

Copper-containing wastewater treatment and copper recovery by using a continuous flow microbial fuel cell

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Abstract. A microbial fuel cell is a device of directly converting chemical energy into electricity with the microbial metabolism. Graphite rods were used as electrodes, organic wastewater was used as substrate, anaerobic activated sludge was used as anaerobic bacteria and copper-containing wastewater was used as catholyte. A continuous flow dual chamber microbial fuel cell was constructed. The feasibility of electricity producing via degradation of wastewater by anaerobic bacteria in anode chamber and copper recovery from copper-containing wastewater were studied. The results showed that a continuous flow microbial fuel cell could produce electricity and could be used to treat copper-containing wastewater, the maximum current density was $4.4 \text{ mA}\cdot\text{m}^{-2}$, the removal rate of Cu^{2+} was 99%, and the sediment on the cathode was a mixture of Cu and Cu_2O .

1. Introduction

With the development of industry, electroplating, metallurgy and oil industry discharge a large amount of copper-containing wastewater annually, which has a disastrous effect on the environment and has wasted a lot of copper resources [1,2]. The traditional methods of copper-containing wastewater treatment include chemical precipitation [3,4], ion exchange [5], electrolytic process [6], etc, but it is difficult to recover copper by these methods, and secondary pollution may be caused.

A microbial fuel cell (MFC) is a device which can convert chemical energy of organic matter, sludge or wastewater into electricity with the microbial metabolism at normal temperature and pressure [7], it has many advantages such as a wide range of substrate sources, higher energy utilization, safety, and so on. The research of MFCs in the field of wastewater treatment began in the 1980s. The technology of microbial electricity generation has achieved great breakthroughs and the practical application of MFCs has ensued since 1990s.

The important application of the MFC is that metal ions can be used as electron acceptors, and the valuable metals can be recovered. Choi *et al* [8,9] studied Ag and Cd recovery using an MFC. Li *et al* [10] found that the removal rate of Cr^{6+} in the MFC was 97% under irradiation of visible light. Zhang *et al* [11] showed that the removal efficiency of V^{5+} and Cr^{6+} was 67.9% and 75.4% respectively. Ter Heijne *et al* [12] adjusted the pH of Cu-containing solution to 3 and attained Cu^{2+} removal rate of 99.8%. An MFC of using Cu^{2+} as cathode electron acceptor is a new issue in the fields of environmental engineering. The feasibility of current generated by the MFC instead of the traditional



power in the electrolytic to treat copper-containing wastewater has been confirmed [13]. The copper could be recovered when simulate molasses wastewater was used as anode substrate and electroplating wastewater was used as cathode fluid [14].

In this paper, organic wastewater was used as anode substrate, copper sulfate solution was used as catholyte, a continuous flow MFC was constructed. The copper-containing wastewater treatment and the recovery of copper were studied.

2. Materials and methods

2.1. MFC devices

The dual chamber MFC was used in the experiment. The anode and cathode chamber were made of polyethylene, they were separated by the pretreated cation exchange membrane (CEM). The anode and cathode materials were graphite. Two outlets were set on the both sides of the anode chamber and cathode chamber. Two electrodes were connected via copper wires.

Three kinds of MFCs were used in the test, named MFC1, MFC2 and MFC3 respectively, and each external resistance was 10 Ω . CuSO_4 solution of $6400 \text{ mg}\cdot\text{L}^{-1}$ was used as cathode liquid in the MFC1, MFC2 and MFC3. All MFCs were operated at indoor temperature. A peristaltic pump was used to supply the wastewater to the anode chamber.

MFC1: Phosphate buffer solution (PBS) and simulated wastewater (COD of $874 \text{ mg}\cdot\text{L}^{-1}$) were added into the anode chamber.

MFC2: which had not PBS and the COD was $972 \text{ mg}\cdot\text{L}^{-1}$.

MFC3: which had PBS and the COD was $874 \text{ mg}\cdot\text{L}^{-1}$.

2.2. Materials

Simulated organic wastewater: the components include K_2HPO_4 , $(\text{NH}_4)_2\text{SO}_4$, NH_4Cl , Na_2CO_3 , glucose, and tap water. Wastewater had been anaerobic domesticated for ten days and the COD was approximately $900 \text{ mg}\cdot\text{L}^{-1}$.

Simulated wastewater in the cathode chamber was CuSO_4 solution of $6400 \text{ mg}\cdot\text{L}^{-1}$ and the pH was 4.5.

Sludge: anaerobic sludge in the anode chamber was taken from Qingtan sewage treatment plant. The inoculum dose of sludge in the anode chamber was 50 mL.

CEM and electrodes: CEM (Zhejiang Qianqiu Environmental Water Treatment Company) has been immersed in deionized water for 24 hours before using. Graphite rod (surface area of 25 cm^2 , Shanghai Mount Young Electrical Carbon Company) was used as anode and cathode.

