Removal of copper from aqueous solution by electrodeposition in cathode chamber of microbial fuel cell

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ABSTRACT

Based on energetic analysis, a novel approach for copper electrodeposition via cathodic reduction in microbial fuel cells (MFCs) was proposed for the removal of copper and recovery of copper solids as metal copper and/or Cu_2O in a cathode with simultaneous electricity generation with organic matter. This was examined by using dual-chamber MFCs (chamber volume, 1 L) with different concentrations of $CuSO_4$ solution (50.3 ± 5.8, 183.3 ± 0.4, 482.4 ± 9.6, 1007.9 ± 52.0 and 6412.5 ± 26.7 mg Cu^{2+}/L) as catholyte at pH 4.7, and different resistors (0, 15, 390 and 1000 Ω) as external load. With glucose as a substrate and anaerobic sludge as an inoculum, the maximum power density generated was 339 mW/m³ at an initial 6412.5 ± 26.7 mg Cu^{2+}/L concentration. High Cu^{2+} removal efficiency (>99%) and final Cu^{2+} concentration below the USA EPA maximum contaminant level (MCL) for drinking water (1.3 mg/L) was observed at an initial 196.2 ± 0.4 mg Cu^{2+}/L concentration with an external resistor of 15 Ω, or without an external resistor. X-ray diffraction analysis confirmed that Cu^{2+} was reduced to cuprous oxide (Cu_2O) and metal copper (Cu) on the cathodes. Non-reduced brochantite precipitates were observed as major copper precipitates in the MFC with a high initial Cu^{2+} concentration (0.1 M) but not in the others. The sustainability of high Cu^{2+} removal (>96%) by MFC was further examined by fed-batch mode for eight cycles.

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1. Introduction

Copper is found in many wastewater sources including printed circuit board manufacturing, electronics plating, wire drawing, copper polishing, paint and wood preservative manufacturing and printing operations [1]. Typical concentrations vary from hundreds mM (e.g. plating bath waste) to less than 0.01 mM (e.g. copper cleaning operations). It is a toxic metal, causing many health hazards and harmful biochemical effects on human beings. Numerous treatment technologies have been developed for copper removal, including biosorption [2], adsorption with nanoparticles [3] or zeolites [4], and hybrid processes [5]. Copper is a valuable industrial metal and the recovery of copper from wastewater is attractive. Therefore, electrochemical electrolysis cells, such as electrochemical reactors with plate electrodes [6], three-dimensional foam electrodes [7], porous electrodes [8] and membranes [9,10] have become attractive by using cathodic deposition of Cu^{2+} from wastewater. These electrochemical methods are especially effective for copper removal but require an electricity supply.

Microbial fuel cells (MFCs) are devices that use exoelectrogenic bacteria as catalysts to oxidize organic and inorganic matter and generate current [11–17]. Recently, MFCs have been tested for biological chromium(VI) reduction [18–21], ferric iron reduction and ferrous iron oxidation in cathode chambers [22,23]. The results indicate that MFCs can also be used to treat oxidized metal pollutants in cathode chambers with removal organics in anode chambers.

In this study, we propose to treat copper-containing wastewater using an MFC system via cathodic Cu(II) reduction based on electrochemical and thermodynamic analysis using published data [24,25]. The cathodic reduction of Cu^{2+} in a cathode chamber is incorporated with the oxidation of organics (such as glucose) in an anode chamber of an MFC as shown in Fig. 1. During electrodeposition, two major Cu^{2+} reduction reactions have been reported i.e. formation of metal copper (Cu) and cuprous oxide (Cu_2O) [26]:

$$Cu^{2+} + 2e^- \rightarrow Cu \quad (E^0 = 0.337\,V) \qquad (1)$$
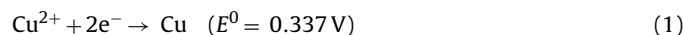
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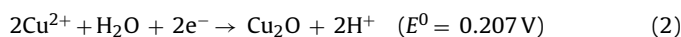 E-mail addresses: taohc@pkusz.edu.cn (H.-C. Tao), wei-min.wu@stanford.edu (W.-M. Wu).
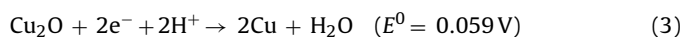 [1] Tel.: +1 650 724 5310.
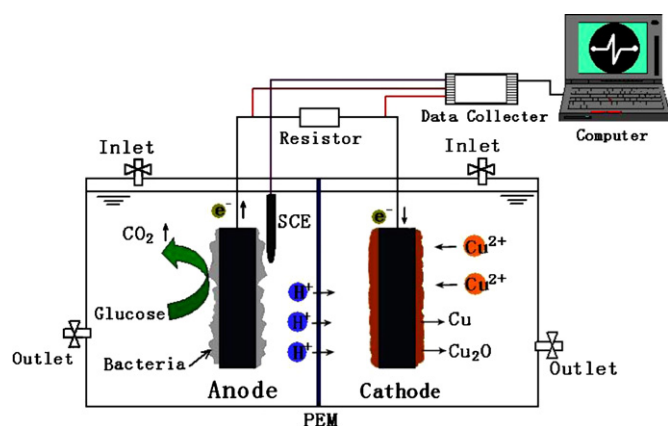
Fig. 1. Schematic diagram of the MFC and monitoring system for cathodic Cu(II) reduction. SCE = saturated calomel electrode. PEM = proton exchange membrane.

