Electrochemical characterization of gold mining wastewater for recovery of mercury using electrochemical method

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Abstract. An experimental study to determine optimum operating conditions for mercury recovery from gold mining wastewater has been conducted. Electrochemical characterization of gold mining wastewater was carried out by using steady-state polarization experiment in a batch system. The polarization curves obtained were then utilized to determine the optimum operating conditions. The polarization experiments were conducted by an electrochemical cell with two electrodes of copper (Cu), carbon (C), or stainless steel (SS) and an electrolyte solution of the wastewater. Variations of electrodes used were pairs of copper (Cu), carbon (C) and stainless steel (SS) which were arranged randomly. To obtain the polarization curves, the electrical potentials between 0 V and 3 V were applied and its corresponding currents were recorded at an interval potential of 0.1 V. The highest current density was achieved on electrode pairs of stainless steel-carbon (SS-C) and carbon-carbon (C-C). This is an early indication that the most optimum electrode pairs for mercury recovery possibly are SS-C and C-C. EDX analysis confirmed the presence of mercury in the deposited materials, this leads to a conclusion that mercury can be deposited on to carbon electrode from the wastewater using electrochemical method which then eventually it can be recovered.

1. Introduction
A large number of conventional gold mining activities in Indonesia cause severe environmental problems due to mercury (Hg) pollution [1]. One of the International media, Worldpolluted.org reported that mercury contamination occurred due to the gold mining waste in Kalimantan was ranked seventh in the 'Top Ten' Threats in 2013 or the 10th most threatening thing in 2013. Estimated by The United Nations Industrial Development Organization (UNIDO) more than 1000 tonnes of mercury pollute the environment every year and 30% of it is anthropogenic mercury. In 2008, the Journal of Water and Environment Technology found a mercury concentration of 2,260 μg / L in the Kahayu river of Central Kalimantan [2].

Mercury is a heavy metal that has toxic effects on living things. Due to its high toxicity and ability to accumulate into the human body, continuous exposure to mercury may cause adverse effects to human health [3]. The element has been declared to be one of the most toxic pollutants [4]. The first identified case of mercury poisoning occurred in the Gulf of Manimata, Japan from 1930 to 1960. The case revealed that bioaccumulation of toxic materials (methyl mercury) naturally occurred in fishes could kill about a hundred people and caused genetic damage in large populations. The Minamata incident was followed by a more tragic report, Hg poisoning in Iraq in 1972 in which 450 villagers died after eating grain using mercury-containing pesticides [4,5].

Therefore, it is crucial to look for a technology that is capable of overcoming the mercury contamination. The technology has to be able to reduce the mercury in the wastewater without causing another environmental problem which so-called Green technology. The technology becomes a choice to gear up sustainable development. An electrochemical method was selected to be used in this study as it is green and offers a number of advantages [4]. Electroplating has attracted much attention because of its simple process, cheap equipment, ease of operation, shorter retention times, high
deposition speed and reduction of generated sludge [6]. There have been a number of studies dedicated to apply the electrochemical method, however the types of electrodes used are still in limited quantities, such as aluminum [7], magnetite [4] and graphite-titanium [8]. In this research various electrodes would be used which were graphite-stainless-steel-copper. The electrodes were arranged by copper (Cu), carbon (C) and stainless steel (SS) which composed alternately as anode and cathode. In addition, operating conditions (current density and voltage) would also be determined systematically based on electrochemical fundamental theory through steady-state polarization experiments. So that an electrode pair that has the best efficiency and the most optimum operating conditions could be determined.

2. Experimental

All experiments were carried out at room temperature in the laboratory of chemical engineering, faculty of engineering, Universitas Muhammadiyah Surakarta. The gold mining wastewater used in this research was obtained from small and medium conventional gold mining industries from Wonogiri, Central Java. Initially, the waste was analyzed to determine its mercury content using Mercury analyzer. The analysis was carried out 3 times repetition to ensure the results were accurate.

