Recovery of Alum from Surabaya Water Treatment Sludge using Electrolysis with Carbon-Silver Electrodes

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ABSTRACT

Untreated alum sludge from Surabaya water treatment plant (WTP), which contained high concentration of alum was directly discharged into Surabaya River. It might cause problems because of the accumulation of aluminum in the lower part of the river. Alum could be recovered from the drinking water sludge using the electrolysis method. Aims of this study were to determine the optimum pH and electrical current for electrolysis using carbon-silver electrodes to recover aluminum coagulant from the sludge, and to determine the amount of the recovered alum. The sludge was acidified prior to electrolysis. Acidification was done by adding sulfuric acid at pH 3 and 4. Polarization test was conducted at 100, 200, and 300 mA, in order to determine the optimum electrical current. The electrolysis was performed in one compartment batch recirculation reactor, using silver as cathode and carbon as anode for 10 hours. Values of pH were measured every hour. The precipitated matter in the cathode was weighed, and analysed by means of *Inductively Coupled Plasma*. The optimum conditions of the electrolysis were achieved at initial pH 3 and electrical current 300 mA. The electrolysis resulted in the highest precipitate of 2.6112 g in the cathode.

Keywords: alum, drinking water, electrolysis, recovery, sludge

INTRODUCTION

Clean water, as one of the basic needs of urban population, is provided by municipal water supply companies, with post raw water treatment sludge as residue. The rapid population growth in large cities in Indonesia, especially in Surabaya, has caused the water demand to increase. Therefore, the drinking water sludge, which contains high amounts of aluminum would increase too [Selintung, 2012]. The high aluminum content in the drinking water sludge results from the use of aluminum sulfate ($Al_2(SO_4)_3$) as coagulant to reduce turbidity and total suspended solids (TSS) in the raw water [Ahmad et al., 2016]. As an example, the aluminum concentration in Code River, Yogyakarta was 128.43 mg/L [Hanim et al., 2007]. Dassanayake [Dassanayake et al., 2015] further stated that the total aluminum concentration in the accelerator unit was 4794 mg/L. The amount of sludge which was discharged into Surabaya River by Surya Sembada Water Treatment Plant (WTP) was 626 m³/day, with the aluminum concentration of 250 mg/L [Primadipta and Titah, 2017]. According to the Government Regulation of the Republic of Indonesia No. 82/2001, the maximum allowable aluminum concentration for Class A water is 0.2 mg/L.

A direct discharge of WTP sludge into a river might cause metal pollution, such as aluminum, lead, chromium, copper, and cadmium to occur [Georgantas and Grigoropoulou, 2005]. Aluminum could be accumulated in the sediment of the lower river part [7], in aquatic biota and humans via food chain [Ippolito et al., 2011]. The bioaccumulated aluminum is potentially toxic to the growing aquatic biota [Cheng et al., 2012]. Furthermore, it may be toxic to humans, resulting,

i.a. in central nervous system failure, dementia, memory loss, lethargy, and severe trembling [Ahmad et al., 2016].

Aluminum recovery from the WTP sludge can be done with a combination of acidification and electrolysis processes. Acidification is aimed at dissolving the aluminum in the sludge [Cheng et al., 2012]. The next stage is electrolysis, which can separate the dissolved aluminum. This last stage has an advantage for not requiring the addition of chemical substances and producing precipitate with high aluminum purity [Huang et al., 2007]. The aims of this study were to determine the optimum pH and electrical current for electrolysis using carbon-silver electrodes to recover the aluminum coagulant from the sludge, and to determine the amount of the recovered alum.

MATERIALS AND METHODS

Alum sludge sampling and characterization

The alum sludge samples were collected from clearator drains of the Surabaya WTP in February 2018. The sludge was dried at 105°C for 24 hours, and characterized according to moisture, alkalinity, pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), volatile solids (VS), total dissolved solids (TDS), sludge volume index (SVI), and metal (Al, Fe, Cu, Cr, and Pb) concentrations. The procedures followed the Standard Methods for Water and Wastewater Treatment Analysis [APHA, 2012].

