidation overpotential [5]. With the development of large area CVD, conductive diamond film electrode can be made by depositing several nanometers boron-doped diamond film on metal or non-metal substrates.

In this article, tantalum-based diamond film electrodes are used to treat tridecane dicarboxylic acid organic wastewater. Also, the electrochemical performances of the electrodes are studied and COD removal rate of wastewater at various technique conditions are stressed in result discussion.

2. Experimental equipment and analytical methods

2.1. Experimental equipment and instrument

As Fig. 1 shows, internal dimensions of the self-made electrolyzer is $5\text{ cm} \times 6\text{ cm} \times 5\text{ cm}$. Both of the anode and cathode are tantalum-based diamond film electrodes. The virtual size of the plate is $3.5\text{ cm} \times 2\text{ cm}$ and the distance of the two plates can be adjusted. The TD3691 potentiostat is used to be the power sources and the wastewater is heated and stirred by CJJ79-1 magnetic stirrer.

In the experiment, chemical oxygen demand analysis instrument COD-571, PH meter PHS-3C and sulfate measuring instrument are also used.

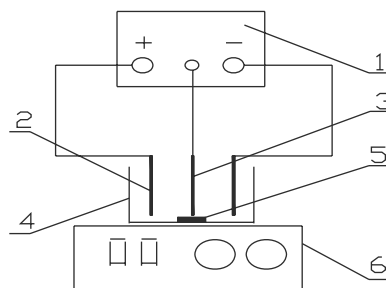


Fig. 1. Schematic of experimental equipment. 1. Power sources, 2. electrode plates, 3. reference electrode (SCE), 4. electrolyzer, 5. stirrer, 6. stir rotor.

2.2. Testing items and analytical methods

The COD of tridecane dicarboxylic acid ferment wastewater is between 10,000 and 12,000 mg/L. The pH value of the solution is from 3 to 5 and the sulfate concentration of the wastewater is between 12,000 and 15,000 mg/L.

2.2.1. Cyclic voltammetry

In the electrolyzer without diaphragm, both of the working electrode and counter electrode (with virtual area 14 cm^2) are diamond film electrodes, while SCE being the reference electrode. The electrolyte is 0.5 mol/L sulfuric acid solution. The voltage sweep range is from -4 to 3 V and the sweep rate is 50 mV/s .

From Fig. 2 we can see, the hydrogen and oxygen evolution potentials in sulfuric acid are -2.5 V and 1.5 V , respectively. The potential window of the electrode is as wide as 4 V , while those of the platinum and graphite electrodes are 1.8 V and 1.2 V [6], respectively. Because of this character it is propitious to produce hydroxyl radical. So, high catalyzing-oxidation efficiency of this kind of electrode can be performed.

2.2.2. Instantaneous current efficiency

Instantaneous current efficiency (ICE) can be calculated by the difference between the CODs

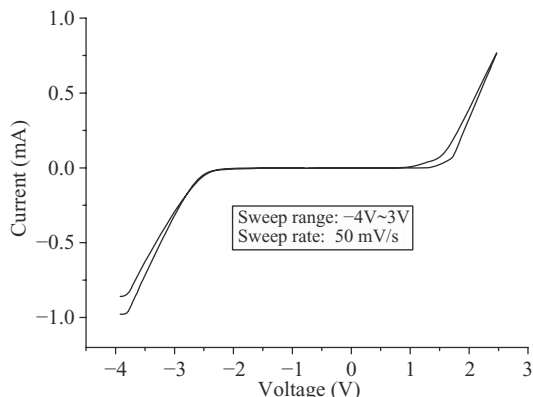


Fig. 2. CV curve of diamond film electrode.

before and after the electrochemical reaction. That is:

$$\text{ICE} = \frac{[(\text{COD})_t - (\text{COD})_{t+\Delta t}] FV}{8I\Delta t} \quad (1)$$

In this equation, $(\text{COD})_t$ and $(\text{COD})_{t+\Delta t}$ are chemical oxygen demand value at the time t and time $t + \Delta t$, respectively. Their units are g/L. I is current, A; F is Faraday constant, 96,487 C/mol; V is volume of the solution, L.

