P-ISSN 2586-9000
E-ISSN 2586-9027

Homepage : *https://tci-thaijo.org/index.php/SciTechAsia* **Science & Technology Asia**

Vol.22 No.4 October - December 2017 **Page: [1 – 10]**

Original research article

Recovery of Silver from Mixed Metals Solution Using a Bio-Electrochemical System

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Received 15 May 2017; Received in revised form 26 September 2017
Accepted 18 October 2017; Available online 1 December 2017

ABSTRACT

There are many conventional technologies used for recovery of precious metals from wastewater, but most of them are chemical intensive and consume high energy. This paper focuses on silver recovery using bio-electrochemical system (BES), which basically consists of two separated chambers, the anode and cathode chamber. The anolyte, containing either acetate or glucose as substrate, was fed into the anode chamber, in which microorganisms were employed to produce electrons through anaerobic oxidation. The catholyte was a synthetic mixed metals solution containing silver Ag(I), copper Cu(II), and iron Fe(III), which acted as terminal electron acceptors. Two BES reactors, in which anion exchange membrane (AEM) and cation exchange membrane (CEM) served as separators, were investigated. Experiments were conducted at different initial Fe(III) concentrations (10 mM and 20 mM), while the concentrations of Ag(I) (10 mM), and Cu(II) (1 mM), were kept constant. The silver recovery obtained in the CEM-based reactor (> 99%) was higher than that in AEM-based reactor (58-75%). However, diffusion of Ag(I), Fe(III), and Cu(II) through the CEM was unavoidable. In terms of power generation, a power density of 4515.63 mW/m^3 was found in AEM-based reactor, which was higher than that in CEM-based reactor (1542.56 mW/m^2). However, the substrate loss was found in the AEM-based reactor due to the transport of negative-charged organic matter through the AEM, which caused a fast decrease of cell voltage. This study successfully demonstrated the feasibility of using a bio-electrochemical system to recover silver coupled with power generation from a synthetic mixed metals solution.

Keywords: Anion exchange membrane; Bio-electrochemical system; Cation exchange membrane; Power generation; Silver recovery

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1. Introduction

Silver (Ag) is a valuable and important metal because of its use in different types of industries. Diverse applications of Ag also make it a major metal found in wastewater and aqueous solutions. As much as 3.9 million USD dollars' worth of Ag has been found in 10 million gallon of wastewater [1]. Silver-rich wastewater is released from different sources, such as photographic and printing processes, electroplating, and electronic devices manufacturing. The Ag toxicity is a serious problem as it accumulates in the environment if it is not removed from wastewater properly before discharging. Thus, silver recovery are required in order to reduce the economic and environmental impacts.

There are many conventional methods (e.g. chemical precipitation, electrolysis, metallic replacement) to recover silver from wastewater aqueous solutions. However, these methods have many disadvantages. A chemical precipitation process is inherently not favorable due to the addition of chemicals and toxic gas production. Further treatments are also required to extract pure silver. Electrolysis requires high energy and equipment costs [2]. Metallic replacement has low cost but uses highly active metals (e.g. copper, iron, and zinc) to recover more-valued metals (e.g. silver). Furthermore, this technique still required wastewater treatment at the end [2].

BES technology is a promising technology to recover metals from aqueous solution [3, 4]. BES has many strong points as compared to other methods. First, it does not produce toxic sludge, because the process requires minimum or no chemical additions to reduce metal ions [5]. Second, a BES normally uses minimum energy to acquire precious metals (i.e. the energy consumption is very low and the BES actually generates its own electricity [1]). However, a BES is very dependent on the substrate conversion and enzymatic efficiency [6, 7]. Many types of reactor configuration have been designed and investigated, such as batch reactor, dual-chamber, single chamber, and tubular reactor [5]. For dual-chamber design, an ion exchange membrane (e.g. anion, cation, and proton exchange membrane) is usually used as a separator [1, 8, 9]. Basically, a BES use microorganisms as the media to produce electrons by feeding them with a substrate [1, 7]. Mixed cultures of anaerobic micro-organisms were employed in most BES studies due to their stability and easy adaptation compared to a single strain [6].

The principle of the BES method for silver recovery is to convert chemical energy stored within a substrate into electrical energy in the form of electrons [1, 10]. There are many substrates that can be used in BES method, but acetate and glucose are the most commonly used [7]. Acetate is metabolized by shorter metabolic pathways, as compared to glucose. The substrate is consumed by exoelectrogen to produce the electron as below (Eq.1.1 and Eq. 1.2).