All reagents used in the experiments were analytical reagents.

2.3. Analysis methods

Sealed catalytic digestion method was used to measure COD, a multimeter was used to measure the voltage. ICP-AES (Optima 2100DV, Perkin Elmer Inc., USA) was used to detect Cu^{2+} concentration, and X-ray diffraction (XRD, X'Pert PRO, PANalytical B.V., The Netherlands) was used to analyze the sediment on the cathode.

The current density is shown as

$$I_{\text{An}}=I/A_{\text{An}}$$

where I is the current (mA), and A_{An} is the effective area of the anode (m^2).

The removal rate of copper ions is shown as

$$\text{Cu}^{2+} \text{ removal rate} = (\text{Cu}^{2+}_{\text{initial}} - \text{Cu}^{2+}_{\text{effluence}}) / \text{Cu}^{2+}_{\text{initial}}$$

where $\text{Cu}^{2+}_{\text{initial}}$ is the initial concentration of copper ion ($\text{mg}\cdot\text{L}^{-1}$) and $\text{Cu}^{2+}_{\text{effluence}}$ is the effluent concentration of copper ion ($\text{mg}\cdot\text{L}^{-1}$).

3. Results and discussions

3.1. The influence of PBS on the copper recovery

The effect of the PBS on the copper recovery was studied. Comparison of current density when adding and not adding PBS was shown in figure 1.

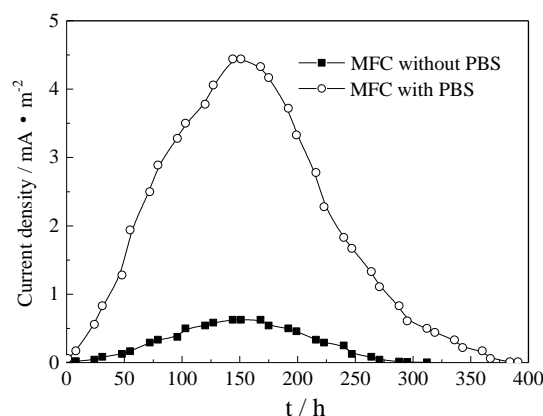


Figure 1. Comparison of current density when adding and not adding PBS.

Figure 1 showed that the current density was low when PBS was not used, the maximum current density was $0.6 \text{ mA} \cdot \text{m}^{-2}$. After adding PBS, the maximum current density was $4.4 \text{ mA} \cdot \text{m}^{-2}$, which was 7.1 times of the MFC without addition of PBS. It is mainly caused by the reduction of internal resistance, due to the addition of a large number of conductive ions, the entire solution ionic strength increased, thereby increasing the conductivity of the solution and reducing the system resistance [15].

After the operation, scrap the sediment on the cathode graphite rod into the production collector, and the XRD spectrum was shown in figure 2.

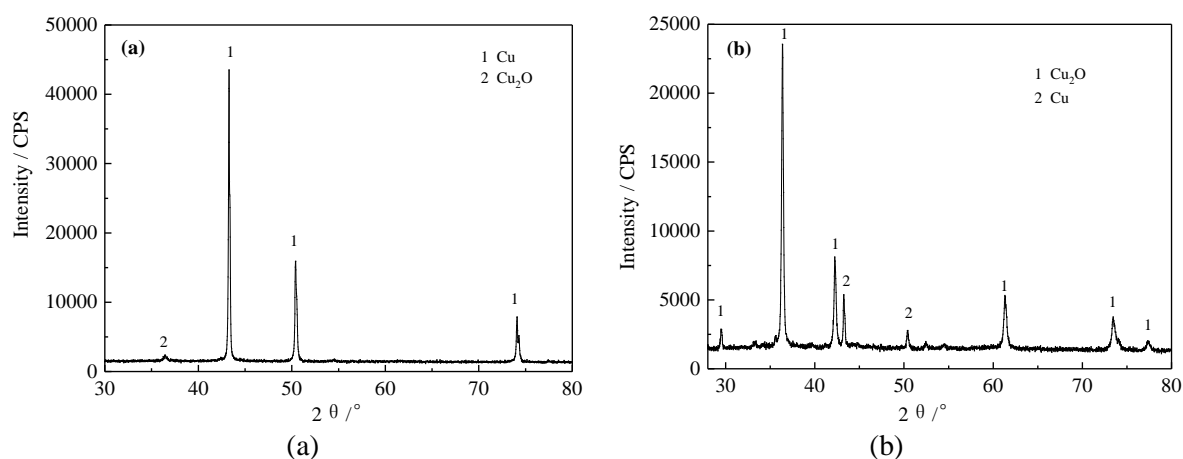


Figure 2. XRD of the sediment on the cathode. (a) MFC with PBS, (b) MFC without PBS.

