Cathodic Reduction of Cu\(^{2+}\) and Electric Power Generation Using a Microbial Fuel Cell

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When Cu\(^{2+}\) was used as an electron acceptor, removal of Cu\(^{2+}\) was achieved from the synthesized wastewater (SW) in the cathode compartment of a microbial fuel cell (MFC). By addition of KNO\(_3\), the different initial pH of the SW showed no effect on the removal efficiency of Cu\(^{2+}\). For Cu\(^{2+}\) concentration of 50 mg/L, the removal efficiencies were found to be 99.82%, 99.95%, 99.58%, and 99.97% for the KNO\(_3\) concentrations of 0, 50, 100, and 200 mM, and to be 99.4%, 99.9%, 99.7%, and 99.7% for pH values of 2, 3, 4, and 5, respectively. More than 99% Cu\(^{2+}\) was removed for the Cu\(^{2+}\) concentrations of 10, 50, and 100 mg/L, while only 60.1% of Cu\(^{2+}\) was removed for the initial concentration of 200 mg/L (pH 3). The maximum power density was affected by both KNO\(_3\) concentration and initial concentration of Cu\(^{2+}\). It was increased by a factor of 1.5 (from 96.2 to 143.6 mW/m\(^2\)) when the KNO\(_3\) concentration was increased from 0 to 200 mM (50 mg/L Cu\(^{2+}\)) and by a factor of 2.7 (from 118 to 319 mW/m\(^2\)) when Cu\(^{2+}\) concentration was increased from 10 to 200 mg/L (pH 3).

Key Words: Copper ion removal, Electron acceptor, Electric power generation, Microbial fuel cell

Introduction

Heavy metals from contaminated water are of major concern because of their high toxicity and susceptible carcinogenic effect to many life forms. Unlike organic contaminants, which are mostly biodegradable, metal ions do not degrade into harmless end products. Cu\(^{2+}\) may be present in wastewaters from a variety of sources that use copper salts or copper catalysts. Some sources include chemical manufacturing processes and plating baths. Thus the effective removal of copper from polluted waters is ecologically very important. Many technologies were reported for the removal or recovery of copper from wastewater including bio-sorption,\(^1\) activated carbon adsorption,\(^2\) chemical precipitation,\(^3\) acidification,\(^4\) and adsorption on minerals.\(^5,6\) Majority of the technologies mentioned above have their inherent limitations, such as high costs and harmful effluents. Therefore, it is very important to develop new technologies to remove copper ions from wastewater efficiently and economically.

MFCs raise more attention due to the benefits of both wastewater treatment and power generation.\(^7,8\) In a dual-compartment MFC, anode and cathode compartments are separated by an ion exchange membrane, such as proton exchange membrane (PEM),\(^9\) cation exchange membrane (CEM), anion exchange membrane (AEM), and ultrafiltration membrane,\(^10\) and bipolar membrane.\(^11\) In the anode compartment microorganisms attach to the anode surface, and degrade organic pollutants under anaerobic conditions to generate electrons. The generated electrons flow through an external circuit to the cathode, reacting with electron acceptors and producing an electric current. Several variations of wastewater have been used as electron donors, including artificial wastewater,\(^12\) brewery wastewater,\(^13\) vegetable products,\(^14\) landfill leachate,\(^15\) chemical wastewater,\(^16\) etc. Even if the majority of wastewaters were used as electron donors in the anode compartment until now, only a few studies were focused on the treatment of wastewater used as electron acceptors. Li \(\text{et al.}^{17}\) tried treatment of electroplating wastewater containing Cr\(^{6+}\) by using MFC. They got Cr\(^{6+}\) removal efficiency as high as 99.5% and maximum power density of 1600 mW/m\(^2\). Clauwaert \(\text{et al.}^{18}\) removed up to 0.146 kgNO\(_3\) N/m\(^2\) day for the cathode compartment volume, and the highest power output was 8 W/m\(^2\) for the net cathode compartment volume by using a bio-cathode of the MFC.