At anode, acetate is oxidized as

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-,$$
$$E^0 = -0.293\ V \qquad \text{(Eq. 1.1)}$$

Glucose is oxidized as

$$C_6H_{12}O_6 + 12H_2O \rightarrow 6HCO_3^- + 30H^+ + 24e^-,$$
$$E^0 = -0.41\ V \qquad \text{(Eq. 1.2)}$$

At cathode the electrochemical reaction could be;

$$Ag^+ (aq) + e^- \rightarrow Ag(s),\ E^0 = 0.799\ V \qquad \text{(Eq. 1.3)}$$

The electrons are then transferred through different extracellular electron transfer (EET) mechanisms to the anode, where they are transported to the cathode through an electrical circuit. On the cathode side, the reduction of silver ions occurs spontaneously (Eq. 1.3) and metallic silver deposits form on the cathode surface.

There are several studies reporting silver recovery from wastewater using BES technology. The BES was used to recover silver from ammonia chelated silver wastewater with high silver removal (99.9%) after 8 hours of operation. It can produce 3.2 joules of electricity and 160 C of charge, and removed 83% of COD in the anode chamber [11]. Another study used AgNO3 in synthetic wastewater to remove silver up to 95% and 97% after 10 hours of operation when adding 0.1 M and 0.2 M of NaClO4 into the catholyte, respectively [12]. Silver thio-sulfate (Ag2SO3$^-$) and free silver ion (Ag$^+$) in synthetic wastewater were also investigated as catholytes in BES reactors to recover silver. The results showed that Ag$^+$ was removed more rapidly than that $Ag_2SO_3^-$. A high pH value was favorable for the reduction of $Ag_2SO_3^-$ complex [13].

The above studies mostly used simple synthetic wastewater, which contains only free silver ion (Ag$^+$) in the catholyte. Thus, it is not comparable to a real wastewater. Real wastewater normally contains different metals, such as Ag(I), Fe(III), Cu(II), and Ag2SO3$^-$. Therefore, in this study, a synthetic mixed metals solution is prepared based on the major metals found in the fixer solution of a local photographic shop, to investigate the silver recovery. The mixed solution contains Ag(I), Fe(III), and Cu(II) ions as main constituents. This research focuses on the recovery of silver from synthetic mixed metals solution at different initial Fe(III) concentrations in a BES system. Effects of ion exchange membranes on silver recovery are also investigated.

2. Materials and Methods

2.1 Material preparation

Before the BES reactors were set up, all materials need to be prepared and pre-treated first. Carbon brush, obtained from Thai carbon fiber, Thailand serves as the anode. It was first cleaned by soaking in acetone solution overnight. Afterward the carbon brush was cleaned with acid treatment by soaking it in ammonia peroxydisulfate (200 g/L) and sulfuric acid (100 mL/L solution) for 15 minutes. The carbon brush was then heat-treated in a muffle furnace at 450 °C for 30 minutes [14, 15]. For the cathode, graphite plate obtained from China was employed. It was immersed for more than 24 hours in 2 mM potassium permanganate solution and washed with distilled water [13]. The anion exchange membrane (AEM) and cation exchange membrane (CEM), obtained from Membranes international INC, USA, were pre-treated by immersing into 5% NaCl, solution for 12 hours before used.

2.2 BES reactor assembling

Two dual-chamber BES reactors were made from acrylic plates. Each reactor was comprised of two cover ends (21×16×1 cm, H×W×T), an anode, and a cathode chamber (12×6×6 cm, H×W×T). Two chambers were separated by an ion exchange membrane (i.e. AEM and CEM) (22×12 cm, H×L). The carbon brush anode and graphite plate cathode were connected through an electrical circuit made from titanium wire and an external resistance (Rext). The cell voltages produced from the system was recorded every 10 minutes by using a PC equipped with a data logger, using Squirrel View Assistant software.

2.3 Start-up and operation

The microorganisms used for the anodic inoculation was anaerobic sludge obtained from a digester of Pathum Thani brewery wastewater treatment plant. The chemical characteristic of sludge was: VSS of 28,693 mg/L, COD of 13,104 mg/L. The microorganisms, in a mixed culture (100 mL), were fed into the anode chamber with the anolyte (900 mL) as following.