Figure 2(a) showed that the sediment diffraction in the 2θ of 43° , 50° and 74° has sharp diffraction peaks, which were consistent with the characteristic diffraction peaks of pure copper through computer retrieval. Brick red sediment on the cathode graphite rod of the continuous flow MFC were proved that the sediment was mainly copper. Sediment diffraction in the 2θ of 36° has a diffraction peak, which was consistent with the characteristic diffraction peaks of Cu_2O , there is a small amount of

Cu₂O in the sediment.

Figure 2(b) showed that sediment diffraction in the 2θ of 43° and 50° has diffraction peaks, which were consistent with the characteristic diffraction peaks of copper through computer retrieval, which proves that copper is in the presence of cathodic reduction products. Sediment diffraction in the 2θ of 29° , 36° , 42° , 61° , 73° and 77° has sharp diffraction peaks, which were consistent with the characteristic diffraction peaks of Cu₂O.

3.2. The influence of substrate concentration on the copper recovery

The effect of the anode substrate concentration of MFCs on the copper recovery was studied. Comparison of current density with different initial concentration of COD was shown in figure 3.

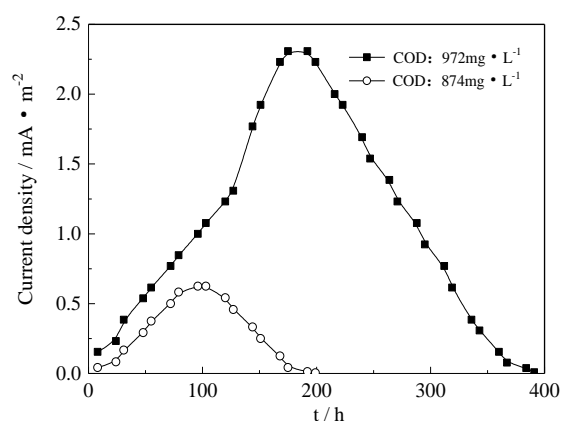


Figure 3. Comparison of current density with different initial concentration of COD.

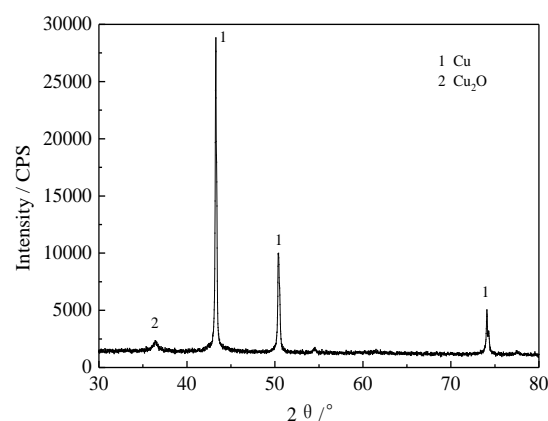


Figure 4. XRD of the sediment on the cathode.

It was showed in figure 3 that the maximum current density was $2.3 \text{ mA} \cdot \text{m}^{-2}$ with the COD of $972 \text{ mg} \cdot \text{L}^{-1}$, and relative to $0.6 \text{ mA} \cdot \text{m}^{-2}$ of $874 \text{ mg} \cdot \text{L}^{-1}$. The higher the content of organic matter, the more the amount of hydrolyzed into small molecular substances, and the more the electricity generation. The reason may be that wastewater contains complex organic and rich nutrition, macromolecular organic matter, which was not readily biodegradable, can be decomposed into small molecules through the hydrolysis of microorganism [16].

When the COD of the substrate was $874 \text{ mg} \cdot \text{L}^{-1}$, the XRD spectrum of the sediment was shown in figure 4.

Figure 4 showed that the sediment diffraction in the 2θ of 43° , 50° and 74° has sharp diffraction peaks, which were consistent with the characteristic diffraction peaks of copper through computer retrieval. Sediment diffraction in the 2θ of 36° has a diffraction peak, which was consistent with the characteristic diffraction peaks of Cu₂O.

3.3. Copper-containing wastewater treatment in the cathode chamber

The removal rate of Cu²⁺ in the MFC1, MFC2 and MFC3 was shown in table 1.

Table 1. Comparison of the removal rate of Cu²⁺.

MFC	Removal rate of Cu ²⁺ (%)
MFC1	99.8
MFC2	99.4
MFC3	99.9

Table 1 showed that the removal rate of Cu²⁺ of the continuous flow MFCs could reach above 99%. The reason is that Cu²⁺ and electron from anode occur reduction reaction and the products deposit on

the graphite rod with the pattern of Cu or Cu₂O.

4. Conclusions

A continuous flow MFC can produce electricity, at the same time it can be used to treat copper-containing wastewater and to recover copper.

When PBS was added into the anode chamber, the maximum current density was 4.4 mA·m⁻², and the sediment on the cathode graphite rod was mainly copper.

The removal rate of Cu²⁺ by the continuous flow MFCs can reach above 99%.

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