Acidification

Two hundred g of dried alum sludge was added with distilled water up to 1000 mL. Then, sulfuric acid was added for acidification in order to achieve solutions with the pH of 3 and 4. The acidified sludge solution was homogenized using magnetic stirrer with 800 rpm for 120 minutes. Centrifugation was applied to separate the solid fraction from the solution, which contained metal ions. The solution was used as electrolyte during the electrolysis.

Polarization test

The polarization test was carried out to determine electric current and potential ranges in the electrolysis. In this study, three current variations from polarization curve would be used.

Cell potential and current density for aluminum coagulant recovery using electrolysis could be determined from the polarization curve.

The previous studies showed that the cell potential was around 0,2 V [Widayatno et al., 2016]. In this study, polarization test was conducted at pH 3 with cell potential ranges of 0.0–6.0 V and 6.0–10.0 V, by putting significant TDS value decrease into consideration. The increase of cell potential values was adjusted every 3 minutes, and the TDS as well as current were measured. The polarization test data were used for preparing a polarization curve using TDS data and the cell potential value within 0.0–6.0 V and 6.0–10.0 V ranges. Electric current at the cell potential value, which showed a significant TDS decrease, was selected to run the electrolysis.

Electrolysis process

A laboratory scale batch recirculation reactor with one compartment (Figure 1a) was used, following Selvakumar et al. [2016]. The reactor was made from acrylic with a dimension of 5 cm (l) × 2 cm (w) × 20 cm (h). Silver was used for cathode for its highest conductivity, compared to other metals. The high conductivity, softness (low hardness), and high resistance to oxidation make silver an excellent choice for contact materials. Carbon was selected as anode for its corrosion resistant, high electronic conductivity, and its abundant and low cost reasons. The electrodes were of plate forms with a dimension of 2 cm (l) × 5 cm (w). The thickness of carbon anode and silver cathode was 0.1 cm and 0.5 cm, respectively. The distance between electrodes was 1 cm. Configuration of the reactor is shown in Figure 1b. The electric current source was DC Power Supply. A peristaltic pump was used for flowing the electrolyte from 1 L feed tank to the cell with a discharge rate of 5 mL/s.

The initial pH values of the electrolysis were adjusted to 3 and 4, following Sengupta [2002] and Bahena et al. [2002]. The electric current values were obtained from the results of polarization tests. The operation time of electrolysis was 10 hours. TDS and pH were measured every hour. The recovered deposited matter at the cathode was weighed, and then soaked with 50 mL nitric acid [Ahmad, 2011]. The dissolved aluminum and metal impurities were measured using *Inductively Coupled Plasma* (ICP) type Agilent Technologies series 700 ICP-OES. The results were used to determine the amount and purity of aluminum coagulant from the electrolysis.
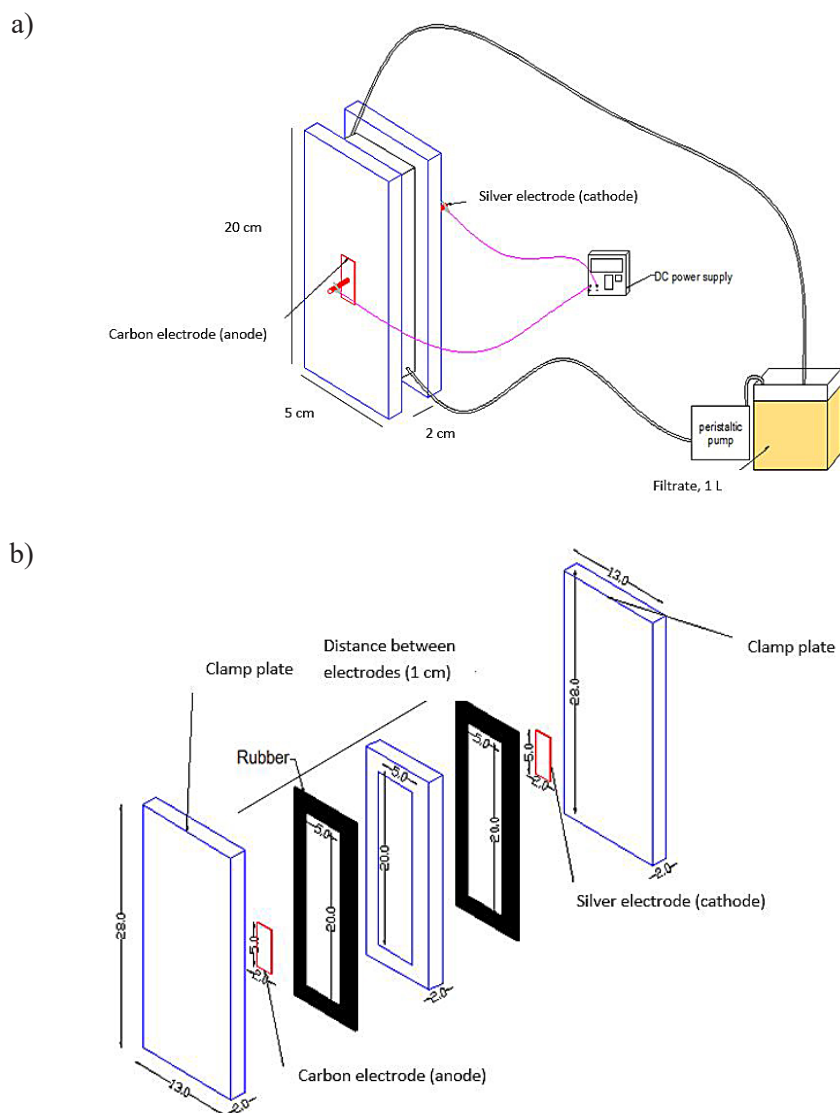
a)