- For the AEM-based reactor, the anolyte contained (per 1L): glucose, 0.935 g; NH4OH, 1 mL; Na2HOP4, 3.55 g; KH2PO4, 3.4 g; Yeast extract, 0.2 g. The anolyte pH was 6.8-7.0. Glucose was used instead of acetate in order to minimize the substrate loss from the anode to cathode chamber.
- For the CEM–based reactor, the anolytes contained (per 1 L): CH3COONa, 1.28 g; NH4Cl, 0.31 g; Na2HPO4, 3.55 g; KH2PO4, 3.4 g; yeast extract, 0.2 g. The anolyte pH was 6.8-7.0

The anolyte was supplied into the anode

chamber directly from bottom to top of the chamber by a plastic tube. This anolyte went through the sludge layer, and the effluent can be withdrawn from the top sampling port. The anode chamber was purged with N2 gas for 15-30 minutes to remove the dissolved oxygen. During the inoculation period, the cathode chambers were filled with 1 L of phosphate solution containing (per 1 L): NaH2PO4.2H2O, 4.22 g; Na2HPO4, 1.090 g; NaCl, 2.93 g, at pH 7.0. The cathode chambers were continuously purged with air to supply O2 as a final electron acceptor. Two electrodes were connected through an electrical circuit with a Rext of 1000 Ω. The output cell voltage was recorded vs. time to monitor the behavior of the reactors during the inoculation. After several days, the voltage decreased due to depletion of substrate in the anode chamber. The anolyte and catholyte were replaced by fresh solutions. After obtaining repeatable stable voltages with air supplied in the cathode chamber, the BES reactors were successfully inoculated.

The operation for silver recovery was then conducted, as described below. During the operation stage, the anode and cathode were connected through titanium wires with a Rext of 5 Ω to maximize the current transferred from the anode. Both reactors were purged with N2 gas for 15-30 min and sealed with septa, in order to maintain anaerobic conditions.

- Effect of separator on Ag recovery: To study the effect of separator, the AEM and CEM were used in two BES reactors. The catholytes in both reactors were replaced by the synthetic mixed metals solution containing AgNO3 (10 mM), Cu(NO3)2 (1 mM), and Fe(NO3)3 (10 mM), at pH 2-3. The anode chambers were also filled by fresh anolytes each times of catholytes replacement.
- Effect of Fe(III) concentration on Ag recovery: For this, the initial concentration of Fe(NO3)3 was increased from 10 mM to 20 mM in both reactors while the concentrations of AgNO3, and Cu(NO3)2 were kept constant (i.e. 10 mM and 1 mM, respectively).

After finishing the above experiments, fresh anolytes and catholytes were replaced in both reactors for polarization curve analysis to characterize the fuel cell. The polarization curve experiments were conducted by varying the Rext in a range of 10,000 – 5 Ω, using the catholyte solution containing Ag(I) (10 mM), Cu(II) (1 mM), and Fe(III) (10 mM). The cell voltage was recorded at pseudo-steady state.

2.4 Analytical methods and calculations

The concentrations of Ag(I), Fe(III), and Cu(II) in synthetic mixed metals solution were determined by using an inductively coupled plasma (ICP) spectrometer (Optima 8000, USA). Morphology and chemical composition of metallic deposits on the cathode surface was observed by using scanning electron microscope (SEM) (S-3400N, Hitachi, USA and JSM-5410LV, Oxford) and energy dispersive spectroscopy (EDS) (Metek, Apollo XP 2060, USA and LINK ISIS300, Oxford). The internal resistance and power density of the reactors were obtained by plotting the polarization curves and power curves. The polarization curves were recorded from the highest (i.e. 10,000Ω) to the lowest (i.e. 5Ω) external resistance. The cell voltage was taken only when pseudo-steady state conditions had been established. The polarization curves represented cell voltage E, measured by the data logger, as a function of current density I, which is calculated by Ohm’s law as $I = E/(Rext \times Vanode)$. The internal resistance (Rint) of BES reactor was then obtained by calculating the slope of the polarization curve. The power density, calculated by $P = E^2/(Rext \times Vanode)$, described the power as a function of the current (density). The peak of power curve was the highest power density that can be produced from reactor. In the above equations, Vanode is the working volume of the anode chamber (1.0 L).