2.2.3. Electricity consumption ratio

Electricity consumption ratio (ECR) is the electricity consumption when 1 kg COD is used, as follows:

$$\text{ECR} = \frac{Iu\Delta t}{((\text{COD})_t - (\text{COD})_{t+\Delta t})V} \quad (2)$$

In the above equation, u is voltage, V; Δt is electrolysis time, s. The other items are the same as before.

3. Result and discussion

3.1. The effect of current density

Current density is one of the most important parameters in electrolysis technique. In electrochemistry, anodic current density reflects

oxidation reaction speed on the anode. There is a linear relationship between cell voltage and current density, as follows:

$$u = a + Ki [7] \quad (3)$$

In this formulation, K and a are constants. a is apparent decomposition voltage, V; K is voltage grads, $\text{V m}^2/\text{A}$. They are important parameters to judge a electrolyzer.

By comparison with current density, the cell voltage is easier to be controlled. Therefore, in this study, by adjusting and controlling the cell voltage, the result of electrolysis is investigated at different current densities. The relationship between the cell voltage and current density is seen in Fig. 3.

From Figs. 4 and 5 we can see, as electrolysis time being 60 min, the COD removal rate increases with the cell voltage going up. Because as cell voltage rising, the anode potential will be higher, this boosts up the oxidation of the anode. And with the cell voltage climbing, the current density increases, which speed up the reaction rate. At the same time, the current efficiency decreases and the energy consumption increases. When cell voltage is higher than 3 V, that is, current density is higher than 9 A/cm^2 , the current efficiency decreases abruptly while the COD removal rate decreasing trend with cell voltage going up or

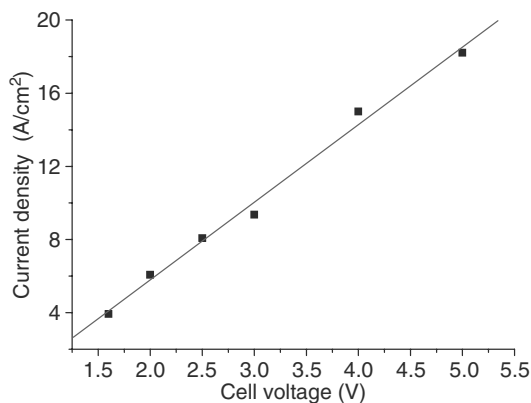


Fig. 3. Voltammety curve of the cell.

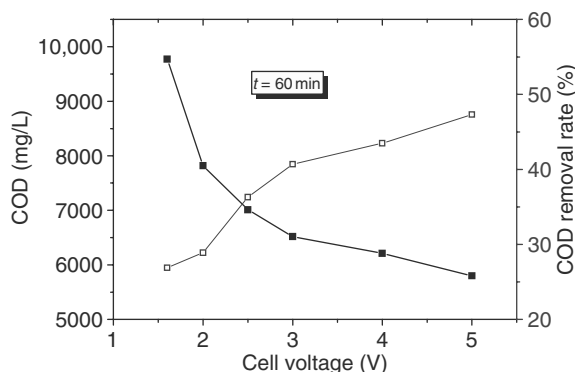


Fig. 4. The relationship of COD or COD removal rate and cell voltage.

current density rising relaxes. The main reason is that the side reaction increases with the cell voltage climbing or the current density going up. Therefore, the organic degradation rate reduces.

3.2. The effect of electrolysis time

Generally, the organic concentration in wastewater reduces with the electrolysis time increasing. With enough electrolysis time, the concentration of the organic can reach very low. But, in financial terms, the electrochemical oxidation should be done as soon as possible to reduce the electricity consumption. Thus, the cell voltage, the current density and the time should be considered together.

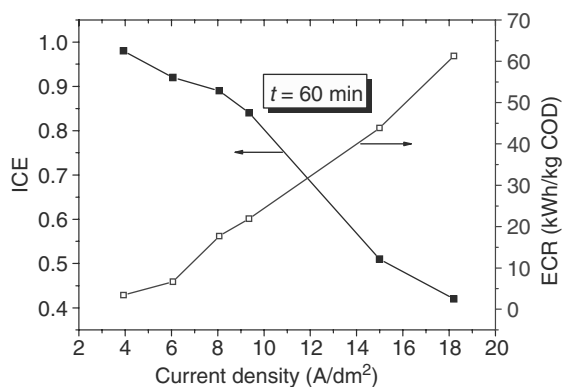


Fig. 5. The relationship of ICE or ECR and current density.