The reduction potential of Cu\(^{2+}/\text{Cu}\) is as follows:

\[
\text{Cu}^{2+} + 2e^- = \text{Cu} \quad \text{E}^0 = 0.337 \text{ V} \quad (1)
\]

The reduction potential of HCO\(_3^-/\text{CH}_3\text{COO}^-\) at pH 7 is as follows:

\[
\begin{align*}
\text{HCO}_3^- + 8\text{H}^+ + \text{CO}_2 + 8e^- & = \text{CH}_3\text{COO}^- + 3\text{H}_2\text{O} \\
\text{E}^0 & = -0.284 \text{ V} \quad (2)
\end{align*}
\]

From Eq. (1) and (2), the cell voltage (\(E_{\text{cell}}\)) of a MFC using acetate as electron donor and Cu\(^{2+}\) as electron acceptor can be calculated:

\[
E_{\text{cell}} = E^0_{\text{ca}} - E^0_{\text{an}} = 0.337 \text{ V} - (-0.284 \text{ V}) = 0.621 \text{ V}
\]

Therefore, the \(E_{\text{cell}}\) is theoretically enough to remove Cu\(^{2+}\) and to generate electric power as well. Our goal of this study is to remove Cu\(^{2+}\) contaminants from the wastewater, while generating power at the same time, and to evaluate factors that could affect the removal of Cu\(^{2+}\) and power generation. To avoid the transfer of Cu\(^{2+}\) from the cathode chamber to the anode chamber, which would be toxic to microorganism, AEM was selected as a separator of the reactor chambers instead of usually used PEM, such as Nafion membrane. This study is the first time to combine the removal of Cu\(^{2+}\) contaminants and power generation by using a MFC.

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Experimental Section

MFC fabrication. A tubular dual-compartment MFC reactor fabricated with a plexi-glass tube (diameter = 5 cm) was used in this study (Figure 1). Both anode and cathode compartments held a volume of 137 mL (length = 7 cm), and the effective volumes were 120 mL and 100 mL, respectively. The anode and cathode compartments were separated by AEM (AMI-7001, Membrane International, Inc., USA) with a surface area of 19.6 cm² (diameter = 5 cm). The AEM was preconditioned by immersing in NaCl solution as described in the published paper.10 Both anode and cathode were graphite felts with the same geometrical surface area of 35.6 cm² (length = 3.5 cm, width = 3 cm, height = 1.12 cm, Alfa Aesar, USA). The electrodes were treated by soaking in acetone overnight; afterwards the electrodes were rinsed with distilled water 5 times, and then heated for 30 min at 450 °C in a muffle furnace as reported by Wang et al.19

Inoculation. Anaerobic sludge, collected from the anaerobic digester of Okchen wastewater treatment plant in Okchen, Korea, was used as inoculum in the anode compartment. To start up the MFC reactor, a mixture of 30 mL anaerobic sludge and 90 mL artificial wastewater (AW) was pumped into the anode compartment after purging with nitrogen gas for 5 min. The AW contained 1.36 g/L CH₃COONa·3H₂O, 1.05 g/L NH₄Cl, 1.5 g/L KH₂PO₄, 2.2 g/L K₂HPO₄, and 0.2 g/L yeast extract.20 Each time the voltage decreased below 25 mV, 0.2 g medium was added to the anode compartment until a repeatable maximum voltage was obtained. The cathode compartment was filled with 0.1 M KH₂PO₄ solution and purged with air (80 mL/min). The effect of ionic conductivity of catholyte solution in the cathode compartment on power generation was evaluated by adding different amounts of KNO₃ to the SW. In order to determine the removal efficiency of Cu²⁺ under different pH values, the pH of SW was adjusted with diluted HNO₃.

Calculations. Voltage was measured with a potentiostat (WMPG 1000, Won-A Tech, Korea) every minute. The power density was calculated according to:

\[ P = \frac{V^2}{RA} \]

where V is the voltage, R is the external resistance, and A is the geometrical surface area of the anode.

