Silver Recovery and Power Generation from Ammonia Chelated Silver Solution in a Bio-Electrochemical Reactor

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Abstract. Silver has valuable features and limited availability, and thus recovery from wastewater or aqueous solutions plays an important role in environmental protection and economic profits. In this study, silver recovery along with power generation and COD removal were investigated in a bio-electrochemical system (BES). The BES comprised of an anode and a cathode chamber which were separated by a cation exchange membrane to prevent the crossover of electrolytes. During the biological oxidation of acetate as an electron donor in the anode chamber, the reduction of ammonia chelated silver ions as electron acceptors in the cathode side occurred spontaneously. Results showed that a silver recovery of 99% and COD removal efficiency of 60% were achieved at the initial silver concentration of 1,000 mg/L after 48 hours of operation. The power generation improved 4.66%, from 3,618 to 3,795 mW/m², by adding NaNO₃ of 850 mg/L to the catholyte containing 2,000 mg/L of silver ions. Deposits on the cathode surface were characterized using scanning electron microscope (SEM) and energy dispersive X-ray (EDX). Metallic silver with dendritic structures and high purity were detected. This study demonstrated that BES technology can be employed to recover silver from complex chelating solution, produce electricity, and treat wastewater.

1. Introduction
Silver ions in the form of complexes and chelating agents usually exist in the effluents of silver plating plant and photographic processes. The toxicity of silver to freshwater and marine organisms is an environmental concern, thus its release into the environment is strictly regulated. Silver also has valuable features and limited availability. Therefore, for both economic and environmental aspects, it is important to recover silver from wastewater or aqueous solutions.

Recently, the bio-electrochemical system (BES) technology has been demonstrated as an attractive approach for recovery of metals [1-3]. Basically, BES uses organic waste as the electron donor during the biological conversion in the anode chamber to supply for the reduction of metal ions as the electron acceptors in the cathode chamber. Recovery of silver from aqueous solution using the BES technology has been studied by several researchers [4-6]. However, the above studies mostly employed simple free silver ions (Ag⁺) in acidic solutions (e.g. AgNO₃) as the model catholyte. Meanwhile, the practical waste solutions may be alkaline due to the existence of complex compositions such as chelating agents like ammonia, cyanide and EDTA [7]. Thus, the aqueous solutions containing silver in complex forms need to be investigated further.

In this study, the recovery of silver was conducted in a BES reactor using ammonia chelated silver solution as the synthetic wastewater in the cathode chamber. Acetate served as the substrate for microbial activities in the anode chamber. The BES performance was characterized by recovery
efficiency, power generation, and substrate removal. The addition of sodium nitrate (NaNO₃) to the catholyte, which may affect the ionic conductivity of solution and power generation, was also evaluated.

2. Materials and Methods

2.1. BES reactor fabrication
A cubic-shape BES reactor consisting of an anode and a cathode chamber (1.0 L working volume) was fabricated. Two chambers were separated by a cation exchange membrane (CMI-7000S, Membrane International, Inc. USA) (figure. 1). The membrane (264 cm² surface area) was pre-treated by immersing in 5% NaCl solution for 12 hours to allow for the hydration and expansion. Carbon brush (15 cm x 6 cm) prepared by twisting carbon fiber (ThaiCarbonfiber Co., Thailand) with Ti wire of 1.0 mm in diameter (Prolog Titanium Co., Ltd), served as the anode, while the cathode was a graphite plate (90 cm², Fujian, China). Before making the electrical connection with Ti wire, both of electrodes were pre-conditioned according to previous studies [6, 8].

![Figure 1. Schematic drawing of BES reactor.](image)

2.2. Start-up and Operation
Anaerobic sludge (100 mL) from the digester of a brewery wastewater treatment plant (Pathum Thani, Thailand) was used as an inoculum in the anode chamber. The anolyte (900 mL) included (per liter): CH₃COONa (1.28 g) as electron donor, Na₂HPO₄ (3.55 g), KH₂PO₄ (3.4 g), NH₄Cl (0.31 g), yeast extract (0.2 g). During the inoculation stage, the cathode chamber was filled with phosphate buffer solution (1.0 L, pH 7.0) and purged continuously with air (80 mL/min). The anode and cathode were connected through an electrical circuit made by Ti wire and 1,000 Ω resistance. The system was considered to be successfully acclimated when measured cell voltage was stable after several feeding cycles.

Air was then stopped in the cathode chamber, and the catholyte was replaced by the ammonia chelated silver solution. The chelated solution was prepared by dissolving Ag₂SO₄ at different Ag⁺ concentrations (1,000-2,000 mg/L) in the excess amount of 30% NH₃OH solution along with de-ionized water. Silver existed in the form of the chelated agent as Ag(NH₃)₂⁺. The catholyte pH was around 10.2. The anolyte was refilled with fresh solution each time the catholyte was replaced. Two chambers were purged with N₂ (80 mL/min) for 15 min to remove the effect of dissolved oxygen and
then sealed with septa during the operation. A 5 Ω resistance was connected to maximize the current transferred from the anode to the cathode. The effect of ionic conductivity of solution on power generation was investigated by adding a different amount of NaNO₃ to the catholyte containing 2,000 mg/L of silver ions.

2.3. Analytical methods and calculation
The cell voltage E (mV) was monitored through a data logger (Grant Instruments, Cambridge Co., Ltd) every 10 min and analyzed by SquirrelView software 2010 series. Power density P (mW/m³) was calculated as $P = \frac{1000E^2}{R_{\text{ext}}V}$, in which $R_{\text{ext}}$ (Ω) is the external resistance, V (m³) is the working volume of anode chamber. The COD measurement was based on the Closed Reflux, Titrimetric method. The silver concentration (mg/L) was measured by Inductively Coupled Plasma (ICP) Spectrometer (Optima 8000, PerkinElmer, USA). Before analysis, all aqueous samples were filtered through syringe filters NY 0.45 µm (Allpure). Deposits scraped from the graphite plate surface were characterized for morphology and chemical composition by using SEM (S-3400N, Hitachi, USA) and EDX (Metek, Apollo XP 2060, USA). All analytical procedures were performed in triplicate.