The electrochemical cell used in the experimentation was made of vertical cylindrical glass with a volume of 250 ml. Stainless steel (SS), carbon (C) and copper (Cu) used for the electrodes were obtained from metal stores (Moro Dadi) in Surakarta with a minimum purity of 95%. At first, the metal was cut so that a surface area of 11.76 cm² was obtained. The electrodes were then mechanically and chemically cleaned. Mechanical polishing was carried out by using sandpaper to obtain smooth surface. The chemical cleansing was conducted by dipping the electrodes into a solution of nitric acid (10%). Thereafter, the electrodes were washed by deionized water before installing it into the electrochemical system. The electrodes were attached to copper wire which was then connected to the power supply (Sanfix SP3050).

To achieve the aims and objectives of the research, first, polarization experiments were carried out in the previously described electrochemical cell. To see the effect of the electrodes used, the electroplating system was set with variations of electrodes pairs (anode/cathode) which were C-C, C-SS, C-Cu, SS-C, SS-SS, SS-Cu, Cu-C, Cu-SS, and Cu-C. The electrolyte solution used was 200 ml in a 250 ml beaker. The electrodes were connected to the power supply by using copper wire. An electrical potential was applied to the system started from 0.1 to 3 V with a potential interval of 0.1. Corresponding current responses were recorded when the system has reached steady-state conditions (usually at around 1 minute). The current responses were measured by using a digital multimeter of Fluke 17B+.

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The initial concentration of mercury in the waste before the treatment was 0.052 ppm. It shows that the concentration of the waste was required as the mercury content exceeds the concentration that is allowed to be disposed to the environment, i.e. 0.000048 ppm under the threshold of 0.001 ppm. The next stage was to electrochemical characterization of the waste by using steady-state polarization experiments.

Polarization data obtained from the experiments were plotted to create polarization curves. The cathodic polarization curves for the wastewater containing mercury at various electrodes pairs are shown in Figure1. It can be seen in Figure 1 that at low potentials (0.1 – 0.4 V), small electrical
current flow was observed. This indicates that the reduction reaction of Hg has not occurred yet. The cathodic currents increase gradually with the increase of applied potentials from 0.4 V to 1.8 V. At potentials greater than 1.8 V, significant increases of the cathodic current densities are observed. However, at a potential of 2.2 - 2.4 V gas (H₂) evolution was visible. It is generally seen that the current at the cathode flows since the low cell potential, however, at the potentials of the cell between 0-2 V do not show any mercury plating on the working electrode. The mercury reduction reaction most likely to occur at potentials between 1.8 V and 2.4 V which is indicated by a significant increase in cathodic current densities [4,9,10]. The corresponding current densities for mercury electroplating range from -0.075 to -0.175 mA/cm².

Figure 1. Steady-state polarization curves showing the relationship between the cell potentials with the current densities

The effect of electrodes pairs was also observed. Figure 1 also shows that the electrode pairs of SS-C and C-C are identified to be the most appropriate electrode pair characterized by an increase of the current flows significantly at a relatively low potential. The cathodic current flows indicate that the reaction of Hg electroplating began to take place and the more negative of the cathodic current results in higher rate of reduction reaction [11, 12, 13]. The characterization experiments showed that higher cathodic currents were obtained when the electrodes pairs of SS-C and C-C were used. This is an early indication that the SS-C and C-C pairs of electrodes are the most appropriate for use in the electrodeposition of mercury from the gold mining wastewater [9,10].

To see whether the mercury was deposited on to the electrode or not, the surface of the cathode was analyzed by using scanning electron microscopy (SEM) and EDX method. Figures 2 and 3 show the micrograph of SEM and EDX analysis results respectively. The SEM micrograph in Figure 2 indicates that due to the electroplating process, material from the wastewater was deposited on to the surface of the cathode. EDX analysis in Figure 3 confirmed the presence of mercury in the deposited materials [14]. This leads to the conclusion that mercury could be deposited on to carbon electrode from the wastewater using electrochemical method which then eventually can be recovered.
4. Conclusion
Hg or mercury recovery from gold mining waste could be achieved by using the electroplating method. Stainless steel-Carbon and Carbon-Carbon couples electrode become the most potential cathode-anode pair to be used. The optimum electroplating potential for Hg ranges between 1.8 V-2.4 V indicated by a significant cathodic current increase. The corresponding current densities for mercury electroplating range from -0.075 to -0.175 mA/cm². The experiment also showed that mercury could be deposited on to carbon electrode from the wastewater using electrochemical method which then eventually can be recovered.

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