The columbic efficiency (CE) was calculated as follows:

\[ CE = \frac{8\int_idt}{FvACOD} \]

where 8 is a constant used for COD, based on MO₂ = 32 for the molecular weight of O₂ and 4 for the number of electrons exchanged per mol of oxygen, t is the reaction time interval (60 s), F is the Faraday’s constant (96485 C/mol e⁻), v is the effective volume of anode chamber, and ΔCOD is change of the chemical oxygen demand consumed, I is current calculated as:

\[ I = \frac{V}{R} \]

Analysis. The concentration of total copper was analyzed with an ICP emission spectrometer (ICPE-9000, Shimadzu, Japan). Observation of removal product attached on the surface of the cathode was performed with SEM (XL-30S FEG, Philips, Holland). The chemical elements of the deposit on the cathode surface after reaction was identified with EDS (Quantax 200, Bruker, Germany).

Results and Discussion

Effects of KNO₃ concentration. KNO₃ was not necessary for the reduction of Cu²⁺. As shown in Figure 2A, the removal efficiency of Cu²⁺ was not affected by the addition of KNO₃.
within a reaction time of 11 hours, which was at least 99.6%, while the maximum power output was greatly improved (Figure 2B). The maximum power density was increased from 96.2 to 143.6 mW/m², when KNO3 concentration was increased from 0 mM to 200 mM. The reason for this is that the addition of KNO3 could decrease the internal resistance of the MFC by improving the ionic conductivity of the solution. Similar phenomenon was reported by Liu et al.,21 when KCl was used to improve the ionic conductivity. In this study, the internal resistance was decreased from 239.4 to 136.1 ohm due to the improved ionic conductivity by increasing KNO3 concentration from 0 to 200 mM (pH 5.8, unadjusted). According to electron stoichiometry calculation, the coulombs used to generate electric current were increased from 18.45 C to 18.97 C according to the increase in KNO3 concentration from 0 to 200 mM, and they were a little larger (1.5% to 4.4%) than those used to reduce Cu2+. The loss of electrons was likely due to the reduction of dissolved oxygen in SW during the early stage of N2 purge.

**Effects of initial pH.** To determine the effects of pH on the removal efficiency of Cu2+, SW was prepared by dissolving 50 mg/L Cu2+ in 200 mM KNO3 solution. The pH was adjusted from 2 to 5. After operating the cell for 11 hours, the removal efficiencies were found to be 99.4%, 99.9%, 99.7%, and 99.7% for pH values of 2, 3, 4, and 5, respectively. From the result, it can be concluded that the Cu2+ removal was not affected by the initial pH of the SW. The conclusion was consistent with the principle that the reduction of Cu2+ did not involve protons according to Eq. (1), which meant that no adjustment of pH was needed for treatment of practical wastewater containing Cu2+ by using MFC. This is different from other reported technologies5,6 indicating that higher pH led to higher removal efficiency of Cu2+. Although the existence of H+ in SW had no effect on the reduction of Cu2+, the adjustment of pH also affected the power generation due to the decrease of internal resistance by increasing ionic conductivity (data not shown). This also differed from other kinds of electron acceptors, such as Cr6+17 and MnO422 showing that reduction is largely affected by H+ concentration.

**Effects of initial Cu2+ concentration.** Effects of initial concentration of Cu2+ on the removal efficiency and power generation were also evaluated by adjusting the concentration of Cu2+ to 10, 50, 100, and 200 mg/L (200 mM KNO3, pH 3). Figure 4A shows that, within 11 hours, the removal efficiencies of Cu2+ reached 99.72%, 99.86%, and 99.92% for the Cu2+ concentrations of 10, 50, and 100 mg/L, respectively, while only 60.1% of Cu2+ was reduced for the concentration of 200 mg/L. This was probably due to the fact that the electrons produced by the microorganisms in the anode compartment was insufficient for the reduction of Cu2+ compared to its high concentration and limited operation time as shown in Figure 4B.