3. Results and Discussion

3.1 Effect of separator on silver recovery and power generation

The experiment was conducted for 48 hours. During the operation, the remaining concentration of Ag(I), Fe(III), and Cu(II) in the catholyte were measured every 4 hours by using an ICP spectrometer. The cell voltages produced from both reactors were also recorded by the data logger. During the first 6 hours, higher cell voltage production was found in the AEM base-reactor (Fig. 1). However, it declined quickly, compared to that of CEM-based reactors. This can be attributed to the substrate loss problem occurring in the AEM-based reactor. In this reactor, glucose served as the substrate, which is fermentable, and takes part in different metabolisms. During its fermentation, simpler organic matter (e. g. butyrate, propionate, acetate) is produced, which diffuses through the AEM due to their negatively charged form.

The reduction of metals in the catholyte is shown in Fig. 2. The Ag(I) reduction occurred quickly during 8 hours for the AEM-based reactor (Fig. 2A) and 24 hours for the CEM-based reactor (Fig. 2B). In both reactors, the Fe(III) concentration slightly decreased with time, compared to Cu(II) concentration. The Cu(II) concentration was quite constant until 48 hours of operation

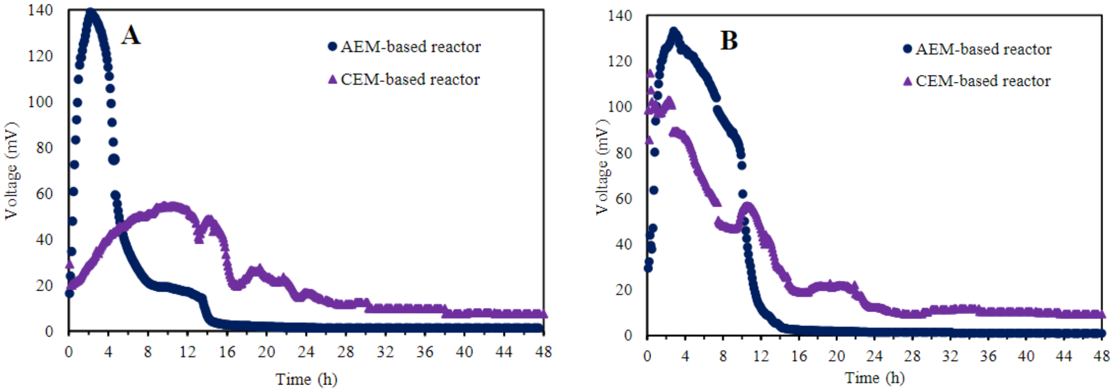

Fig.1. Cell voltage progression during the operation in BES reactor at A). Ag(I) 10 mM, Fe(III) 10 mM and Cu(II) 1 mM, and B). Ag(I) 10 mM, Fe(III) 20 mM, and Cu(II) 1 mM

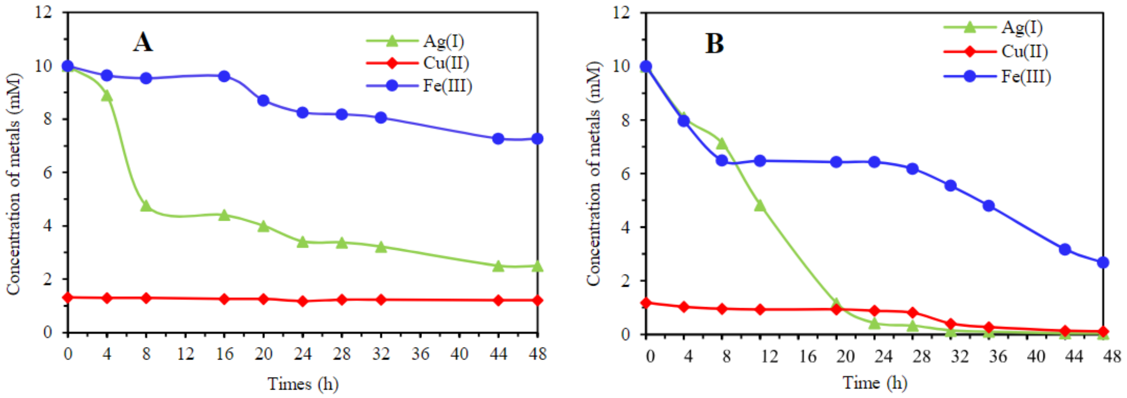

Fig. 2. Reduction of metal ions vs. time in the catholyte of A). AEM-based ractor, B). CEM-based reactor at Ag(I) 10 mM, Fe(III) 10 mM, Cu(II) 1 mM