b)

Figure 1. (a) Electrolysis reactor design, (b) Electrolysis reactor configuration

RESULTS AND DISCUSSIONS

Alum sludge characteristicss

The alum sludge samples were collected from clearator drains in Surabaya WTP. Metals and organics were the main components of the sludge. The alum sludge characteristics were applied as references for proper treatment methods.

As shown in Table 1, the largest metal concentration in the sludge corresponded to aluminum (1194 mg/L). This high concentration of the aluminum creates a potential for recovery. According to National Pollutant Discharge Elimination System (NPDES), this concentration exceeded the daily maximum limitation of 1,5–10 mg/L [EPA, 2011]. Other metals in the sludge were Fe (515 mg/L), Cu (0.559 mg/L), and Cr (0.217 mg/L). Iron was present in considerably high concentration. The source of iron was the high concentration of suspended solids in the sludge (12,511 mg/L), which was mainly soil particulate in the raw water. Copper and chromium in the sludge were originated from improperly treated industrial waste water which was commonly discharged into Surabaya river.

The BOD and COD concentrations of the sludge were 936.8 mg/L and 9,000 mg/L, respectively. These concentrations exceeded the effluent standards of the State Ministry for The Environment Decree of Republic Indonesia No. 5/2014, which were 50 mg/L and 100 mg/L, respectively. The BOD/COD ratio of 0.1 indicated that the organic content in alum sludge was non-biodegradable [Dahou, 2017]. Such a high organic content originated from industrial and domestic wastewater sources.

Table 1. Alum sludge characteristics

Parameters	Concentration	Unit
Water content	98.4	%
Alkalinity	75	mg/L HCO$_3^-$
pH	7.46	-
COD	9,000	mg/L
BOD$_5$	936.8	mg/L
Volatile Solids	12,816.7	mg/L
Total Dissolved Solids	370.4	mg/L
Total Suspended Solids	12511	mg/L
Al	1194	mg/L
Fe	515	mg/L
Cu	0.559	mg/L
Cr	0.217	mg/L

Polarization test

The polarization test, which was performed at a cell potential range of 0–6 V at pH 3, generated electrical current 0–500 mA. During the test, the TDS values in the electrolyte decreased from 5.3 g/L to 1.6 g/L at the cell potential 5.8 V (Figure 2). The polarization test which was carried out in the cell potential range of 6–10 V, generated current in the range of 500–1000 mA (Figure 3). The TDS concentration decreased abruptly from 5.28 to 0.014 g/L at cell potential 6.0–9.0 V. A drastic decrease of TDS during the second polarization test might cause water electrolysis, which needs high energy consumption [Songa et al., 2008]. Therefore, cell potential range of 0–6 V with electrical current 0–500 mA were considered to be appropriate for performing the electrolysis of the alum sludge.