The open circuit potential (OCP) of the cathode was determined by placing an Ag/AgCl (3.3 M KCl) reference electrode in the cathode compartment. Then it was converted with respect to Standard Hydrogen Electrode (SHE). Power density was greatly affected by the initial concentration of Cu2+ as shown in Figure 4C. The maximum power density increased by a factor of 2.7 from 118 to 319 mW/m², when the initial concentration of Cu2+ was increased from 10 to 200 mg/L. The OCV increased from 563 to 590 mV for the same increase in the concentration of Cu2+ (Figure 4D). The improvement of maximum power density might be due to the increase in the OCP of the cathode which was influenced by Cu2+ concentration. This result was generally consistent with the trends expected by analysis using Nernst equation based on Eq. (1):

\[
E = 0.337 + 0.030 \log [\text{Cu}^{2+}]
\]
A similar phenomenon was observed by You et al.,\textsuperscript{22} when permanganate was used as an electron acceptor. Another reason for the improvement of the maximum power density would be the reduction of internal resistance caused by the increase in ionic conductivity with high initial Cu\textsuperscript{2+} concentration. The internal resistance was further reduced from 85.9 (10 mg/L Cu\textsuperscript{2+}) to 63.7 ohm (200 mg/L Cu\textsuperscript{2+}). The redox potential of NAD\textsuperscript{+}/NADH on the anode of our MFC was about °0.340 V, which was close to that of °0.32 V reported by other researchers.\textsuperscript{23} The CE increased from 0.66\% for 10 mg/L Cu\textsuperscript{2+} and from 3.43\% for 200 mg/L Cu\textsuperscript{2+} (Figure 4C). This increase in CE was due to the increase of number of electron acceptors provided at higher Cu\textsuperscript{2+} concentrations, which led to relatively longer discharge time with higher voltage under the fixed load resistor (Figure 4B).

Figure 5 shows the power density curve as a function of current density for the Cu\textsuperscript{2+} concentration of 50 mg/L at pH 3. The external resistance was changed from 1000 to 50 Ohm. As it is illustrated, the maximum power density of 284 mW/m\textsuperscript{2} was achieved at a current density of 0.893 A/m\textsuperscript{2} with an external resistance of 100 ohm.

Characteristics of the cathode surface after MFC operation. The cathode surface was observed using SEM and analyzed by EDS. As seen from the SEM picture (Figure 6), a deposit was clearly observed on the surface of the cathode after MFC operation in the Cu\textsuperscript{2+} solution. From the EDS analysis (Figure 7), the peaks at 0.943, and 8.096 keV verified that the copper metal exists on the surface of the cathode.\textsuperscript{24} As discussed in the above, Cu\textsuperscript{2+} can be efficiently reduced and removed by accepting electrons generated by decomposition of acetate by microorganisms using a MFC. Compared to other technologies, the removal of Cu\textsuperscript{2+} using MFC has the following advantages: (1) It is not
necessary to adjust the pH, while, as it was reported by Shukla and Roshan, lower pH led to lower Cu²⁺ removal efficiency, thus costing extra to adjust the pH in order to get higher Cu²⁺ removal efficiency; (2) Electric power, a useful energy source, can be generated at the same time; (3) Pure copper can be easily recovered. From the EDS analysis and a color change of the cathode surface (from black to wine), the final product attached to the surface of the cathode was found to be copper metal. Actually, the graphite felt cathode would gradually turn to a copper cathode as the reduction of Cu²⁺ proceeded, which made it easy to recover the copper. Otherwise, a physical process, such as adsorption, made it impossible to recover copper directly. In this study, the effective removal of Cu²⁺ from SW was achieved. However, further test of this technology should be performed using real wastewater containing Cu²⁺. Its real application would depend on the development of a large scale-up of the MFC.

Conclusions

This study successfully verified dual functions of Cu²⁺ removal from the synthesized wastewater and power generation of a dual-compartment microbial fuel cell. Addition of KNO₃ and initial pH of SW showed no effect on the removal of Cu²⁺, while the addition of KNO₃ and adjustment of pH greatly affected the maximum power density due to the decrease of internal resistance. Initial concentration of Cu²⁺ affected both the removal efficiency and the maximum power density. The maximum power density increased from 96.2 to 143.6 mW/m² when the KNO₃ concentration was increased from 0 to 200 mM (50 mg/L Cu²⁺), and from 118 to 319 mW/m² when the Cu²⁺ concentration was increased from 10 to 200 mg/L (pH 3). The high removal efficiency of Cu²⁺ and high power generation achieved by our MFC makes the MFC a promising technology to treat Cu²⁺ contaminated water and recovery of copper metal.

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