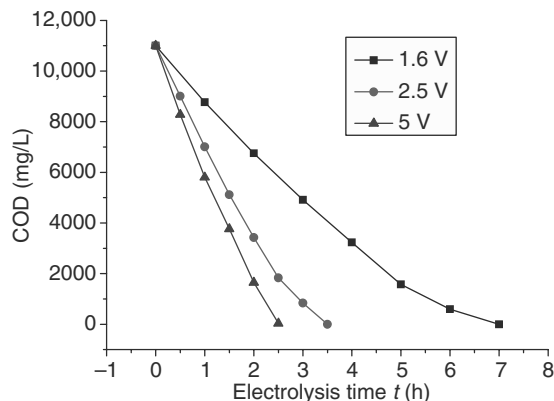


Fig. 6. The relationship of COD and electrolysis time at different cell voltage.

For this reason, electrolysis time is a very important factor for electrochemical oxidation.

From Figs. 6 and 7 we know, with the time going on, the organic concentration reduces quickly and will be removed almost. However, at later period, COD decreasing speed is slower, current efficiency is lower and the specific electricity consumption is increasing. The reasons are as follows: (1) as the electrolysis going along, the organic concentration is lower and lower, that weakened the indirect oxidation; (2) the current density is too big, which makes the side reaction increases and the current efficiency reduces.

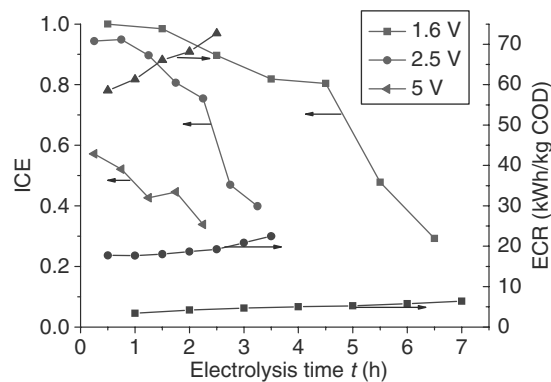


Fig. 7. The relationship of ICE and ECR and electrolysis time at different cell voltage.

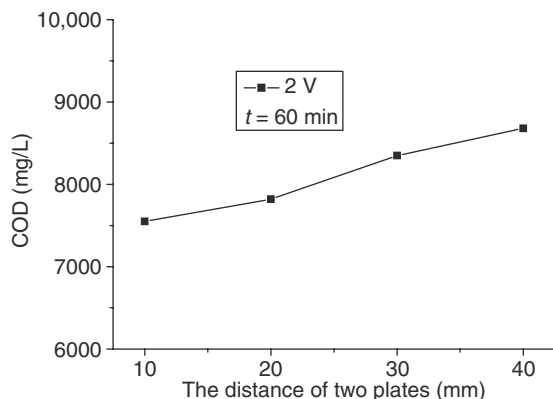


Fig. 8. COD value at different distances.

3.3. The effect of the two electrode plates distance

In the electrolysis process, there is a close relationship between the cell voltage, current density and the distance of the two plates. At 2 Volts, when the electrolysis time is 60 min, the distance of the two plates is adjusted and the correlative data are recorded.

From Figs. 8 and 9 we can see, with the distance reducing, the COD decreases. This is because that the shorter distance will speed up the anion discharge on the anode and improve the oxidation. With the distance decreasing, the

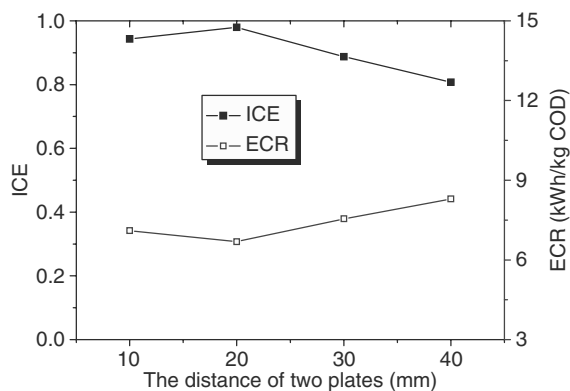


Fig. 9. ICE, ECR at different distances.

resistance, the electricity consumption and the cost of the wastewater treatment are all reducing. When the distance of the two plates is 10 mm, the ECR is a little higher, that may arise from more bubbles and worse mass transfer because of short distance. At this condition, the current density is higher and lead to a certain waste of electricity. Whereas, in engineering, there is a forced cyclic movement of the electrolyte on the surface of electrodes. So, the mass transfer is better and the distance of the two plates can be reduced further.