potential of Ag(I) (i.e. Ag^+/Ag^0 = 0.799 V versus the Standard Hydrogen Electrode (vs. SHE)) as compared to that of Cu(II) (i.e. Cu^{2+}/Cu^0 = 0.337 V vs. SHE) and Fe(III) (i.e. Fe^{3+}/Fe^0 = -0.44 V vs. SHE). The CEM-based reactor had higher performance for metal ions reduction and silver recovery than the AEM-based reactor. However, in the CEM-based reactor, some diffusion of Ag(I), Fe(III), and Cu(II) through the membrane was observed. The digestion of the biomass in the anode chamber of this reactor at the end of operation showed the presence of Ag(I) (0.073 mM), Fe(III) (3.283 mM), and Cu(II) (0.403 mM), which were higher than that found in the original sludge obtained from the wastewater treatment plant (Ag(I) 0.057 mM, Fe(III) 2.182 mM, and Cu(II) 0.190 mM).

3.2 Effect of Fe(III) on silver recovery and power generation

The experiment was conducted by increasing the concentration of Fe(III) from 10 mM to 20 mM while the other metal ions were kept constant (i.e. Ag(I) 10 mM, and Cu(II) 1 mM) in the catholyte. The catholyte is based on a photographic shop's fixer solution which mainly contains Ag(I), Fe(III), and a small amount of Cu(II). There was no significant change in the cell voltage production in AEM-based reactors when the Fe(III) concentration increased (Fig.1A and B). Similarly, it declined quickly in 12 hours due to substrate loss through the membrane as mentioned above. For the CEM-based reactor, higher cell voltage production was observed when the Fe(III) concentration increased (Fig.1A and Fig.1B). It can be explained by increase of ionic conductivity in the catholyte, which further decreased the internal resistance.

Although AEM-based reactor produced higher cell voltage at the beginning of operation, it actually dropped sharply in a short time (12 hours), whereas CEM-based reactor maintained the high voltage state for a longer time.

When the initial Fe(III) concentration increased from 10 to 20 mM, the reduction rate of Fe(III) was increased accordingly in both reactors (Fig.3). However, the increase of Fe(III) concentration affected the reduction rate of Ag(I) ions (r_{Ag}). Specifically, the r_{Ag} decreased from 0.16 mM/h to 0.12 mM/h for the AEM-based reactor, and from 0.21 mM/h to 0.16 mM/h for the CEM- based reactor, along with the increase of Fe(III) concentration from 10 mM to 20 mM, respectively.

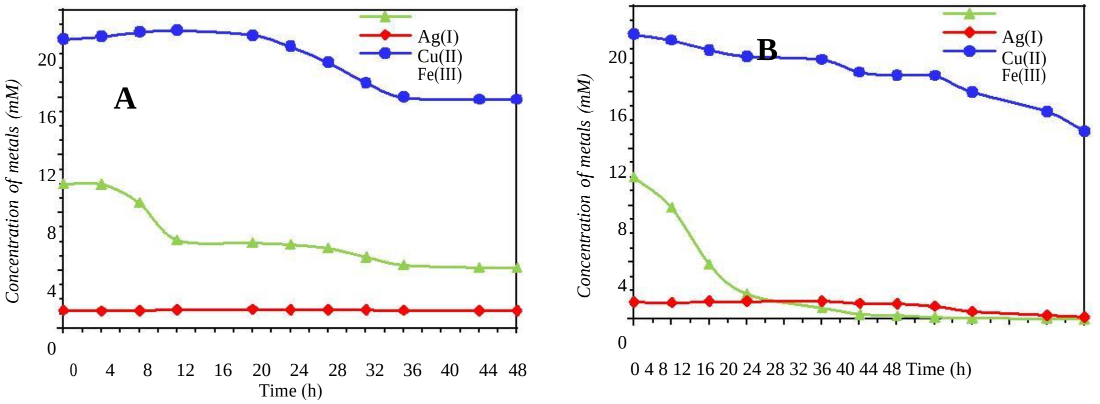

Fig. 3. Reduction of metal ions vs. time in the catholyte of A). AEM-based ractor, B). CEM-based reactor at Ag(I) 10 mM, Fe(III) 20 mM, Cu(II) 1 mM.

