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Recovery of silver metal and electric power generation using a microbial fuel cell

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ABSTRACT

The purpose of this study was to model recovering silver metal from wastewater using a two-chambered silver (I) microbial fuel cell (Ag(I)-MFC) with carbon felt electrodes. Both anode and cathode chambers held a volume of about 900 mL. The anode and cathode were graphite felts with a surface area of 122.3 and 34.6 cm^2. The chambers were separated by an anion exchange membrane with a surface area of about 78.3 cm^2. The MFC was discharged by connecting a 1,000 Ω load resistor. The anode chamber contained 10 mM sodium acetate with 4-(2-hydroxyethyl)-1-piperazine-ethanesulfonic acid buffer medium as electron donors, and the cathode chamber contained synthetic wastewater with silver nitrate. It was verified that the Ag(I)-MFC system in the present study could successfully be operated. The effluent silver concentration was in the range of 0.003–0.153 ppm, representing that the recovery efficiencies for silver ion were in the range of 98.2–92.3% for the Ag(I) concentration range from 50 to 4000 ppm after operating the reaction for 10 h. Initial Ag(I) concentration affected the power generation by both increasing the cathode potential and decreasing the internal resistance of the MFC. The highest maximum power density and current density was 1.93 W/m^2 and 4.25 A/m^2 (for 2,000 ppm Ag(I)), respectively. Shinny silver metals on the graphite felt cathode were visible and they were verified to be very pure silver by scanning electron microscope and energy dispersive spectroscopy. A charge transfer resistance of 1,687 Ω was obtained for 1,000 ppm Ag(I) by electrochemical impedance spectroscopy.

Keywords: Effluent silver concentration; Electric power generation; Silver (I) microbial fuel cell; Recovery efficiency

1. Introduction

Removal of heavy metals from wastewater is a very important issue in recent years because of their high toxicity and susceptible carcinogenic effect to human. Heavy metals, such as copper, silver, chromium, and mercury, cannot be degraded into harmless end products. Silver ions are placed in wastewater for sources that use silver nitrate, silver sulfate, like film processing, spent electrical and electronic applications, jewellery and ornament, and

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mining wastewater [1,2]. In common, the only soluble silver salt is silver nitrate, which is a main component of the silver-containing wastewater. Silver nitrate is widely used in radio, chemicals, machinery manufacturing, ceramics, photography, electroplating, and ink manufacturing industry. There are broad application and growing demand for silver in the industries. Thus, it is very important to recover silver from the wastewaters. Silver ions could be recovered and/or removed by preferably utilizing hydrometallurgical methods, which include adsorption by ion exchange [3–6], extraction [7], reduction by reagents [8], and electrochemical reduction [9]. Most of these technologies mentioned have their advantages and limitations. So, it is important to develop efficient and cost-effective new technologies to recover silver from wastewaters.

Microbial fuel cell (MFC) technology can form a novel, cost-effective approach for recovering silver metal and bioelectricity from the system that consists of biomass, anaerobic bacteria, silver ion-containing wastewater, electrodes, and ionic exchange membrane. In the MFC reactor, the micro-organism, which is a key factor, attaches to the surface of the anode, anaerobically decomposes the organic matters in its plasma, and generates reduced electron carriers NADH, and $FADH_2$, which transport electrons to flavin mononucletide-containing protein, coenzyme Q, and cytochromes. The electrons on the membrane can be transported by mediators, such as flavins, to the anode, where the electrons can pass through a load and are trapped by electron acceptors at the cathode.

Silver recovery by MFC has been reported in literature [10]. In this work, carbon brush anode and carbon cloth cathode were used with the highest recovery efficiency of 99.91% and the highest maximum power density of 4.25 W/m^2. However, in the present study, graphite felt was applied to obtain visible silver metal and find out the industrial application opportunities. Factors that can affect silver recovery efficiency and power generation, such as initial $NaClO_4$ concentration as an electrolyte and initial silver ion concentration, were evaluated. The surface morphology by scanning electron microscopy (SEM) and the internal resistance analysis of the Ag(I)-MFC by electrochemical impedance spectroscopy (EIS) were performed.