and

$$2Cu^{2+} + H_2O + 2e^- \rightarrow Cu_2O + 2H^+ \quad (E^0 = 0.207\,V) \quad (2)$$

where E^0 is the standard electrode potential, calculated using published data (Table S1). The Cu_2O produced can be further reduced to Cu:

$$Cu_2O + 2e^- + 2H^+ \rightarrow 2Cu + H_2O \quad (E^0 = 0.059\,V) \quad (3)$$

The cathode potentials (E_{Cat}) of the three reactions at different conditions (pH, temperature and Cu^{2+} concentrations) can be calculated based on the Nernst equation, shown in Eqs. (4)–(6):

$$E_{Cat}(Cu^{2+}/Cu) = E^0(Cu^{2+}/Cu) - \frac{RT}{nF}\ln\frac{1}{[Cu^{2+}]} \quad (4)$$

$$E_{Cat}(Cu^{2+}/Cu_2O) = E^0(Cu^{2+}/Cu_2O) - \frac{RT}{nF}\ln\frac{[H^+]^2}{[Cu^{2+}]^2} \quad (5)$$

$$E_{Cat}(Cu_2O/Cu) = E^0(Cu_2O/Cu) - \frac{RT}{nF}\ln\frac{1}{[H^+]^2} \quad (6)$$

where F is the Faraday constant (9.6485×10^4 C/mol), R is the gas constant (8.314 J/K mol), T is absolute temperature (K), and n is the number of moles of electrons transferred in the half-reactions. As shown in Fig. 2, the cathode potentials calculated for Eqs. (4)–(6)
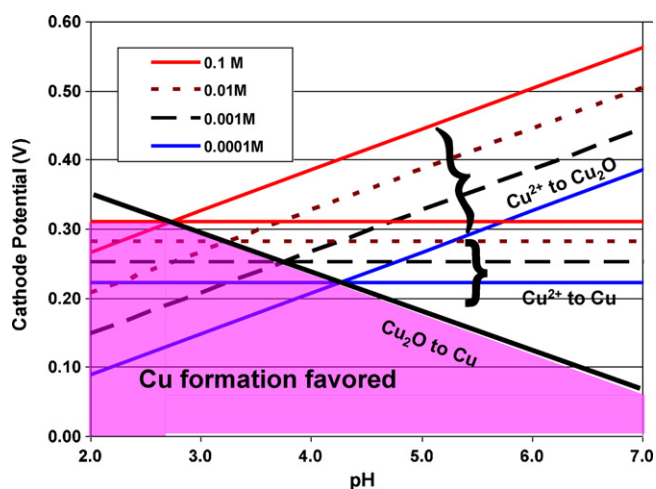
Fig. 2. Cathode theoretical potentials for half-reactions of Cu^{2+} to Cu_2O, Cu^{2+} to Cu and Cu_2O to Cu at different Cu^{2+} concentrations and different pH. The area in pink shows that formation of metal Cu is favored. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

at 25 °C with data in references [24,25] indicate that (a) the reduction of Cu^{2+} to Cu(s) depends solely on Cu^{2+} concentration; (b) Cu^{2+} to Cu_2O is a function of both Cu^{2+} concentration and pH; the half-reaction has high potential or is thermodynamically more favorable as pH increases; (c) further reduction of Cu_2O to Cu is only a function of pH and favored within a low pH range; and (d) when pH drops below a critical value with decreasing Cu^{2+} concentration (e.g. pH 2.75 for 0.1 M Cu^{2+} or pH 3.75 for 0.01 M), the potential for Cu^{2+} to Cu becomes more favorable than Cu^{2+} to Cu_2O. For example, at a pH of 4.7 and Cu^{2+} concentration of 0.1 M, $E_{Cat}(Cu^{2+}/Cu)$ is calculated as 0.310 V, less favorable than $E_{Cat}(Cu^{2+}/Cu_2O)$ which is calculated as 0.426 V but it becomes more favorable at pH 3.0 and 0.001 M Cu^{2+} concentration because $E_{Cat}(Cu^{2+}/Cu)$ is 0.251 V while $E_{Cat}(Cu^{2+}/Cu_2O)$ is 0.207 V (Fig. 2).

In the anode chamber, organic matter from wastewater could be used as electron donor by exoelectrogenic bacteria to generate electrons. Using commonly used substrates like glucose, lactate and acetate as example, the anode potential (E_{An}) can be calculated using the data from references [24,25]. The standard potentials at pH 7.0 ($E^{0\prime}$) of glucose, lactate and acetate in an anode are −0.411, −0.325 and −0.277 V, respectively (Table S2). Under selected test conditions (e.g. pH 7.0, initial 5.0 g substrate/L and 3.0 g/L of $NaHCO_3$ in the anode chamber) as described later, the E_{An} is −0.393, −0.310 and −0.263 V for glucose, lactate and acetate, respectively (Table S3). The overall electromotive force (emf) which equals $E_{Cat} - E_{An}$ in the MFC system for cathodic Cu^{2+} reduction can be estimated and positive emf values for Cu(II) reductions are obtained using glucose, lactate and acetate (Table S4). In general, reduction of Cu^{2+} to Cu_2O is more favorable than Cu^{2+} to Cu. For example, at 200 mg Cu^{2+}/L (3.125 mM, pH 4.7), the emf value for the reduction of Cu^{2+} to Cu in the cathode is estimated at 0.641 V and for Cu^{2+} to Cu_2O at 0.730 V, with glucose as the substrate (Table S4). The positive emf values imply that cathodic Cu^{2+} reduction is thermodynamically favorable and an MFC could be modified to electrodeposit copper precipitates from a cupric sulfate solution on the cathode using organics of wastewater as an electron donor in the anode chamber. This analysis also suggests that reducing Cu^{2+} to Cu_2O would be more favorable at pH 4.7 or higher (Table S4). At the same Cu^{2+} concentration, the sequence of emf values for the substrates are glucose > lactate > acetate (Table S4). However, the value is not a sole factor influencing reduction reaction. The utilization of substrate by exoelectrogenic bacteria may significantly influence reaction rate and efficiency.

