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Bio-electrochemical system for recovery of silver coupled with power generation and wastewater treatment from silver(I) diammine complex

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ABSTRACT

In this study, a bio-electrochemical system was used to investigate the recovery of silver from diammine complex $[Ag(NH_3)_2]^+$, coupled with power generation and wastewater treatment, measured in terms of chemical oxygen demand (COD) removal. Acetate was oxidized by anodic microorganisms to produce electrons, which were transported to the cathode for the reduction of $[Ag(NH_3)_2]^+$ complex. After 48 h of operation at different initial $[Ag(NH_3)_2]^+$ concentrations (1000–3000 mg Ag/L), a Ag removal of over 96%, along with a COD removal of 60–76.80%, and a columbic efficiency of 8.55–14.69%, were achieved. Maximum power density slightly increased by 4.66%, from 3618 to 3795 mW/m^3, when 10 mM $NaNO_3$ was added to the catholyte containing 2000 mg Ag/L. The diffusion of $[Ag(NH_3)_2]^+$ ions through the membrane affected the performance, as the inorganic fouling at the membrane surface increased the internal resistance. This transport was confirmed by the accumulation of silver in anodic biomass (0.853 mg Ag/g biomass) after 58 days. Scanning electron microscope (SEM), energy dispersive X-ray (EDX), and X-ray diffraction (XRD) analysis demonstrated Ag deposits with a dendritic structure formed at the cathode surface. A deeper understanding on bio-electrochemical technology used for Ag recovery and electricity production from $[Ag(NH_3)_2]^+$ complex was achieved in this study.

1. Introduction

A large amount of silver (Ag) has been used in the plating industry and for photographic manufacturing. Accordingly, the effluents from these processes normally contain Ag at high concentration. Waste fixer solutions from photographic manufacturing, for example, contain Ag in the range of 5000–10,000 mg/L [1]. Furthermore, the waste composition is relative complex, where a variety of organic and inorganic substances, such as ammonia, EDTA, and thiosulfate, usually exist [1–3]. The toxicity of silver and other recalcitrant compounds to freshwater and marine organisms is an environmental concern. Thus, the discharge of silver-rich wastewater into the environment is regulated stringently. The maximum daily discharge of Ag into surface water is 0.22 mg/L according to the Environmental Protection Agency (EPA) (USA, 2000). Moreover, silver is a valuable metal and is not considered as a waste requiring disposal, but as a recoverable material. Therefore, for both economic and environmental aspects, recovery of silver from effluents is essential.

Recently, bio-electrochemical system (BES) technology offers an attractive approach for integrated wastewater treatment along with energy and resource recovery [4]. Basically, a BES consists of an anode and a cathode chamber, which are normally separated by an ion exchange membrane (IEM) to prevent the cross-over of electrolytes. In the anode chamber, microorganisms are employed to convert organic wastes and produce electrons, which are then transferred through an electrical circuit to the cathode. Electricity, thus, can be produced spontaneously instead of used. The conversion of biodegradable wastes to electricity by using BES technology has been demonstrated by several researchers [5,6]. By acting as electron acceptors in the cathode chamber, metal ions are reduced electrochemically, and metallic deposits are formed at the cathode surface, which can be recovered. BES technology has been found to be a new method for recovery of metals from aqueous solutions or wastewater [7–9].

Recovery of silver from aqueous solution using BES technology has been studied by several researchers [10–13], in which the effects of operational parameters (e.g. pH, initial Ag concentration) were investigated. The influences of different IEMs on BES performance was also examined [14]. However, the above studies mostly used acidic solutions containing simple free silver ions (Ag^+) as the model catholyte, except $Ag[S_2O_3]^-$ was considered by Tao et al. [12]. Due to a

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high standard redox potential (Ag^+/Ag^0, $E^0 = 0.799$ V versus the standard hydrogen electrode (vs. SHE) [8]), Ag^+ ions can be reduced spontaneously in the cathode chamber. There are not many studies on recovery of silver from complexes in alkaline waste solutions. Silver complexes (e.g. $[Ag(NH_3)_2]^+$, $[Ag(S_2O_3)_2]^{3-}$) have a lower standard redox potential (i.e. $E^0 = 0.373$ V, 0.01 V vs. SHE, respectively) as compared to free silver ions (i.e. $E^0 = 0.799$ V), which may not facilitate spontaneous reduction in BES reactor.

Silver(I) diammine complex contaminated wastewater ($[Ag(NH_3)_2]^+$) was firstly studied by Wang et al. [2] to recover Ag accompanied with electricity production. It was reported that 3.2 J and 160C could be produced and 1.6 g Ag could be recovered on the cathode after 9 h of operation while 1 g COD was removed from the anode chamber [2]. The experiment was conducted in a small bio-electrochemical cell (i.e. working volume < 50 mL) in which a bipolar IEM (BPM-I, Beijing Ting Run Co., China) was used as a separator between the anode and the cathode chamber. Basically, a bipolar IEM consists of an anion and a cation exchange layer (AEM and CEM) mounted together and allows the simultaneous migration of proton (H^+) and hydroxide (OH^-) ions generated from the water splitting reaction at the interface of the CEM and AEM layers. However, due to the permeability of electrolyte, the transition area (or interface) always contains a certain concentration of electrolyte salts diffusing from both chambers. Under an electric field, there is also migration of the anions through the AEM layer toward the anode, and the cations through the CEM layer toward the cathode, which increases the polarization potential of the separator and leads to elevated internal resistance [15,16]. Furthermore, in a bipolar IEM-based system, the pH balance between anode and cathode chambers is severely affected due to the competition for migration of electrolytes at the interface [16]. These drawbacks of bipolar IEM were also pointed out by Wang et al. [2], which caused low performance in electricity production in their research. Also, a detail discussion on columbic efficiency, power density, and their relation to internal resistance were lacking in this research. Therefore, alternative materials for electrodes and membranes, which may have an influence on the internal resistance, should be investigated to improve the performance. In addition, in the study of Wang et al. [2], the operation for silver recovery in the bio-electrochemical cell was carried out at one concentration of $[Ag(NH_3)_2]^+$ (i.e. 10 mM), and the effect of initial $[Ag(NH_3)_2]^+$concentration was not considered. Thus, further studies should be conducted to investigate thoroughly the reduction of $[Ag(NH_3)_2]^+$ complex in a BES reactor.