3.4. The effect of pH value

From Fig. 10 we can see, when the cell voltage is 1.6 V, the COD removal rate is increasing with the pH value decreasing. The reasons are (1) the lower pH value is propitious to produce strong oxidation substance; (2) on the anode, oxygen evolution is one of the most important reactions of water electrolysis. From Eq. (4) [8], we know that oxygen is easier to separate out in alkaline than in acid, which makes the organic degradation easier.

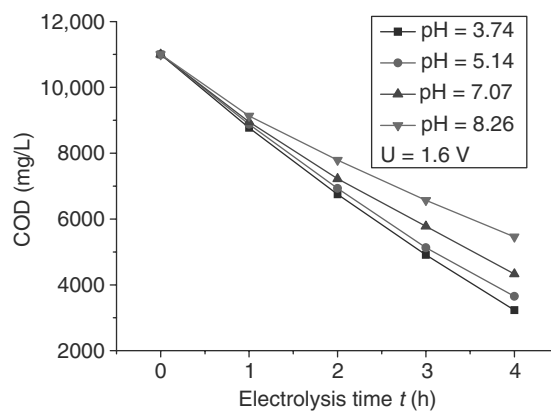
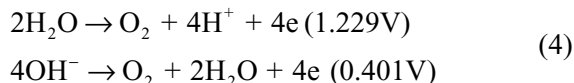


Fig. 10. The relationship of COD and time at different pH value.

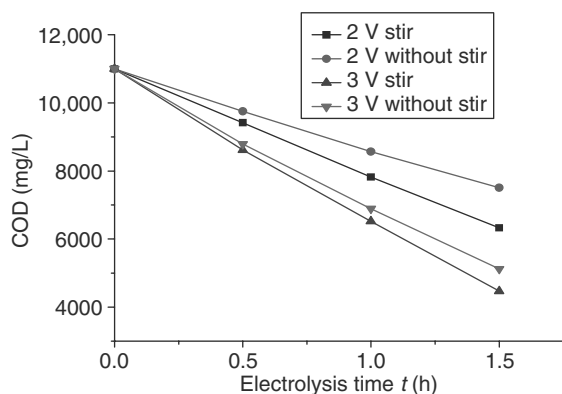


Fig. 11. The effect of stir on COD.

3.5. The effect of stir

In electrochemical reaction, mass transfer is important to organic degradation.

From Fig. 11 we can see, at two different voltages, the COD is lower with stir than that without stir. That means improving mass transfer can increase organic degradation rate. By comparison with 3 V cell voltage, the effect of stir is more apparent at 2 V. This may be because that at 3 V cell voltage, gas evolution effect is more drastic, which makes mass transfer better.

4. Conclusion

By testing the performance of the diamond film electrode with cyclic voltammetry (CV), a wide potential window of this kind of electrode is found. So, it is propitious to the indirect oxidation of organic in wastewater and higher current efficiency is performed.

Different electrolysis conditions are investigated. As a result, COD removal rate and specific electricity consumption are increasing with the cell voltage increasing and electrolysis time going on. Moreover, the distance of the two plates reducing, lower pH value and drastic stir will benefit to the degradation of the organic.

As the wastewater investigated has high salinity and high conductivity, low current density should be applied by considering the effect of various electrolysis conditions on COD removal rate, electrolysis efficiency and specific electricity consumption. The best technique should be 1.6 V cell voltage, 7 h electrolysis and 20 mm distance of the two plates. Moreover, without changing the pH value of the wastewater and with stir, the COD removal rate can reach 99%, which meets the discharge standard of China. As a result, the specific electricity consumption is 6.4 kWh/kg COD.

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