The objective of this study was to investigate the feasibility of electrochemical Cu^{2+} reduction in the cathode of dual-chamber MFCs with proton exchange membranes and cupric sulfate solution as catholyte. We tested glucose as the substrate to examine the feasibility of cathodic Cu^{2+} reduction. The performance of the MFCs was characterized in terms of power generation, Cu^{2+} removal efficiency, and the composition of deposited products on the cathode under different Cu^{2+} concentrations.

2. Materials and methods

2.1. MFC system design

The dual-chamber MFCs used consisted of a cathode chamber and an anode chamber (1.00 L working volume) (Fig. 1). The two chambers were separated by a proton exchange membrane (PEM, Nafion[TM] 212, Dupont Co., USA) with a 121 cm^2 cross section. Prior to use, a fresh PEM was pre-treated in accordance with the literature [14]. After use, the PEM was regenerated via the same procedure. Graphite plates (14 cm × 10.5 cm, 0.5 cm thickness, Nanguang Co., Ltd., China) were used as anode material in the first test of MFCs (A_0 and A_1), while graphite felt (Beijing Sanye

Carbon Co., China) was used in all the other MFCs. All cathodes were graphite plate (6 cm × 4.5 cm) with stainless steel wire for electrical connection. Resistors (15, 390, 510 and 1000 Ω) were used as an external load depending on the test. Cell voltage was recorded every minute by a PC equipped with a data acquisition unit (ADAM-4017 Analog Input Model, Advantech Co., Ltd., China).

2.2. MFC start-up and experiments

The anode chamber of the MFC was inoculated with anaerobic sludge (0.10 L, collected from an anaerobic digester at Luofang Wastewater Treatment Plant, Shenzhen, China) and a medium (0.90 L) containing (per L) glucose, 5.00 g; NaCl, 1.00 g; NaHCO₃, 3.00 g; NH₄Cl, 0.40 g; MgCl₂·7H₂O, 0.33 g; CaCl₂, 0.28 g; and trace vitamins and minerals, 5 mL [11]. A saturated calomel electrode (SCE) (212, Shanghai Luosu Technology Co., China) was placed in the anode chamber as a reference probe. The MFCs were maintained in a temperature-controlled chamber (SPX-150, Shanghai Yuejin Medical Instruments Factory, China) at 35 °C and operated in fed-batch mode. Three batch experiments were conducted. During inoculation, the cathode chamber was filled with the phosphate buffer (1.00 L, pH 7.0) containing (per L) Na₂HPO₄, 2.75 g; NaH₂PO₄·H₂O, 4.22 g; and NaCl, 2.93 g. The cathode chamber was continuously sparged with air to supply O₂ as electron acceptor. After acclimation, the air sparging stopped and the phosphate buffer was replaced with 1.00 L of CuSO₄ solution of desired initial concentration. Power generation and the change in Cu²⁺ concentrations were monitored.

The first experiment was to examine the feasibility of cathodic Cu²⁺ reduction. Two MFCs (named A_0 and A_1) with graphite plates as anodes were operated with an external resistor of 1000 Ω. The anode chamber of A_1 was inoculated with the anaerobic sludge while that of A_0 was not inoculated as a control. After an acclimation stage of 48 h, the phosphate buffer catholyte of both MFCs was replaced with a CuSO₄ solution of 6400 mg Cu²⁺/L (0.1 M).

The second experiment was to determine the effect of external resistance on copper removal and electricity generation. Three MFCs (R_1, R_2 and R_3) with graphite felt anode material (which enhances power generation in comparison with the graphite plates used in the first set) were operated at an initial Cu²⁺ concentration of 200 mg/L with different external resistors (R_{ext} = 15, 390 and 510 Ω for R_1, R_2 and R_3, respectively).

The third experiment was to investigate the effect of initial Cu²⁺ concentration on MFC performance. Four MFCs (C_1, C_2, C_3 and C_4) were started with initial Cu²⁺ concentrations of 50, 200, 500 and 1000 mg/L, respectively. The external resistor was removed from the MFC system i.e. the operation was conducted under short circuit.

The sustainability of Cu²⁺ removal was further tested in a modified MFC (55 mL cathode chamber volume) with a fed-batch mode by refilling CuSO₄ solution (350 mg Cu²⁺/L) and with a 500 Ω external resistor. Each feed cycle lasted about 20 h at 35 °C.

2.3. Analytical procedures and calculations

The cell voltage (V) across an external resistor (R_e) in the MFC circuit was monitored at 0.5 min intervals. When the cell voltage output was stable, a stepwise change of external resistance from 90,000 to 30 Ω was used to obtain a polarization curve for the maximum power generation. The current (I) through the electrical circuit was calculated based on the measured cell voltage (V) and resistance by $I = V/R_e$. Power density (P) was calculated by $P = VI$ based on the volume of the anolyte or the area of the cathode. The
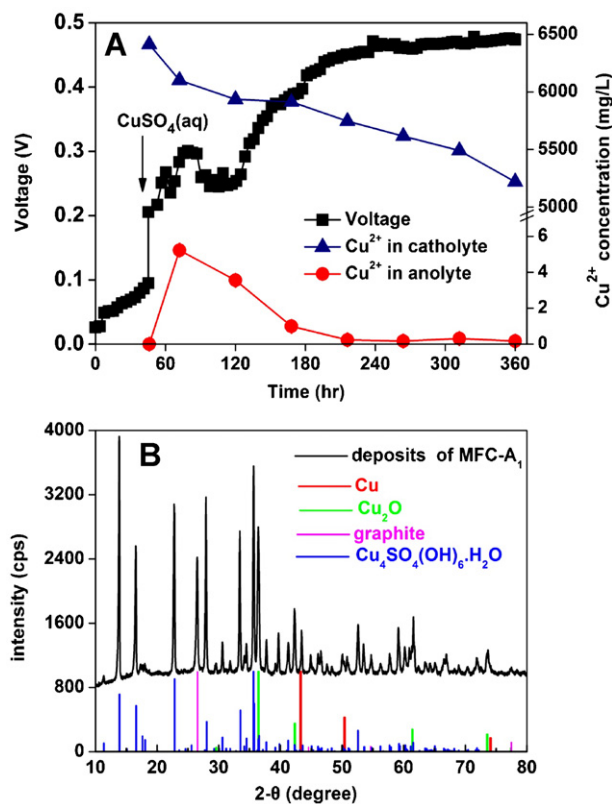