It can be explained that large amount of Fe(III) ions in the catholyte may compete with Ag(I) ions to accept the electrons transferred from the anode. However, the increase of Fe(III) concentration did not affect the Cu(II) reduction rate in both reactors (0.002 mM/h for AEM-based reactor, and 0.02 mM/h for CEM-based reactor). As a result, the Ag removal in AEM-based reactor and CEM-based reactor was 58.02% and 99.70%, respectively. When comparing the results of Ag recovery in all of the cases as presented in Fig.2 (A and B) and Fig.3 (A and B), the CEM-based reactor showed a better performance.

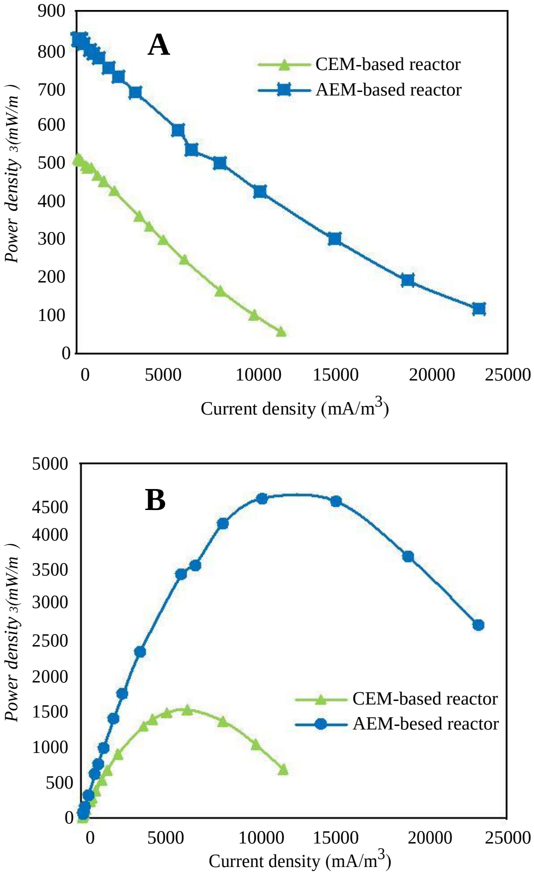

Fig.4. A) Polarization curves and B) Power and and power curves obtained in the AEM and CEM-based reactors. density of BES reactors obtained with the catholyte containing Ag(I) 10 mM, Fe(III) 10 mM, and Cu(II) 1 mM

3.3 Polarization and Power curves

Fig.4 showed the polarization curves and power curves obtained in the AEM and CEM-based reactors with the catholyte containing Ag (l) 10 mM, Fe(III) 10mM, and Cu(II) 1mM.

The internal resistance (Rint) of each reactor was determined as the slope of the polarization curves. Specifically, the Rint of the AEM-based reactor and CEM-based reactor were 30.58 □ and 38.58□, respectively (Fig.4A).

The diffusion of metal ions through the CEM due to their positive charge increased the internal resistance of membrane, which accordingly increased the total internal resistance of CEM-based reactor, as compared to AEM-based reactor. The maximum power density (Pmax) was also determined, in which a higher Pmax of 4515.63 mW/m^3 was found in AEM-based reactor as compared to that in CEM-based reactor (1542.56 mW/m^3) (Fig.4B). This result was ascribed to the higher cell voltage found in the AEM-based reactor at the beginning of operation.

3.4 Characterization of deposits on the cathode and membrane surfaces

After 30 days of operation, the graphite plates and membranes were taken out from both reactors for SEM-EDS analysis.

Prior to use, the graphite plates showed a black carbon color. During the experiment, bright deposits grew from small particles to film-like structures on the graphite plate surface when the reaction time elapsed. At the end of BES operation, the graphite plates in both reactors were covered with lustrous white deposits which could be observed visually. Under the SEM analysis, silver with thin shinny film-like structure was found on the cathode surface of the AEM-based reactor Fig.5 A1 while silver the in form of dendritically crystal structures was detected in the CEM-based reactor Fig.5 B1.

These results were then confirmed by the EDS spectrum, in which the sharp peak at an energy level of 2.98 keV indicated that the deposits on the cathode surfaces of both reactors were comprised of pure silver (Fig.5 A2 and B2).