When conducted at the electrical current of 100–300 mA, electrolysis of the acidified alum sludge worked, as indicated by the appearance of gas bubbles around the cathode and anode. Both gases were formed vigorously at electrical current above 300 mA. This might indicate that the unexpected electrolysis of water occurred. Therefore, the electrical current variations for the electrolysis in this experiment were 100, 200, and 300 mA.

Electrolysis process

pH Values

The pH values of the electrolyte showed a slight decrease during the electrolysis process. At the electrical current of 100 mA, the electrolyte with initial pH 3 showed stable pH values, whereas the electrolyte with initial pH 4 showed a decrease in pH from 4.01 to 3.00 (Figure 4). When performed at 200 mA, the pH values of the electrolyte decreased from 3.07 to 2.52 and 4.09 to 2.65, at initial pH 3 and 4, respectively (Figure 5). If the current was increased to 300 mA, the pH of the solutions with the initial value of 4 tended to be relatively constant. However, the solution with initial pH 3 decreased from 3.2 to 2.47 (Figure 6).
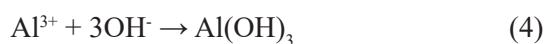
The slight pH decrease during electrolysis with electric currents 100 to 300 mA can be explained as follows. A simultaneous formation of H$^+$ ion from H$_2$O occurred in the cathode (Eq. 1), and H$^+$ ion was used for the formations H$_2$SO$_4$ at the anode (Eq. 2) and H$_2$ at the cathode (Eq.3). During the electrolysis, Al(OH)$_3$ was formed in the cathode (Eq. 4) from Al^{3+}, which was present in the acidified electrolyte. These reactions are shown in Eq. 1–4 [Chen et al., 2000]:

Reactions at anode:

$$2H_2O \rightarrow 4H^+ + 4e^- + O_2 \qquad (1)$$
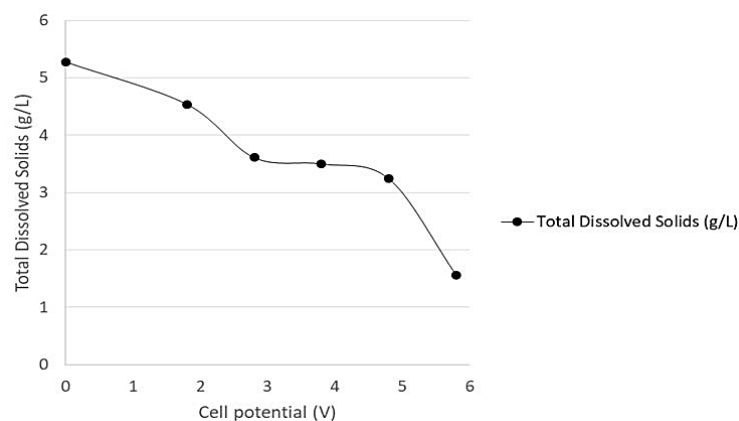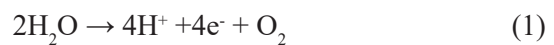
Figure 2. Influence of the cell potential to TDS values (i=0–500 mA)

$$SO_4^{2-} + 2H^+ \rightarrow H_2SO_4 \qquad (2)$$

Reactions at cathode:

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \qquad (4)$$

Aluminum Deposition at Cathode

The highest weight of deposited matter at the cathode was 2.6112 g, which was gained in electrolysis of acidified sludge with initial pH of 3 at 300 mA. The second and third weights of deposited matter were 2.329 g and 1.2979 g at initial pH
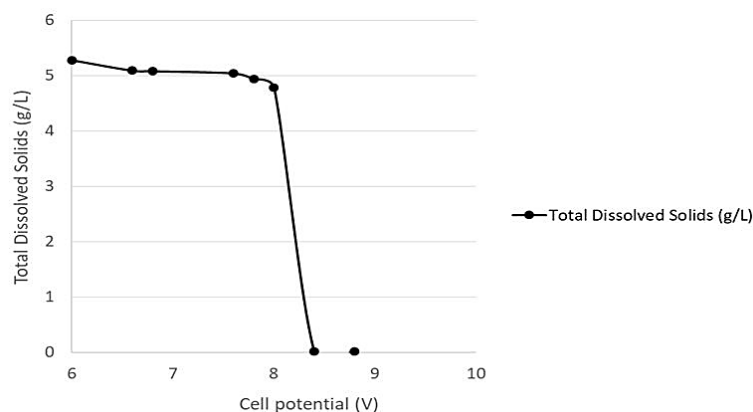

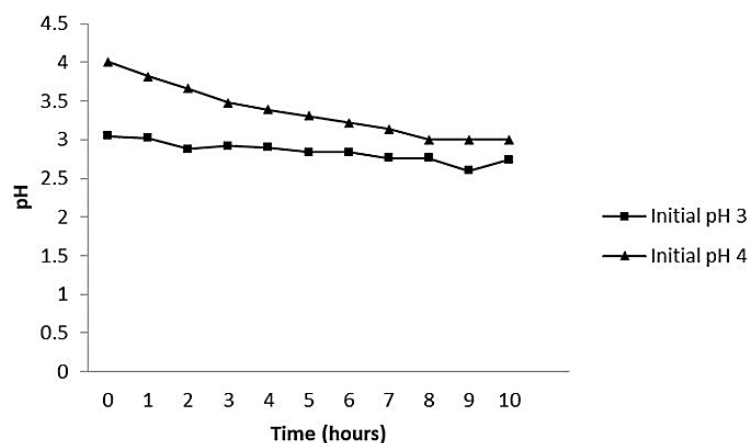**Figure 3.** Influence of the cell potential to TDS values (i=500–1000 mA)

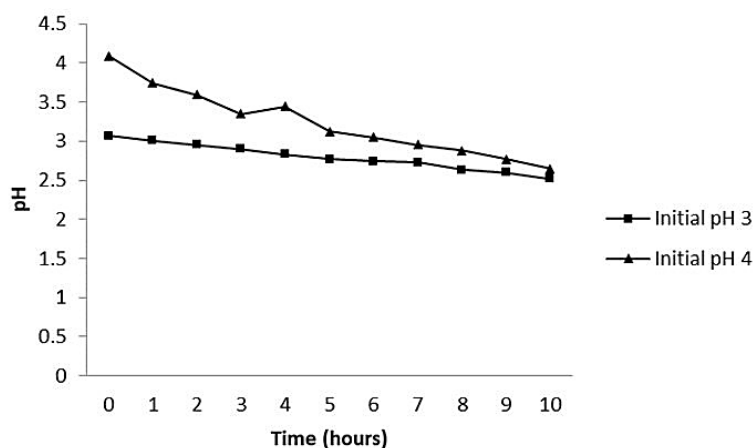**Figure 4.** Comparison of pH values (i=100 mA)

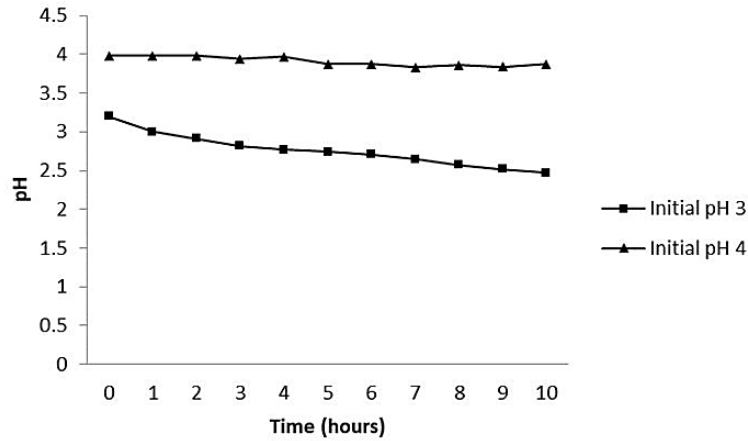**Figure 5.** Comparison of pH values (i=200 mA)

Figure 6. Comparison of pH values (i=300 mA)

4 at 300 mA and 200 mA, respectively (Table 2). This met the Faraday I Law, which stated that the mass of substance in the electrode is directly proportional to the amount of electric charge in the electrolyte solution [Buddhi et al., 2006].