Fig. 3. (A) Cell voltage generation and the Cu²⁺ concentration change in MFC A_1. (B) X-ray diffraction pattern of the deposits on the cathode of A_1. This indicated that the cathode products were metal copper, Cu₂O and non-reduced brochantite.

coulombic efficiency was calculated as [27]:

$$E_c = \frac{\sum_{i=1}^{n} V_i t_i}{RFb \cdot \Delta S \cdot V_{An}} M \times 100\% \tag{7}$$

where E_c is the coulombic efficiency (%); V_i is the voltage (V); t_i is the time duration (s); F is the Faraday constant; b is the moles of electrons produced per mole of substrate ($b = 4$ mol e⁻/mol glucose in this study), ΔS is the overall removal efficiency of glucose as total organic carbon (TOC) (g/L), M is the molecular weight of TOC (12 g/mol) and V_{An} is the volume of the anodic solution (L). TOC of the mixed anolyte was measured by a TOC analyzer (Multi N/C3000, Analytikjena AG, Germany). Cu²⁺ concentration was measured by using flame atomic absorption spectrophotometry (SOLAAR-S4, Thermal, USA). The copper content in deposits on the cathode and PEM was measured after extraction with 1 M nitric acid solution over night. The chemical composition of the cathodic reduced products was analyzed by powder X-ray diffraction (XRD) using a Rigaku D/max 2500PC diffractometer (Japan) with Cu Kα radiation and a graphite monochromator.

3. Results and discussion

3.1. Cu²⁺ reduction and power generation in the MFC

In the first experiment with A_0 (control), neither electricity nor copper reduction occurred. Electrochemical reactions occurred in A_1 with the inoculum. The cell voltage generation of A_1 is shown in Fig. 3A. During the acclimation stage, the cell voltage increased gradually and reached a level of 0.11 V at the end of 48 h. After the Cu²⁺ solution (1.00 L, 6412.5 ± 26.7 mg/L) was injected into the cathode chamber to replace the phosphate buffer, the anodic potential jumped to about 0.22 V immediately, and then gradually

reached a peak level of 0.48 V. The increase in voltage was associated with the decrease in Cu^{2+} concentration (Fig. 3A), i.e. the reduction of Cu^{2+} in the cathode chamber was due to biological electricity generation by exoelectrogens in the anode chamber. A maximum power density of 339 mW/m^3 was obtained at a current density of 1121 mA/m^3 at 355 Ω. The maximum power density was slightly higher than that of a same-sized MFC with oxygen as the electron acceptor (data not shown). The coulombic efficiency was 1.93% as calculated using Eq. (7). The cell voltage reached steady state during the test period. The test was ended after 360 h.

Significant transportation of Cu^{2+} from the cathode chamber across the PEM to the anode chamber was observed in control A_0 with up to 125 mg/L after 24 h (Fig. S1). The mass transfer coefficient was estimated at 8.2×10^{-6} cm/s (Eq. (S4)). The changes in Cu^{2+} concentration were also observed in the anode chamber of A_1 but responded differently (Fig. 3A). After the CuSO$_4$ solution was filled in the cathode chamber, only a small amount of Cu^{2+} penetrated via the PEM into the anode chamber. The Cu^{2+} concentration in the anolyte reached a peak level of 5.23 ± 0.11 mg/L at 72 h, then declined to below 0.99 ± 0.01 mg/L at 168 h and dropped to 0.17 ± 0.08 mg/L at the end of test. The cell voltage did not increase until Cu^{2+} concentration in the anolyte dropped to $\leqslant 3.0$ mg/L, suggesting that a level >3.0 mg/L could be inhibitory for the exoelectrogens. The Cu^{2+} concentration in the anode chamber of A_1 was much lower than that of A_0 and likely due to bioactivities in the anode chamber. Otherwise, the Cu^{2+} level in the anode chamber of A_1 would have reached 125 mg/L at 72 h (24 h after filling with CuSO$_4$ solution) as occurred in the anode chamber of A_0 (Fig. S1). The generation of protons from glucose degradation in the anode chamber hindered the further transportation of Cu^{2+} to the anode chamber. The decrease in the Cu^{2+} concentration in the anode chamber was likely due to precipitation and adsorption of Cu(II) ions to anode biomass.

At the end of the test, the Cu^{2+} concentration in the cathode chamber decreased from 6412.5 ± 26.7 to 5220.0 ± 11.7 mg/L with a removal efficiency of 18.59%. The cathode was covered with crystal deposits of an emerald-green color. Crystals of a similar color were also deposited on the PEM. The pH of the cathode chamber declined slightly from 4.68 ± 0.05 to 4.37 ± 0.06, indicating transportation of protons from the anode chamber. Based on the substrate (glucose) and Cu^{2+} mass removal, the ratio of Cu^{2+} mass to glucose mass removed was 0.298.