2. Meterials and methods

2.1. MFC configuration

An acrylic rectangular two-chambered MFC reactor was used in this study (Fig. 1). Both anode and cathode chambers held a volume of about 900 mL, of which the electrodes were graphite felt electrodes with surface area of 122 and 34.6 cm^2 (Alfa Aesar #42107, USA). The anode and cathode chambers were separated by anion exchange membrane (AEM) (AEM-7001, Membrane international, Inc) with a surface area of about 78.3 cm^2. The AEM was preconditioned by immersing in 10% NaCl solution for 24 h and 5% H_2O_2 for 24 h. Graphite felt (3.0 cm × 3.5 cm × 1.3 cm). electrodes were treated by soaking them in acetone overnight; afterwards, the electrodes were rinsed with distilled water for five times and then heated for 30 min at 450˚C in a muffle furnace. Titanium wire was connected to the carbon felt to collect the current. The external circuit was connected with a 1,000 Ω resistor, as shown in Fig. 1.

2.2. MFC start-up and operation

The anaerobic sludge collected from anaerobic digester was used as inoculums in the anode chamber, as given in literature [10]. When MFC reactor starts up, a mixture of 50 mL anaerobic sludge and 850 mL artificial wastewater was pumped into the anode chamber. The artificial wastewater contained 1.36 g/L $CH_3COONa{\cdot}H_2O$ as electron donor, 0.2 g/L NH_4OH, 2.77 g/L $KClO_4$, 5.79 g/L 4-(2-hydroxyethyl)-1-piperazine-ethanesulfonic acid (HEPES), 1.20 g/L HEPES sodium salt, 0.2 g/L yeast extract, and 0.018 g/L K_2HPO_4. The cathode chamber was filled with 0.1 M $NaClO_4$ solution, and purged with air (50 mL/min) during the inoculation stage. When the microbes were growing, a 1,000 Ω resister was connected in the circuit from the anode to the cathode to discharge, as

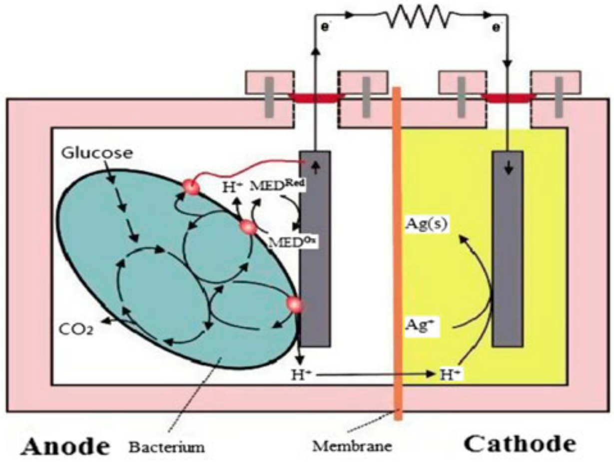


Fig. 1. A MFC reactor used to recover Ag(I).

shown in Fig. 1. A magnetic stirring bar was used to constantly stir the anolyte in the anode chamber.

When the MFC was successfully started, the solution in the anode chamber was replaced with fresh electron donor artificial wastewater. The cathode chamber was refilled with artificial wastewater containing Ag(I), which was prepared by dissolving $AgNO_3$ with distilled water. In order to determine the effect of cathode solution strength on removal efficiency of Ag^+ and power generation, $NaClO_4$ was used as the supporting electrolyte. The solution pH was adjusted with diluted HNO_3. Experiments were performed at room temperature under normal atmospheric pressure.

2.3. Analysis of solutions and surface

Ag(I) remaining concentration in the effluent was analyzed by Mohr method. All electrical measurement and calculation were performed as given in literature [10]. Morphology and chemical composition analysis were performed by SEM and energy dispersive spectroscopy (EDS), as given in literature [11]. EIS was also performed as in literature [11].