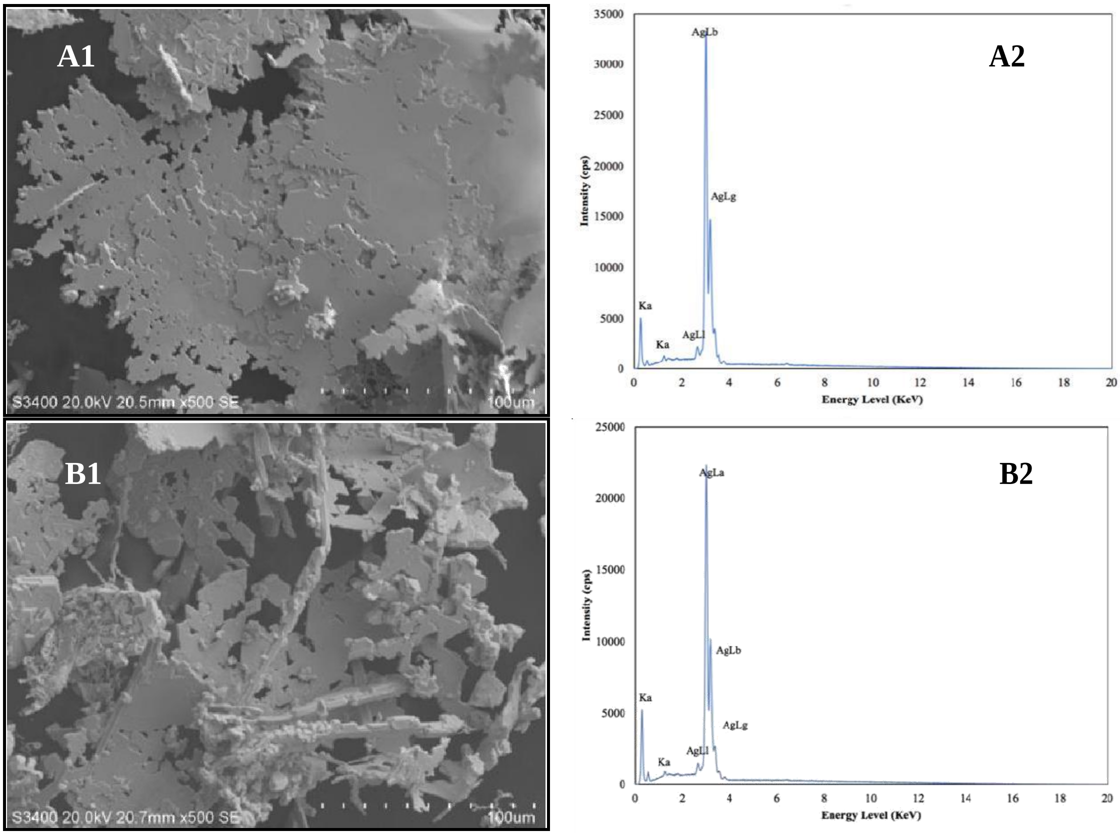

Fig. 5. Characterization of the deposits on graphite plate surface (A) AEM-based reactor, and (B) CEM-based reactor by SEM image (A1 and B1) and EDS (A2 and B2).

The CEM and AEM surfaces before and after operation were also characterized by using SEM-EDS analysis to clarify the deposits on the membrane surface. The original surfaces of the AEM and CEM are shown in Fig.6A1 and B1, respectively. After 30 days of BES operation, membranes were taken out from reactors to observe their morphology. SEM showed the presence of bulk structure on the AEM surface (Fig. 6 A2) and dendritically film-like structure on the CEM surface (Fig.6 B2). EDS analysis confirmed the deposits of silver, iron, and copper on the surfaces of AEM and CEM, as shown in Fig.6 A3 and B3.

4. Conclusions

It was confirmed that bio-electrochemical system technology could recover silver from a synthetic mixed metals solution. Higher recovery efficiency (> 99%) was found in the CEM-based reactor although some diffusion of metal ions as Ag(I), Cu(II), Fe(III) were observed. Increasing initial Fe(III) concentration (10-20 mM) had little effect on the Ag(I) reduction rate in this reactor, but improved significantly the cell voltage production due to the increasing ionic conductivity of the catholyte. In contrast, the AEM-based reactor showed lower recovery efficiency (58-75%) due to the substrate loss problem through the AEM membrane. However, as a higher cell voltage was produced at the beginning of operation, a higher maximum power density (4515.63 mW/m^3) could be obtained from the AEM-based reactor, compared to the CEM-based reactor (1542.56 mW/m^3). Metallic silver was found on the cathode surface in both reactors and