At the end of the experiment, the crystal deposits covered the cathode of A_1 and were scraped for XRD analysis. The diffraction pattern was recorded over a 2θ range from 10° to 80° at a step size of 0.02° as shown in Fig. 3B. The distinct diffraction peaks at $2\theta = 26.54°$ were the graphite scraped from the graphite cathode plate. Six intense peaks at $2\theta = 13.9°, 16.57°, 22.81°, 28.0°, 33.5°$ and 35.7° correspond well with the most intense peaks of brochantite $(CuSO_4 \cdot 3Cu(OH)_2)$ (PDF No. 01-085-1316). Another intense peak at $2\theta = 36.4°$ fit well in the standard pattern of Cu$_2$O (PDF No. 01-078-2076). Metal copper in the deposits was identified as the peak at $2\theta = 43.3°$, which corresponded well with the standard XRD pattern of Cu (PDF No. 01-071-4610). The XRD analysis suggested that under A_1 test conditions, a small fraction of the Cu^{2+} was reduced to Cu$_2$O and Cu while the majority of the copper in the deposits was brochantite. The formation of brochantite does not involve electron transfer and produces protons:

$$4Cu^{2+} + SO_4{}^{2-} + 6H_2O \rightarrow CuSO_4 \cdot 3Cu(OH)_2 + 6H^+ \qquad (8)$$
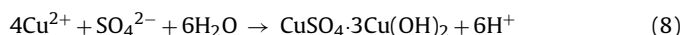
Thermodynamically, this reaction is dependent upon solution pH and Cu^{2+} concentration ($\Delta G^0 = 87.3$ kJ/reaction at pH 0.0 and -151.9 kJ/reaction at pH 7.0, calculated using data from Refs. [24,25]). Energetic analysis indicates that the reaction is favorable ($\Delta G = -56.6$ kJ/reaction) under A_1 conditions (pH 4.7 with 0.1 M Cu^{2+}) (Fig. S2). The deposits on the PEM were not analyzed but
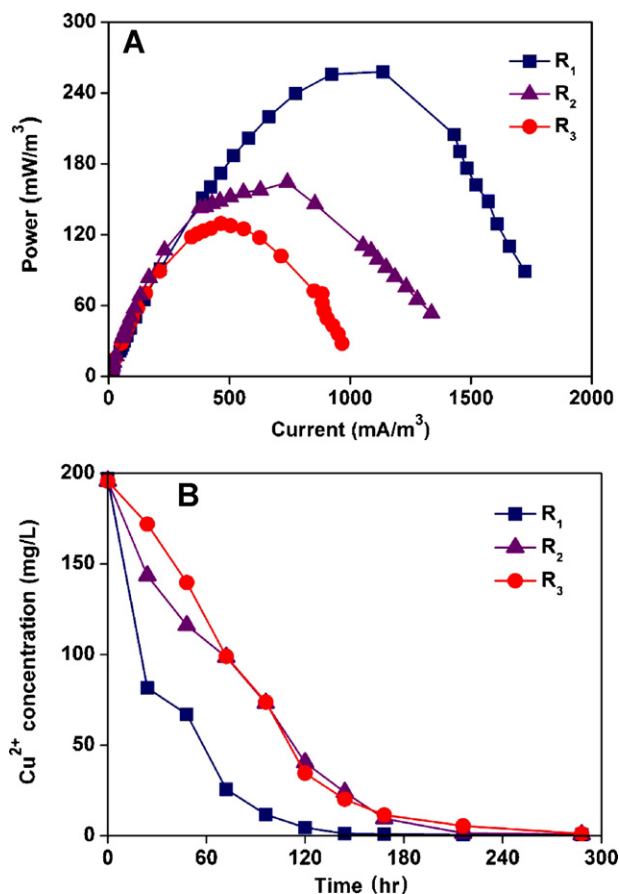

Fig. 4. (A) Effect of external resistance on the power generation (initial Cu^{2+} concentration of 196.2 ± 0.4 mg/L). (B) Change in Cu^{2+} concentrations in the catholyte of R_1 (15 Ω), R_2 (390 Ω) and R_3 (510 Ω).

they were also brochanite-like. In all other tests, described later, with initial Cu^{2+} concentration $\leqslant 1000$ mg/L, no significant formation of brochantite was observed although the ΔG of the reaction could still be slightly favorable. The brochantite deposits were produced only when a high initial Cu^{2+} concentration was applied. In low Cu^{2+} concentrations, the formation of brochanite could be limited by reaction kinetics. This suggested that besides the formation of reduced products, copper and Cu$_2$O, formation of brochantite could also contribute to Cu^{2+} removal in high Cu^{2+} environments.