3. Results and discussion

3.1. Effects of $NaClO_4$ concentration

To determine the $NaClO_4$ concentration effects on power generation, mixtures of $NaClO_4$ solutions from 0 to 0.2 M and 0.1 M silver nitrate solution were used as artificial wastewaters. According to Eqs. (1) and (2) the open circuit voltage would be 0.996 V under the standard state at pH 7. After operating the MFC with a load resistor of 1,000 Ω for about 3 h, the voltage was found to be stable at 0.80, 0.86, 0.95 V for $NaClO_4$ concentrations of 0, 0.1, 0.2 M, respectively (Fig. 2). From these results, it can be concluded that the voltage output increased as $NaClO_4$ concentration was increased. The voltage initially increased for about 2 h, maximized, slowly decreased for about 37 h, and finally decreased rapidly for a longer time. The electrochemical reactions and reduction potentials with respect to the standard hydrogen electrode at 25˚C are as follows:

To determine the $NaClO_4$ concentration effects on the recovery efficiency and remaining concentration of silver, mixtures of different $NaClO_4$ concentrations and 1,000 ppm Ag(I) were used as artificial wastewater in the cathode chamber. If the silver ion is not lost as chemical precipitation, transporting, or leakage of silver ion from the cathode, the amount of concentration decrease in silver ion could be assumed to be deposited on the cathode as silver metal. After 10 h, the recovery efficiencies of silver were found to be 95.3% (with remaining concentration of 47 ppm) and 97.0% (with remaining concentration of 30 ppm) for 0.1 and 0.2 M $NaClO_4$ concentrations; higher $NaClO_4$ concentration showed a little higher efficiency. This means that the $NaClO_4$ concentration range from 0.1 to 0.2 M is enough to support the solution conductivity.

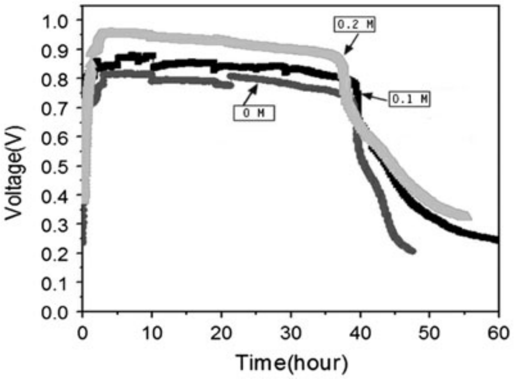


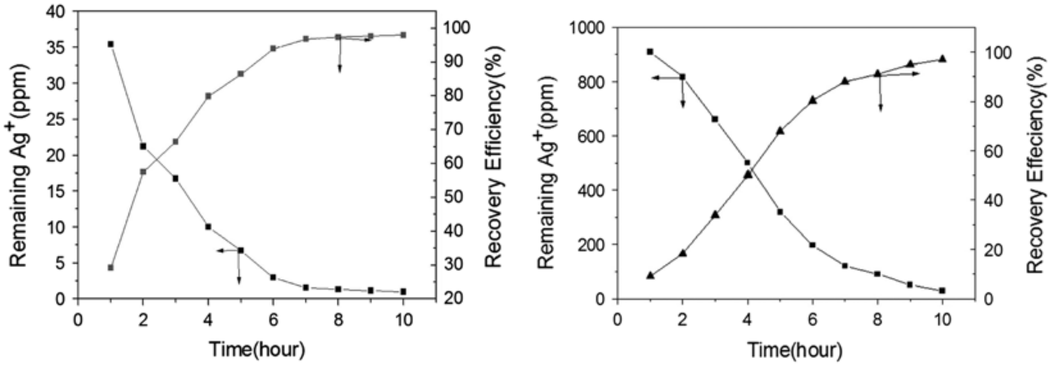
Fig. 2. Discharge curves of different $NaClO_4$ concentrations: The catholyte consisted of the concentration range from 0 to 0.2 M $NaClO_4$ with 0.1 M Ag(I). The anolyte was 10 mM sodium acetate with HEPES buffer medium.

$$\text{Cathode reaction: } Ag^+(aq) + e^- = Ag(s) \quad E^0 = 0.799\,\text{V} \tag{1}$$

$$\text{Anode reaction: } RBFH_2(aq) = RBF(aq) + 2H^+(aq) + 2e^- \quad E^0 = -0.197\,\text{V} \tag{2}$$