The percentage of aluminum recovery, as shown in Table 2 can be calculated from the deposited $Al(OH)_3$ in the cathode. The aluminum concentration in recovered matter from the results of ICP measurement was calculated as well. The percentage of recovery was obtained from Eq. 5.

$$\% \ alumina \ recovery = $$

$$= \frac{mass \ Al \ at \ cathode \ (g)}{mass \ Al \ at \ t0 \ (g)} \times 100\% \quad (5)$$

Percentage of alum recovery was 26.20–28.72 % in the electrolysis with initial pH of 3 and 4 at 300 mA. The percentages of alum recovery also increased along with the increasing of pH values (Table 2). This result was in accordance with the research of Sengupta [Sengupta, 2002], which showed that the optimum alum recovery with electrolysis was at a pH 3 to 4. This researcher further stated that at this pH range, the chemical reactions were faster, and the cations more easily attached in the cathode.

The low alum recovery was most probably caused by the high COD in the alum sludge. The high organic content caused the decrease of conductivity and electron transfer between the anode and cathode [Huitle et al., 2018]. Therefore, it is

Table 2. Calculation of aluminum recovery

Treatment	Al concentration at t_0 (mg/L)	Total weight of Al at t_0 (g)	Weight of deposited matter at cathode (g)	Weight of alum deposit at cathode (g)	Aluminum recovery (%)
pH 3, 100 mA	2816.465	2.816	1.264	1.119	13.76
pH 4, 100 mA	1094.200	1.094	0.792	0.762	24.12
pH 3, 200 mA	3896.900	3.897	1.065	1.011	8.98
pH 4, 200 mA	1337.180	1.337	1.298	1.246	32.24
pH 3, 300 mA	3341.665	3.342	2.611	2.529	26.20
pH 4, 300 mA	2721.600	2.722	2.329	2.258	28.72

Table 3. Metal ion composition in deposited matter at the cathode

Electrolysis condition	Composition (%)				
	Al	Cu	Pb	Fe	Cr
pH 3, 100 mA	88.55	3.72	3.32	0.84	3.56
pH 4, 100 mA	96.21	1.56	0.41	0.42	1.37
pH 3, 200 mA	94.94	1.42	1.35	0.91	1.37
pH 4, 200 mA	95.97	1.77	0.41	0.44	1.39
pH 3, 300 mA	96.86	0.89	0.85	0.79	0.58
pH 4, 300 mA	96.95	1.09	0.61	0.31	1.01

recommended that the organic contaminant to be removed before the electrolysis.

Metal composition in the deposited matter

The metal composition in the deposited matter, as shown in Table 3, was dominated by Al (88.55–96.95%). Other metal contaminants were Cu (0.89–3.72%), Pb (0.41–3.32%), Fe (0.31–0.91%), and Cr (0.58–3.56%). Metal contaminants showed higher composition at initial electrolyte pH 3–4 and electrical current 100 mV.

These metal contaminants can be removed by applying anionic exchange membrane during the electrolysis [Varcoe et al., 2014]. Taking the deposited matter weight and the metal composition into consideration, the optimum conditions for alum recovery using electrolysis method with carbon and silver electrodes occurred at pH 3 and electrical current 300 mA.

CONCLUSIONS

The optimum conditions for alum recovery from acidified drinking water sludge using electrolysis with carbon-silver electrodes were obtained at initial pH 3 and electrical current 300 mA. The low alum recovery and the presence of heavy metal contaminants in the sludge should be considered for removal, when future electrolysis method is applied.

Acknowledgments

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