3.2. Effects of external resistances

In the second experiment, three parallel MFCs (R_1, R_2, and R_3) were operated for 288 h with different external resistors (15, 390 and 510 Ω). The Cu^{2+} concentrations (196.2 ± 0.4 mg/L or 3.1 mM) in this experiment were lower than previous experiments in order to test if the negative effect of migration of Cu^{2+} to the anode chamber could be avoided. The results were positive. The initial Cu^{2+} concentrations in the anolyte of all three MFCs were less than 0.90 ± 0.03 mg/L (data not shown) and electricity was produced without a lag phase. After an acclimation stage, the cell voltage was 0.02 V in R_1; 0.27 V in R_2 and 0.33 V in R_3. Subsequently, polarization curves for the maximum power generation were obtained according to the procedure outlined in Section 2.3 (Fig. 4A). The highest power density (P_{max}) with internal resistance for each MFC was R_1, 258 mW/m^3 and 232 Ω; R_2, 164 mW/m^3 and 479 Ω; and R_3, 130 mW/m^3 and 575 Ω. The coulombic efficiency of R_1, R_2 and R_3 was 3.65%, 3.86% and 2.71%, respectively.
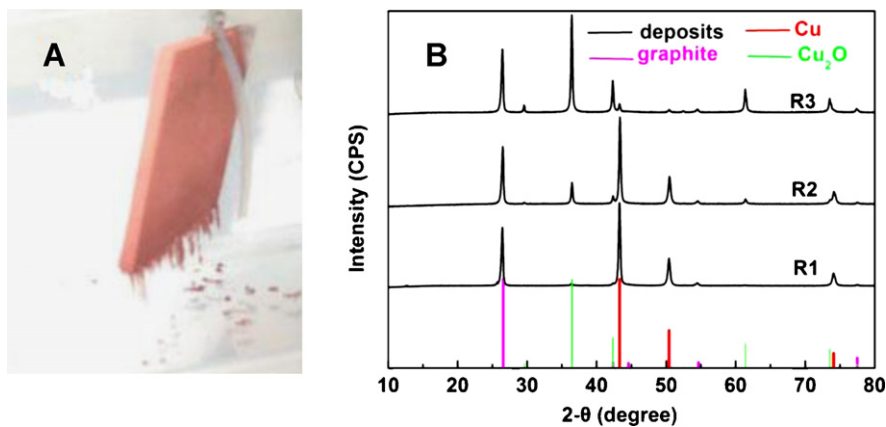
Fig. 5. (A) Picture of the cathode with deposited copper. (B) X-ray diffraction patterns of the deposits on cathode of R_1 (15 Ω), R_2 (390 Ω) and R_3 (510 Ω).

The Cu^{2+} was removed efficiently from the catholyte (Fig. 4B). The reaction duration for Cu^{2+} removal >99% was 144 h for R_1, 216 h for R_2 and 288 h for R_3 with final Cu^{2+} concentrations of 0.52 ± 0.03, 0.65 ± 0.01, and 1.04 ± 0.39 mg/L, respectively, at 288 h. The total Cu^{2+} mass removed was about 195 mg from all MFCs. The results indicated that a Cu^{2+} concentration below the USA EPA MCL i.e. 1.3 mg/L, was achieved and the Cu^{2+} removal rate was influenced by the external resistance. Lower resistance resulted in a higher removal rate. The open circuit potentials of the three MFCs were approximately the same (around 0.54 V) at the initial Cu^{2+} concentration of 196.2 ± 0.4 mg/L. The lower load (or less external resistance) resulted in higher current flowing to the cathode according to Coulomb's law and accelerated Cu^{2+} reduction.

At the end of the experiment, the cathode of R_1 was covered by a reddish-brown colored layer, typical copper-like deposits (Fig. 5A and Fig. S3) and the other cathodes were covered by a brownish-red colored layer. The deposits on the cathodes of the MFCs were scraped for XRD analysis (Fig. 5B). No brochantite was detected in the deposits. The XRD patterns indicated that (a) in R_1 deposits, only metal copper peaks (2θ = 43.3°, 50.4° and 74.1°) were observed, which is consistent with the observation of copper-like deposits covering the cathode; (b) XRD peaks of Cu_2O (2θ = 36.4°, 61.4° and 73.5°) were detected in the deposits of R_2 and R_3 but not R_1 (Fig. 5B); (c) the intensity of metal copper peaks reduced while the intensity of Cu_2O increased as higher resistance applied; the strongest intensity of Cu_2O peaks were observed in the sample from R_3 (510 Ω). With the similar open circuit potentials, the current density generated by the three MFCs followed the order of $R_1 > R_2 > R_3$, which is consistent with the observed XRD peak strength order of metal copper i.e. $R_1 > R_2 > R_3$ (Fig. 5B). Research on electrodeposition indicated that the phase composition of electrodeposition of Cu/Cu_2O films is strongly dependent on the current density [28,29]. Our observation indicated that the extent of Cu^{2+} reduction in the MFCs depended on the current density. The results indicated that decreasing or even eliminating the external resistance may be advisable to achieve high reduction of copper with an MFC.
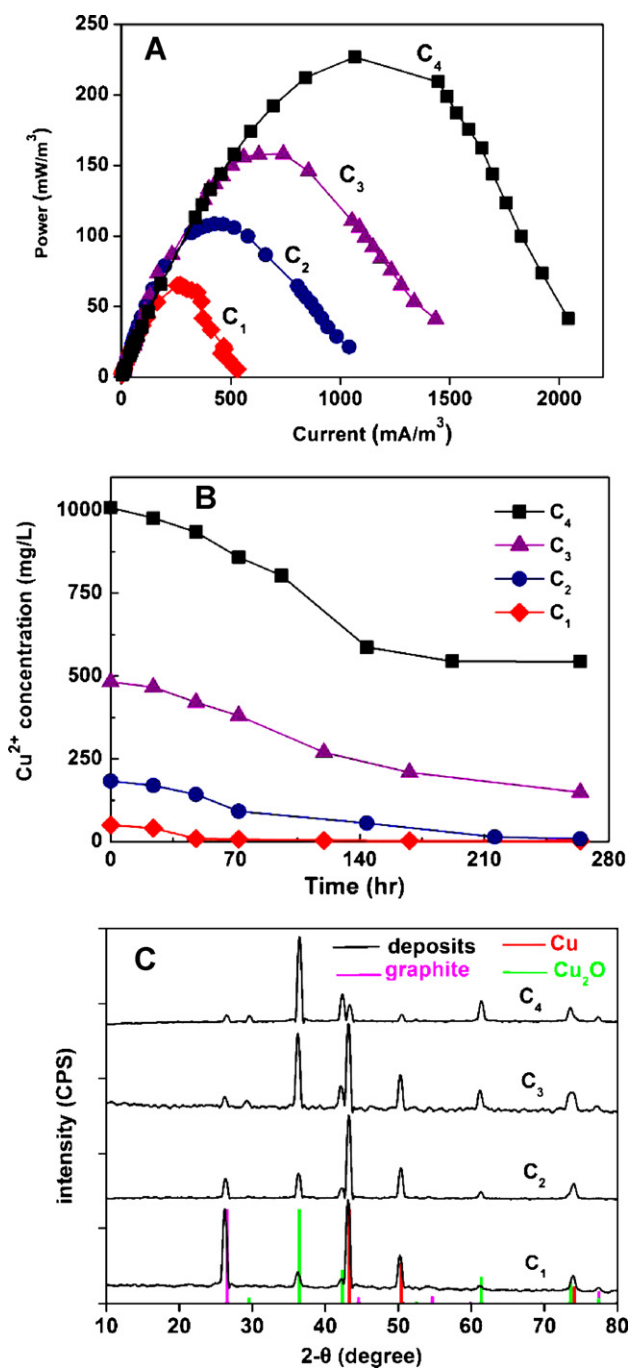
3.3. Influence of initial Cu^{2+} concentrations