3.2. Effects of initial Ag^+ concentration on silver recovery

Effects of initial concentrations of Ag^+ on recovery efficiencies and power generations were also evaluated by increasing the Ag^+ concentration from 50 to 4,000 ppm with 0.2 M $NaClO_4$ concentration as a supporting electrolyte at pH 7. Fig. 3 shows typical examples for 50 and 1,000 ppm that, within 10 h, the removal efficiencies of Ag^+ reached 97.9 and 97.1%, respectively. Higher removal efficiency rate was observed for higher initial Ag^+ concentrations for 3 h, and thereafter, it became similar. For 10 h reaction, the effluent silver concentration was in the range of 0.003–0.153 ppm, representing recovery efficiencies of 98.2–92.3%. The complete recovery would be achieved by increasing electrode area or reaction time.



(A) (B)

Fig. 3. Remaining Ag(I) concentration and recovery efficiency curves for the initial concentration of (A) 50 ppm and (B) 1,000 ppm with 0.2 M $NaClO_4$.

It is a very promising fact from an electrochemical point of view that if one keeps a constant silver ion concentration of 1,000 ppm in the cathode chamber of MFC and a constant concentration of organic electron donor in the anolyte medium as in the MFC start-up, the high discharge voltage of 0.93 V and high apparent current density of 4.25 A/m^2 are achieved, while discharging the cell through a 1,000 Ω load resistor. In reality, there are real wastewater sources containing silver nitrate as high as 31,000 ppm as Ag(I), which leaches out from spent silver oxide button cells [8]. If the present work is applied, the conventional silver recovery processes with precipitation by KCl and replacement reaction of silver chloride with zinc powder can be omitted, leading to economic savings and prevention of secondary water contamination [10].

3.3. Discharge curve of the MFC with different initial concentrations of Ag^+

The initial Ag(I) concentration with 0.2 M $NaClO_4$ as a supporting electrolyte significantly affected the generation of power density and current density. Discharge voltage, with a load resistor of 1,000 Ω, increased from 0.34 to 0.97 V with an increase of the initial concentration of Ag(I) from 50 to 2000 ppm, while the open circuit voltage increased from 0.625 to 1.32 V. At higher Ag(I) concentrations, the higher discharge voltages were kept for much longer time compared to lower concentration. On the other hand, a conventional electrodeposition method was reported to allow only for silver metal recovery by spending electricity at a rate of 3.81 KWh per kg of silver at an optimum condition [9]. This means that the MFC system of the present work would be more economically beneficial for silver recovery because it can produce electric energy as well as recovering a valuable metal like silver without spending electricity. This technology will greatly impact the silver industry.

3.4. Voltage vs. current density (V–J) and power density vs. current density (P–J) curves

To characterize electrochemically MFC in this study, voltage vs. current density (V–J) curves and power vs. current density (P–J) curves were recorded by varying external resistance after the Ag(I) addition to the cathode chamber. Fig. 4 shows the experimental results to characterize MFC. The maximum power density (P_{max}) increased with a Ag(I) concentration increase; the highest P_{max} was 1.93 W/m^2 with maximum current density of 4.25 A/m^2 for 2000 ppm Ag (I). The F·F. specifies the cell performance that relates a maximum power. The high square-like quality of the V–J curve obtained by a fill factor is desirable for achieving a high performance of the cell. The V–J on the carbon felt electrode showed a high activation overvoltage compared to the carbon cloth electrode published by Choi and Cui [10], so that the fill factor was low. Internal resistance, R_{int}, determined by the slope of the voltage vs. current decreased from 457 to 66 Ω, as the Ag(I) concentration was increased from 50 to 2,000 ppm.