The objective of this study is to investigate the silver recovery, combined with power generation and wastewater treatment in a BES reactor operated with different initial $[Ag(NH_3)_2]^+$ concentrations. The overall BES performance is characterized by silver removal efficiency in the cathode chamber, COD removal, and columbic efficiency in the anode chamber. In order to improve the electrical output, the following materials are used: carbon brush as the anode, cation exchange membrane (CMI-7000S) as the separator, and $NaNO_3$ as supporting electrolyte. Since $[Ag(NH_3)_2]^+$ ions can diffuse through the CMI-7000S membrane and adsorb to the anodic biomass, which may have an influence on BES performance, the characterization of the membrane surface and digestion of biomass after BES operation are conducted, to prove the loss of silver. Scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and X-ray diffraction (XRD) are also used to demonstrate the formation of metallic silver deposits at the cathode surface.

The novelty of this study is to understand the fate of $[Ag(NH_3)_2]^+$ complex during the BES operation by investigating the possible diffusion from the cathode to the anode chamber through CMI-7000S membrane and the impacts on internal resistance at different initial $[Ag(NH_3)_2]^+$ concentrations. The determination of Ag amount accumulated in the anodic biomass to prove the Ag loss through membrane, is also investigated.

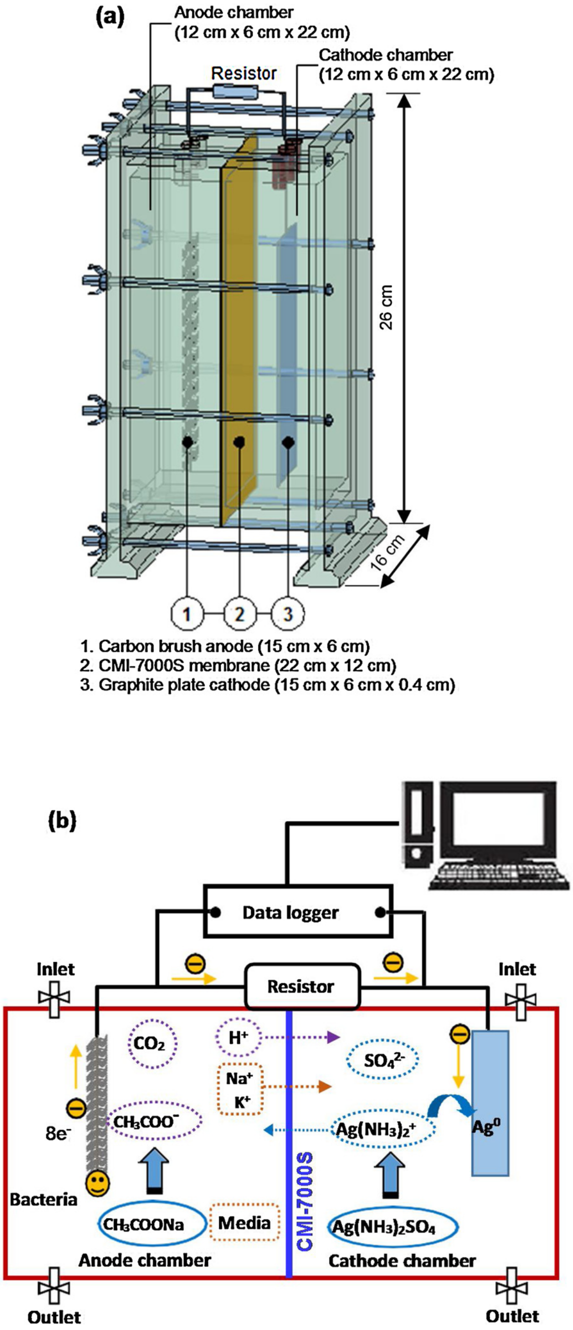

Fig. 1. **(a)** Configuration of a BES reactor and **(b)** Schematic illustration of BES operation.

2. Materials and methods

2.1. BES reactor fabrication

Cubic-shape BES reactors made from acrylic plates, were used in this study. The reactor consisted of an anode and a cathode chamber (i.e. 12 cm long × 6 cm width × 22 cm high, with a working volume of 1.0 L for each chamber) separated by a cation exchange membrane CMI-7000S (Membrane International, Inc. USA). Dimension of the reactor used in the study are shown in Fig. 1a. The membrane (264 cm^2 surface area) was pre-treated by immersing in 5% NaCl solution for 12 h to allow for hydration and expansion. Carbon brush (15 cm × 6 cm), prepared by twisting carbon fiber (Thai Carbonfiber Co., Thailand) with Ti wire of 1.0 mm in diameter (Prolog Titanium Co., Ltd), served as the