Four MFCs (C_1, C_2, C_3 and C_4) were operated simultaneously at initial Cu^{2+} concentrations of 50.3 ± 5.8, 183.3 ± 0.4, 482.4 ± 9.6, 1007.9 ± 52.0 mg/L (0.79, 2.9, 7.5 and 15.7 mM), respectively. The external resistor was removed to maximize the electric currents to the cathode, based on previous experiment results. In this experiment, the migration of Cu^{2+} across the PEM was also limited, peak Cu^{2+} concentrations were less than 2.86 ± 0.24 mg/L in all MFCs.

After acclimation, polarization curves for the maximum power generation were obtained according to the procedure in Section 2.3 (Fig. 6A). The highest power density (P_{max}) of each MFC, with internal resistance was C_1, 65.3 mW/m^3 and 864 Ω; C_2, 108.7 mW/m^3 and 514 Ω; C_3, 58.2 mW/m^3 and 437 Ω; and C_4, 226.8 mW/m^3 and 148 Ω. After the measurement, no external resistor was connected. The P_{max} data indicated that as higher initial Cu^{2+} concentrations were applied, higher power density and lower internal resistance was obtained.

The changes in Cu^{2+} concentrations in the catholyte of the MFCs are shown in Fig. 6B. The experiment lasted 264 h, at which point biodegradable organics in the anode chamber were consumed and TOC concentrations stabilized at about 200 mg/L. The final Cu^{2+} concentration of catholyte in C_1, C_2, C_3 and C_4 was 2.2 ± 0.4, 8.3 ± 0.1, 149.0 ± 0.2 and 544.0 ± 4.6 mg/L, respectively; respective Cu^{2+} removal efficiency was 95.6%, 95.5%, 69.1% and 46.0% and mass Cu^{2+} removed was 48.1, 175.0, 333.4 and 463.9 mg. The Cu^{2+} removal efficiency at higher concentrations was lower, but the total Cu^{2+} removed increased as the higher initial Cu^{2+} concentration was applied. At the end of the experiment, the copper content deposited on the cathodes and PEMs was extracted and analyzed. Results showed that the Cu^{2+} removed was mainly deposited on the cathodes (>90%), with a small fraction on the PEMs except in C_1. Due to a low Cu^{2+} concentration, the copper recovered from the cathode and PEM in C_1 was poor (≈12%). The mass ratios of copper extracted from cathodes to copper extracted from PEMs were 0.6, 3, 10 and 35 fold for C_1, C_2, C_3 and C_4, respectively.

At the end of the experiment, the cathode of C_1 was covered by a reddish-brown colored layer and the other cathodes were covered by a brownish-red colored layer. Based on the XRD patterns, the metal copper peaks were predominant in the deposits with the initial Cu^{2+} concentration ⩽500 mg/L (C_1, C_2 and C_3) while the intensity of Cu_2O was strongest in C_4 with an initial Cu^{2+} concentration of 1000 mg/L. Because all these MFCs were filled with the same anodic medium without external resistor, the electrons potentially generated in all MFCs should have been almost the same. The results showed that the copper removal rate and reduction extent depended upon the Cu^{2+} concentration or the ratio of available electron acceptors (Cu^{2+}) to electron donors (glucose). The higher the ratio (i.e. higher electron acceptor availability) the less reduced copper generated, or less metal copper produced. Based on the difference of cathode potentials between the reduction of Cu^{2+} to Cu(s) and Cu^{2+} to Cu_2O (Fig. 2), a higher Cu^{2+} level at pH 4.7 would favor formation of Cu_2O whereas more available electrons (or a lower Cu^{2+} concentration) would support the further reduction of Cu_2O to Cu. During this experiment, the majority Cu^{2+} in the catholyte (pH 4.7) was first reduced to Cu_2O and the Cu_2O

Fig. 6. (A) Influence of the initial Cu^{2+} concentration on the power generation. (B) Change in Cu^{2+} concentrations. (C) X-ray diffraction patterns of the deposits on the cathodes. C_1: 50.3 ± 5.8 mg/L; C_2: 183.3 ± 0.4 mg/L; C_3: 482.4 ±9.6 mg/L; C_4: 1007.9 ±52.0 mg/L.

was then transferred to Cu, depending on the amount of available electrons. No pH change should be observed after all or most of the Cu^{2+} is reduced to Cu. When electricity generated in the anode was the limiting factor (i.e. at high Cu^{2+} concentration) the reduction of Cu_2O to Cu become limited as observed in C_4.