3.5. Characteristics of deposits on the cathode surface after the reaction

Fig. 5(A) shows color and size of the silver deposits on the graphite felt cathode after metallization of Ag(I) from the 2,000 ppm Ag(I) catholyte for 10 h. The

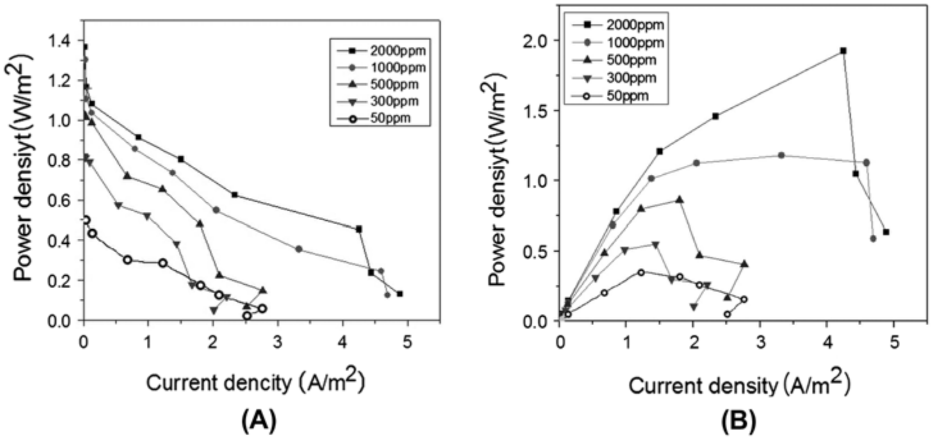


Fig. 4. Voltage vs. current density (A/m^2) and power density vs. current density with respect to the different Ag^+ concentrations in the catholyte. (A) Voltage versus current density and (B) Power density versus current density.

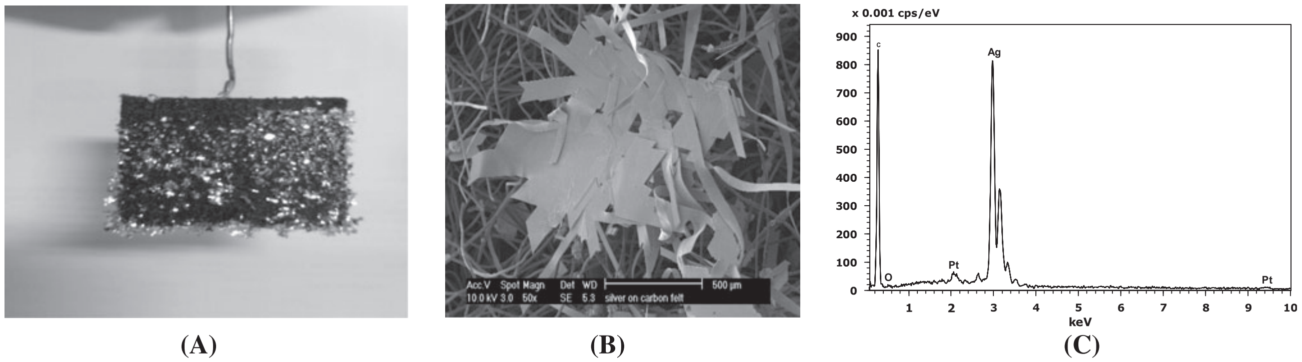
silver metal grew from small particles to shinny rods when the MFC reaction time elapsed. With the passage of time, silver metal on the carbon felt became more shinny.

Morphology and chemical composition of the metals can be observed in more detail by using SEM and analyzed by using EDS. The SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. Fig. 5(B) shows SEM micrographs on the carbon felt cathode with silver metal deposits. The reaction time was 200 h in 2,000 ppm Ag(I) catholyte, the anolyte containing 10 mM sodium acetate with HEPES buffer medium. As the reaction time was increased, the silver deposits were connected, and paper-like silver films appeared on the thin wire-like graphite felt base. EDS analysis showed that very pure silver metals could be obtained from the MFC reaction (Fig. 5(C)).

