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Increasing efficiencies of microbial fuel cells for collaborative treatment of copper and organic wastewater by designing reactor and selecting operating parameters

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HIGHLIGHTS

- High collaborative efficiency for both organics and Cu^{2+} removal was achieved.
- High anodic and cathodic efficiencies and high power densities were achieved under the optimal operation parameters.
- The optimal operation parameters were determined by linear sweep voltammetry.

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ABSTRACT

Organic matters and copper ions can be collaboratively removed from wastewater using a microbial fuel cell (MFC). High collaborative efficiencies for both organic matter and copper ions removal have not been achieved yet in previous studies. We demonstrate here that high collaborative efficiencies can be achieved by designing reactor construction and selecting operational parameters based on the results of linear sweep voltammetry (LSV). When the MFC was constructed as 1:2 volume ratio of anode to cathode chamber and operated at optimal conditions, 83% COD removal and 87% copper ion removal were obtained at the same time. In addition, the Cu-MFC also performed a high coulombic efficiency (CE) of 89% for organic treatment, a cathodic efficiency of 80% for copper ion removal, and a maximum power density of 2.0 W/m^2.

1. Introduction

MFCs are bio-electrochemical systems that can generate electricity via treating organics in wastewater (Logan et al., 2006; Rismani-Yazdi et al., 2008). Recently, the use of MFC to collaboratively treat organic matters and heavy metal ions attracted extensive research interests because of its electricity generation by collaboratively treating two types of wastewater (Choi and Cui, 2012; Heijne et al., 2010; Li et al., 2009; Tandukar et al., 2009; Heijne et al., 2006; Wang et al., 2008, 2011). The MFC for treating copper ion (Cu-MFC) is more attractive than treating other heavy metal ions because the copper ion containing wastewater exists widely (Kim et al., 2002; Periasamy and Namasivayam, 1996; Zamani et al., 2007) and copper ion (Cu^{2+}/Cu) has a high redox potential of +0.286 V (vs. NHE) (Heijne et al., 2010). In Cu-MFC, copper ions can be reduced to metallic copper at cathode while organic waste is oxidized to carbon dioxide at bio-anode with simultaneously electricity generation, according to the following Eqs. (1) and (2):

Anode reaction:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \quad E^{\theta}_{an} = 0.187\ V(SHE). \tag{1}$$

Cathode reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E^{\theta}_{cat} = 0.337\ V(SHE). \tag{2}$$

Alternatively, the other cathode reactions may also occur as Eqs. (3) and (4):

$$2Cu^{2+} + H_2O + 2e^- \rightarrow Cu_2O + 2H^+ \quad E^{\theta}_{cat} = 0.207\ V(SHE). \tag{3}$$

$$2Cu_2O + 2H^+ + 2e^- \rightarrow 2Cu + 2H_2O \quad E^{\theta}_{cat} = 0.059\ V(SHE). \tag{4}$$

Previous studies had shown that the copper ion could be removed in high efficiency using Cu-MFC system. However, the COD removal, the power output and (or) the coulombic efficiency

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were relatively low. For example, Wang et al. (2010) reported a copper ion removal as high as 99.9%, but the system only produced electricity of 0.32 W/m^2 with low CE less than 4%. Tao et al. (2011a) also reported a 99% copper removal in an anolyte fed-batch MFC with only 51 ± 9% COD removal, 0.13 W/m^2 power output and 3.65% CE. In addition, the cathodic efficiency was mostly low, ranging from 22.1% to 43% when oxygen existed in the catholyte. The cathodic efficiency can reach to 84% by flushing catholyte with nitrogen continuously, but it is inevitable to increase the costs and discourage the practical application.

Practical application requires high collaborative treatment efficiencies for both copper ions and organic matters. To reach this requirement, the MFC reactor should be well designed and optimally operated to present high performance for both cathode and anode at the same time. It has been found that the low CE is due to the low activity of the electrogenic bacteria. Microbial community analysis suggests that the electrogenic bacteria dominated when the MFC is acclimated at high anode potential (Jadhav and Ghangrekar, 2009; Katuri et al., 2011; Lyon et al., 2010; Clauwaert et al., 2008). Therefore, it is possible to give a high CE by acclimating microorganism at high anode potential. In addition, high copper ion removal and removal rate can be achieved at a high current density, which is usually obtained by a small external resistance. In previous studies (Heijne et al., 2010; Tao et al., 2011b), MFCs usually performed at a small fixed external resistance (such as 5 Ω) or short circuit to achieve high copper ion removal efficiency. However, the organic removal and power output were accordingly low, especially when the reactor was not well designed. The maximum power density, CE and cathodic efficiency of the system depend on both internal and external resistance. Therefore, an optimal external resistance should be determined to achieve high efficiencies for both organic removal and copper ion removal.

In this study, a Cu-MFC configuration was designed based on the experimental and experiential parameters at specific acetate and copper ion concentrations. Then the optimal external resistance was selected based on LSV and examined in two sets of Cu-MFC with different cathode surface areas. Results suggested that with the proper volume ratio of the anode chamber to the cathode chamber and optimal operation parameters, the MFC could obtain high copper ion and COD removal efficiencies, maximum power output, high columbic efficiency and high cathodic efficiency simultaneously.