3. Results and Discussion

3.1. Silver recovery and COD removal
The experiment was conducted with the catholyte containing 1000 mg/L of silver ions as Ag(NH₃)₂⁺ and the anolyte containing acetate as substrate with COD concentration of 1,000 mg/L. In the anode chamber, the biological oxidation of acetate occurred (Eq. 1), while the ammonia chelated silver ions was reduced spontaneously in the cathode chamber (Eq. 2).

2HCO₃⁻ + 9H⁺ + 8e⁻ $\leftrightarrow$ CH₃COO⁻ + 4H₂O,  $E^0 = -0.290$ V.  (1)

Ag(NH₃)₂⁺ + e⁻ $\leftrightarrow$ Ag⁺ + 2NH₃,  $E^0 = +0.373$ V.  (2)

![Figure 2. Chelated silver ions and COD removal by time.](image)

During the experiment, COD and silver concentration in the anolyte and catholyte were monitored every 4 hours. Figure 2 showed that the silver concentration decreased significantly to below 5 mg/L, indicating > 99% chelated silver ions were removed from the catholyte after 48 hours of operation. Compared with single- form silver (i.e. AgNO₃, $E^0 = 0.799$ V) [4-6], the chelated silver ion had a slower reduction rate due to its lower redox potential ($E^0 = 0.373$ V). In this study, when silver diffusion from the cathode to anode chamber through CEM was ignored, it can be inferred that chelated silver ions were reduced to form deposits on the cathode surface. This finding suggests that high silver recovery of 99% could be obtained in this study. In contrast, the COD concentration in the anolyte decreased slowly. After 48 hours, the remaining COD concentration was 400 mg/L, corresponding to the COD removal efficiency of 60% (figure. 2). It can be attributed to
the biologically uncompleted conversion of organic matter in the anode chamber, which relied on the activated ability of microbial community. Higher COD removal can be achieved when the operation time is extended.

3.2. Effect of NaNO₃ on power generation

The ammonia chelated silver solution containing 2,000 mg/L of silver ions were used as a catholyte in the experiment to investigate the performance of power generation. The catholyte was then added NaNO₃ 425 mg/L and 850 mg/L to test its effect on the power generation and silver recovery. In order to characterize the fuel cell of reactor, the polarization curve analysis was also conducted when the external resistance was varied in a range of 10,000 - 5Ω.

Figure 3 shows that the cell voltage developed rapidly during the first 8 hours and decreased gradually thereafter due to the shortage of substrate in the anode chamber and the reduction of silver ions in the catholyte chamber. The highest cell voltage was found when NaNO₃ of 850 mg/L was added to the catholyte containing 2000 mg/L of silver. It can be ascribed that the addition of NaNO₃ could decrease the internal resistance of reactor by improving the ionic conductivity of the catholyte. It was confirmed by the polarization and power curves (figure 4). The maximum power density ($P_{\text{max}}$) increased by 4.66%, from 3,618 to 3,795 mW/m², with the addition of NaNO₃ of 850 mg/L to the catholyte.

![Figure 3. Cell voltage progression in reactor by time with different catholyte](image)

![Figure 4. Polarization curves (E1 and E2), power curves (P1 and P2) without and with an addition of NaNO₃ 850 mg/L to the catholyte, respectively.](image)

![Figure 5. Deposits on cathode surface were characterized by (A) SEM and (B) EDX](image)
During experiments, the reduction of silver ions in catholyte was not affected by the addition of NaNO$_3$. Results showed that the silver removal was over 99% in all of the cases. Similar results were found by other researchers when KNO$_3$ was used to improve the ionic conductivity of solution for recovery of copper (Cu) and electricity production using a microbial fuel cell (MFC) [9].

3.3. Characterization of deposits on the cathode surface
After 58 days of operation, the BES reactor was emptied. The deposits on graphite cathode surface were scrapped and air dried at room temperature before characterizing by SEM and EDX analysis. Silver with dendritic structures was detected at a magnification of 500 SE (figure 5A). These dendrites have long trunks and short branches which look like a fishbone. This result was also verified by the EDX spectrum (figure 5B), in which the sharp peak at an energy level of 2.98 keV was found, indicating the deposits comprised of pure silver. It was reported that dendritic structures are often produced in electrochemical deposition, especially in fine powder deposition [10]. Other researchers also showed that silver deposits in compact layer structure were found at cathode surface of a MFC used to recover silver from ammonia chelated solution [7].

4. Conclusions
This study demonstrated the feasibility of BES technology for silver recovery and power generation from alkaline solution containing ammonia chelated silver ions Ag(NH$_3$)$_2$$^{+}$ of 1,000-2,000 mg/L. The BES based on the energy obtained from oxidation of acetate in the anode chamber to supply for the reduction of Ag(NH$_3$)$_2$$^{+}$ ions in cathode without external power consumption. High Ag recovery (> 99%) were achieved after 48 hours of operation. The addition of NaNO$_3$ to the catholyte could improve the ionic conductivity of the solution, thus increased the power generation with fewer effects on the silver removal. Pure metallic silver deposits with dendritic structures were found at cathode surface by using SEM and EDX technique. Other silver complexes such as silver thiosulfate [Ag(S$_2$O$_3$)$_2$$^{3-}$] which normally exists in effluent of photographic processing, should be investigated in further studies.

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