3.6. Analysis of R_{int} with EIS

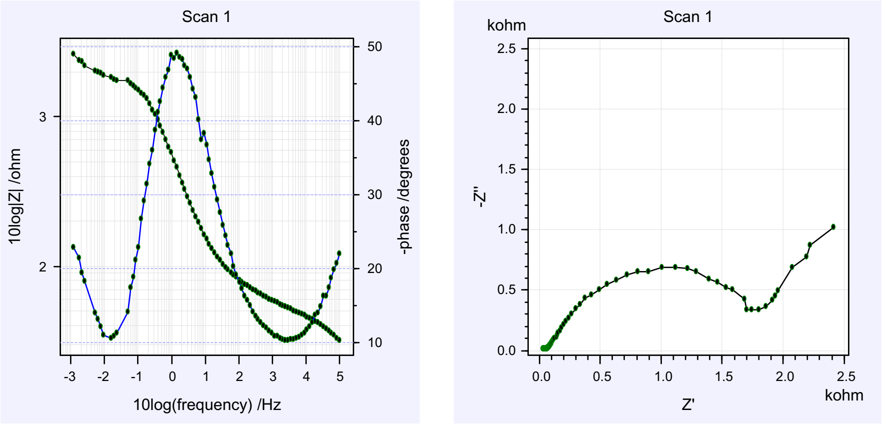
One of the key issues in the MFC studies is to investigate biotic and/or abiotic factors that limit the power output, which can be caused by the internal resistance (R_{int}) of the MFC. This can be measured by the EIS method. The R_{int} consists of three components: charge transfer resistance (R_{ct}), ohmic resistance (R_{s}), and concentration (diffusion) resistance (R_{w}). Both the impedances of individual electrodes and the full cell can be analyzed by this method. EIS is a powerful tool to study chemical and physical processes in solutions as well as in solids. But, only recently, EIS was adopted by MFC researchers to analyze R_{int} and its application in MFC studies requires further clarification [12].

The EIS results of the full cell can be analyzed with two common plots; Bode plots (Fig. 6(A)) and Nyquist plots (Fig. 6(B)). In this experiment, R_{s} is 20.17 Ω, R_{ct}



(A) (B) (C)

Fig. 5. Characterictics of deposits on the graphite felt cathode surface. (A) The cathode appearance with shinny white Ag metal, (B) SEM micrographs (50×) of the silver metal and (C) EDS spectra of the cathode surface of silver metal deposits.



(A) (B)

Fig. 6. (A) Bode plots and (B) Nyquist plot for Ag(I)-MFC. The catholyte contained 1,000 ppm Ag(I) and the anolyte contained 10 mM sodium acetate with HEPES buffer medium.

was 1,687.2 Ω, R_w was 2,027.5 Ω, and C_{dl} was 4.79×10^{-4} F. R_{int} is defined as $R_s + R_{ct} + R_w$, resulting in 3,734.8 Ω by fitting the impedance to the equivalent circuit with two-time constant model. In particular, the charge transfer resistance (or polarization resistance) (R_{ct}) is affected by electrode kinetics. On the other hand, the R_{int} determined, based on the slope of the rising portion of the voltage vs. current curve (polarization curve), was about 600 Ω. If one compares this value with the R_{int} from the EIS measurement, it is found that the EIS value was six times higher than that of the slope method. According to other results, published by Choi and Hu [11], the R_{int} by EIS could interpret the Au(III)-MFC behaviors, such as maximum power density. Therefore, for the Ag(I)-MFC the same argument can also be applied.

4. Conclusion

It was verified that the Ag(I)-MFC system with graphite felt electrodes could successfully be operated. The effluent silver concentration was in the range of 0.003–0.153 ppm, representing that the recovery efficiencies for silver ion was in the range of 98.2–92.3% for the Ag(I) concentration range from 50 to 4,000 ppm and the anolyte containing 10 mM sodium acetate with HEPES buffer medium. Initial Ag^+ concentration affected the power generation by both increasing the cathode potential and decreasing the internal resistance of the MFC. The highest maximum power density and current density was 1.93 W/m^2 and 4.25 A/m^2 (2,000 ppm Ag(I)), respectively. Shinny silver metals on the graphite felt cathode were visible and verified to be very pure silver by SEM and EDS. A charge transfer resistance of 1,687 Ω was obtained for 1,000 ppm Ag(I) by EIS.

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