2. Methods

2.1. Reactor construction

The Cu-MFC was constructed in cylindrical shape (Liu and Logan, 2004) with anode chamber (3 cm in diameter, 2 cm in length) and cathode chamber (3 cm in diameter, 4 cm in length) separated by an anion exchange membrane (AMI7001, Membrane International Inc., USA). The volume ratio of the anode chamber to the cathode chamber was 1:2. The anode was carbon fiber brush (2 cm in diameter and 2.5 cm in length, Hangzhou Jinsheng brush factory, China). The cathode was a graphite rod (10 cm in diameter, Chengyuan Inc., China). A glass fiber separator with 2 mm in thickness was situated tightly to the side of anion exchange membrane and faced to the anode chamber to protect the membrane from biological contamination. The cathode was set 1 cm away from the membrane. Two cathode surface areas were changed as 3.1 cm^2 and 4.7 cm^2 by varying the activated length of graphite rod to study the effect of cathode surface area on Cu-MFC performance.

Catholyte was copper sulfate solution that was adjusted to pH 2 with sulfuric acid and adjusted to the conductivity of 10 mS/cm with Na_2SO_4 before filled into cathode chamber. The copper ion concentration was 0.8 g/L chosen based on the previously reported (Heijne et al., 2010). Anolyte was phosphate buffer solution (PBS) containing 0.75 g/L acetate. The PBS (100 mM) consisted of $Na_2HPO_4{\cdot}12H_2O$ (22.9 g/L), $NaH_2PO_4{\cdot}2H_2O$ (5.0 g/L), NH_4Cl (0.31 g/L), KCl (0.13 g/L) and trace mineral solution (Zuo et al., 2007).

2.2. Inoculation and acclimation of the bio-anode

A single cylindrical chambered MFC (3 cm in diameter, 4 cm in length) with air-cathode was used to inoculate the anode as previously described (Liu and Logan, 2004). The inoculum was obtained from the effluent of an air-cathode MFC that has been operated with PBS and acetate for 2 years. The inoculation of anode was conducted with a mixture (1:1) of inoculum solution and phosphate buffer solution (PBS, 100 mM) containing 1.0 g/L acetate at an external resistance of 1000 Ω for 1 cycle. MFC was then operated with PBS containing 1.0 g/L acetate without inoculum solution for about 5–6 cycles to achieve a repeatable maximum voltage.

In order to achieve the high CE, the MFCs were acclimated with different external resistances from 1000 Ω to 10 Ω (5 downward steps, at each resistance for 48 h), and then operated at an external resistance of 10 Ω for 3 weeks to harvest electrogenic bacteria on anode. After this acclimation, the CE of MFC reached an average value of 76% which was much higher than that previously reported (ranging from 9% to 12%) (Cheng et al., 2006). All the experiments were performed in duplicate in a temperature-controlled room at 30 °C.

2.3. Calculations and measurements

The voltage was monitored at a 5 min interval by a data acquisition system (34901A, Agilent Technologies Inc., USA) connecting to a personal computer. Current (I), power (P), columbic/anodic efficiency (CE) and cathodic efficiency η_{cat} were calculated according to previously described (Heijne et al., 2010; Logan et al., 2006). Power density was calculated as $P_s = P/S$, while current density was calculated as $i = I/S$, where S is the cathode surface area.

The chemical oxygen demand (COD) was measured using standard methods (APHA et al., 1992). The pH and the conductivity of the catholyte were monitored with pH meter (FE20, Mettler Toledo Inc., Switzerland) and conductivity meter (SG3, Mettler Toledo Inc., Switzerland), respectively. An Ag/AgCl reference electrode (corrected with zobell solution) was used to monitor anode and cathode potential. The concentrations of copper ions in both influent and effluent of the anolyte and catholyte were monitored by an Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-OES; iCAP 6000, Thermo Inc., USA). The samples for ICP-OES were extracted from the reactors and acidified with nitric acid before the measurement.

2.4. Linear sweep voltammetry and X-ray photoelectron spectroscopy

Linear sweep voltammetry (LSV) was used to evaluate the electrochemical properties of anode and cathode, and to select the optimal operation parameters such as operational current density, external resistance and cathode area. The LSV test was conducted in a dual chamber MFC with the same configuration as Cu-MFC described above but with different electrode and electrolyte. For LSV of anode, the anode chamber was filled with 100 mM PBS containing 0.75 g/L acetate, while the cathode chamber was filled with Na_2SO_4 solution (conductivity of 10 mS/cm). The counter electrode was a Pt wire placed in the end of the cathode chamber. The Ag/AgCl reference electrode was set closed to the bio-anode in the anodic chamber. The LSV was performed in the potential range from −0.44 V to −0.27 V at a scan rate of 0.1 mV/s.

Carbon rods with different surface areas (3.1 cm^2 and 4.7 cm^2) were examined with LSV to investigate the kinetics of copper