3.4. Sustainability of Cu^{2+} removal in MFCs

To evaluate the sustainability of Cu^{2+} removal with electricity generation in the MFC, a fed-batch mode test was performed with a MFC i.e. by refilling $CuSO_4$ solution (350 mg Cu^{2+}/L) every 20 h. A 500 Ω external resistor was used as load. A total of

Table 1
Results of continuous Cu^{2+} removal in a fed-batch mode MFC.

Number of cycle	Cu^{2+} concentration (mg/L)		Removal (%)
	Start	End	
1	344.34 ± 1.00	11.20 ± 0.10	96.75
2	343.20 ± 1.65	11.29 ± 0.04	96.71
3	361.48 ± 1.22	13.68 ± 0.16	96.22
4	356.01 ± 2.45	13.58 ± 0.08	96.18
5	354.80 ± 2.47	13.88 ± 0.11	96.09
6	353.46 ± 2.87	13.86 ± 0.05	96.09
7	343.55 ± 1.73	11.17 ± 0.04	96.75
8	347.46 ± 1.77	11.19 ± 0.02	96.79
Average	350.54 ± 9.08	12.48 ± 0.62	96.45 ± 0.21

Note: the data values represent 95% confidence intervals. Test temperature was at 35 °C.

eight cycles was continued with an initial COD concentration of 971.21 ± 2.96 mg/L. The COD concentration of 497.34 ± 85.79 mg/L was observed finally. During the test, a stable Cu^{2+} removal greater than 96% was achieved (Table 1). The average maximum power density was 136.7 mW/m² cathode area. At the end of the test, the cathode was covered with brownish-red colored precipitate layer, indicating the formation of Cu_2O and metal copper mixture. This test indicates that the continuous removal of Cu^{2+} in the cathode chamber of MFC with fed-batch mode is feasible and the Cu^{2+} removal performance is sustainable.

3.5. Implementation and further work

This study is one of several attempts to biologically reduce copper(II) using MFCs. The results demonstrated that Cu^{2+} can be removed from the catholyte and recovered as metal copper and/or Cu_2O depending on operational conditions. We demonstrated the feasibility of electrodeposition of metal copper from a cupric sulfate solution on a cathode with simultaneous electricity generation by both single and multiple fed-batch tests. This indicates that MFCs can be modified as a bioreactor to remove, and even recover, copper from a Cu^{2+} containing solution or wastewater in the cathode chamber with electricity generation from the oxidation of organic matter in the anode chamber. Under favorable conditions tested in this study, the Cu^{2+} concentration in the catholyte fell below the USA EPA MCL and copper was mainly deposited as metal copper or/and Cu(I) oxide. The discovery in this study is the potential first step to developing a biological process for the treatment of Cu^{2+}-containing wastewater such as electroplating wastewater.

Based on the results of this study, there was an inverse relationship between power generation and copper removal. The higher the Cu^{2+} mass removed or the higher the removal efficiency, the less available electricity was generated (or lower external resistance was loaded). As we focus on a treatment process for copper removal the power output will not be considered as a primary goal and future process development should address metal removal performance rather than electricity generation.

Our results suggested that metal copper was produced only at relatively low Cu^{2+} concentrations or if excess electrons were applied. If the MFCs were designed for copper removal rather than recovery of metal copper, the deposition of Cu_2O will be more energy-saving than recovery of metal copper and even precipitation of brochanite could be advisable. If metal copper recovery were the target, theoretically, the reduction of Cu^{2+} to Cu(s) could become more favorable if the catholyte were maintained at about pH 3.0 as shown in Fig. 2.

We used anaerobic sludge as inoculum in this study. This culture was not a highly efficient anodophilic functional consortium for the MFC. Therefore, relatively low coulombic efficiency was observed in comparison with those reported by other researchers [30,31]. The

MFC performance for cathodic Cu(II) reduction could be enhanced if the anode biofilm were developed by selected highly efficient exo-electrogens as reported by Wang et al. [31]. We used glucose as the electron donor source for the feasibility study. Based on energetic analysis, the trend of the cathodic Cu^{2+} reduction in MFCs would be the same but the rate and reduction extent may vary if complex organics from wastewater were used. Anode microbial communities would also be influenced by available substrates. Further research should test the effectiveness of other organics from industrial and municipal wastewaters. In this study, we used a simple, synthetic copper solution ($CuSO_4$) in the catholyte to prove the concept of cathodic Cu(II) reduction using MFCs. Future work should focus on electroplating or more complicated wastewater.

4. Conclusion

The electrodeposition of metal copper from a cupric sulfate solution on a cathode, with simultaneous electricity generation by MFCs was feasible. Under the favorable conditions tested, the Cu^{2+} concentration in the catholyte fell below 1.3 mg/L and Cu^{2+} removal >99% was observed at initial Cu^{2+} concentrations of about 200 mg/L. Cu^{2+} was removed from the catholyte and recovered as metal copper and/or Cu_2O depending on operational conditions. Decreasing or even eliminating the external resistance was advisable to achieve a higher reduction of copper. The copper removal rate and reduction extent depended upon the ratio of available electron acceptors (Cu^{2+}) to electron donors (glucose). The sustainability of the removal of Cu^{2+} in cathode chamber was confirmed by continuous fed-batch mode for 8 cycles.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.02.018.

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