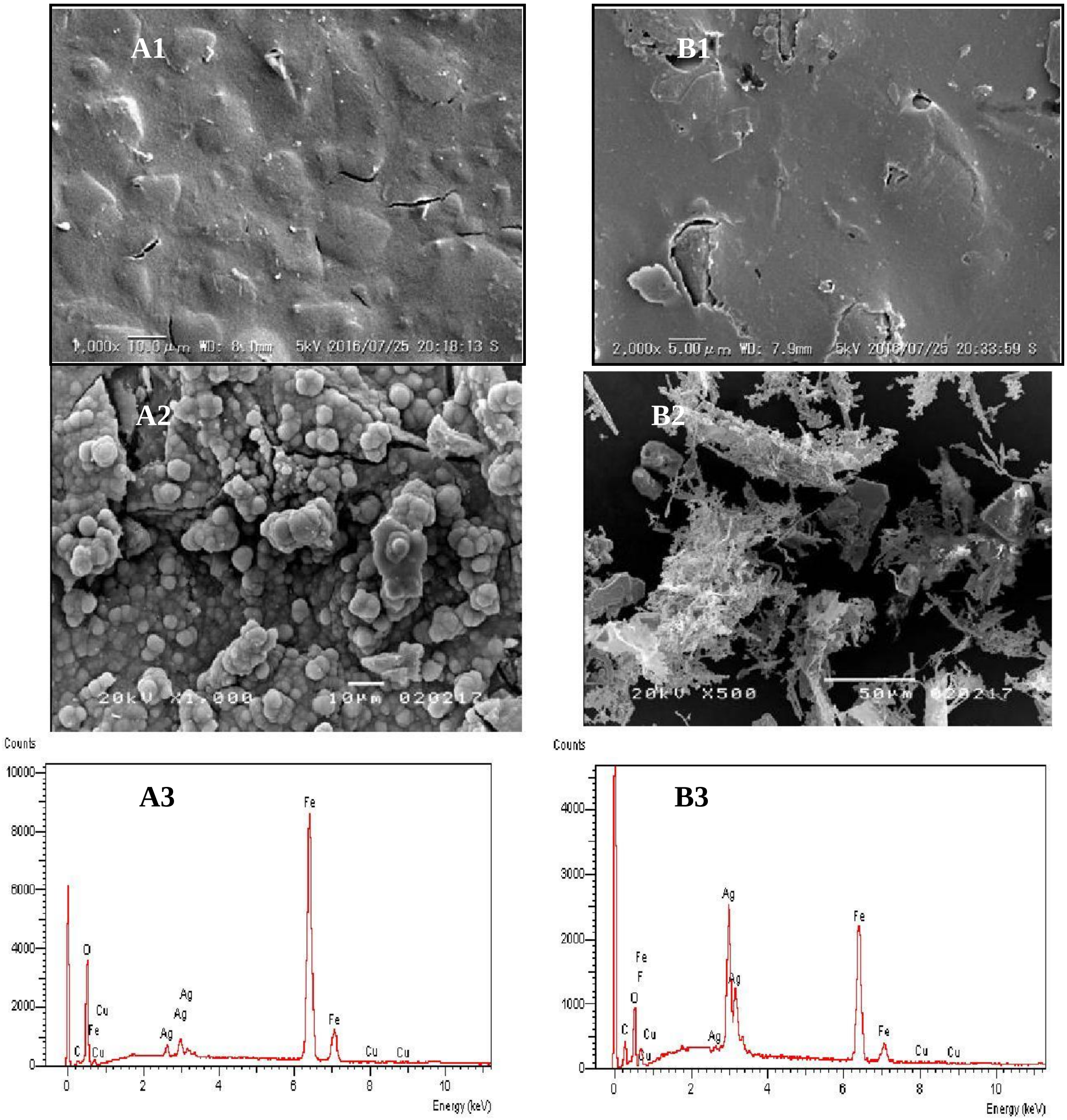

Fig. 6. SEM image of (A) AEM and (B) CEM surface before operation (A1, B1) and after 30 days of operation (A2, B2); EDS (A3, B3) characterizes the chemical deposition on the membrane surface.

also confirmed by SEM-EDS results. Some deposits containing silver, iron, and copper were also detected on the membrane surfaces due to their transport, based on the ion exchange mechanism.

Acknowledgements

The authors would like to acknowledge the financial support from Sirindhorn International Institute of Techno-logy (SIIT), Thammasat University, Thailand

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