Aluminum and Organic Contaminant Removal from Drinking Water Treatment Sludge

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Abstract. Coagulation process using aluminum sulfate (Al₂(SO₄)₃) or alum as coagulant at a drinking water treatment plant generates a large volume of alum sludge. The alum sludge contains high concentrations of aluminum and organic matter, which are harmful to the environment. Organic contaminants can decrease the conductivity and mobility of ions in electrolyte, so it can reduce the effectiveness of electrolysis to remove the aluminum. Aims of this study are: (1) to determine the aluminum and COD removal in electrolysis process using carbon-silver electrodes and (2) to measure the efficiency of COD removal by H₂O₂ oxidation and UV light exposure. The sludge was acidified to pH 3 and 4 and centrifuged prior to electrolysis. The electrical current was 300 mA, based on polarization test using carbon silver as anode and cathode electrodes. Electrolysis was carried out in a batch recirculation one-compartment reactor for 10 hours. Deposited matter of alum at cathode was weighed and analyzed by Inductively Coupled Plasma. The electrolysis pretreatment was meant to remove high organic contaminants in electrolyte. The pretreatment was carried out by oxidation with addition of H₂O₂ with a ratio of [H₂O₂]/[COD] = 1/2 and 254 nm UV light exposure for 4 hours. This study resulted in low aluminum deposit of 3.19 mg at the cathode with COD removal of 11.11% at initial pH 3 using electrolysis. The highest COD removal efficiency by oxidation with addition of H₂O₂ and UV light exposure was 75%. It can be concluded that H₂O₂ oxidation and UV light exposure could be applied prior to electrolysis for optimizing aluminum removal.

Keywords: alum sludge, aluminum removal, carbon-silver electrodes, electrolysis, H₂O₂ oxidation.

1. Introduction
Coagulation process in drinking water treatment plant (DWTP) generates alum sludge. Aluminum coagulant (for example Al₂(SO₄)₃·12H₂O) is a substance with a large positive charge, which is required to form a large aggregate (Arnoldsson et al., 2008). Alum sludge from Surabaya DWTP typically contains various types of metal such as aluminum (126.1 g/L), iron (55.4 g/L), copper (23 mg/L), and chromium (59 mg/L) (Barakwan et al., 2019a). Aluminum and other metals in alum sludge can form as metal ions which are toxic at certain concentrations. The alum sludge from Surabaya DWTP reached 626 m³/year and it was directly discharged into the stream or dumped in a landfill (Primadipta and Titah, 2017). High concentrations of aluminum in alum sludge is harmful to human health and aquatic biota (Keeley et al., 2014).
Alum sludge also has high concentrations of organic matter that can be measured as chemical oxygen demand (COD). The COD of alum sludge from Surabaya DWTP was 9666.7 mg/L (Barakwan et al., 2019a). Organic contaminants could interfere the electrolysis process. Conductivity and mobility of ions in electrolyte would decrease, so it could reduce the effectiveness of aluminum removal with electrolysis (Huitle et al., 2018). Organic contaminant can be reduced during electrolysis with electrosorption process or combined with oxidation process as pretreatment (addition of H2O2 and UV light exposure) (Zou et al., 2008; Chuango et al., 2013). Electrolysis process is influenced by the types of electrode, the potential differences, the characteristics of electrolyte, and pretreatment before process (Wahyono et al., 2017). Aims of this study are: (1) to determine the aluminum and COD removal in electrolysis process using carbon-silver electrodes and (2) to measure the efficiency of COD removal by H2O2 oxidation and UV light exposure.

2. Materials and Methods
Alum sludge samples were collected from clearator drains of Surabaya DWTP. The sludge samples were mashed and acidified using 1 N H2SO4 to pH 3 and 4 (Ahmad et al., 2016). The acidified filtrate was centrifuged for 20 minutes at 4000 rpm. Supernatant from centrifugation was used as electrolyte for electrolysis. Based on polarization test using carbon silver as anode and cathode electrodes, the electrical current was set at 300 mA (Barakwan et al., 2019b). Electrolysis was carried out in a batch recirculation one-compartment reactor with a capacity of 0.2 L for 10 hours (Figure 1). Feed tank capacity used was 1 L. Measurement of pH, total dissolved solids (TDS), conductivity, and COD were done every hour during electrolysis. Deposited matter of alum at cathode was weighed and analyzed by Inductively Coupled Plasma (ICP) type Agilent Technologies series 700 ICP-OES.

Electrolyte solutions were treated with oxidation using H2O2 and UV light exposure. Addition of 30% H2O2 was done in the ratio of [H2O2]/[COD] = ½, and the oxidized filtrate was also added with the same H2O2 with 254 nm UV light exposure (Collivignarelli et al., 2017). Acidified alum sludge solution was stirred using a magnetic stirrer at 700 rpm for 4 hours. The oxidation reactor is shown in Figure 2.
3. Results and Discussions

3.1 Electrolysis Process

3.1.1 TDS and Conductivity Values
Figure 3 shows that the TDS concentrations in the electrolyte during the electrolysis process were fluctuative. The TDS concentrations increased during electrolysis at all electrolyte solutions. The electrolyte pH 3 and 4 showed an increase in TDS concentrations from 3.53 g/L to 3.97 g/L and 4.58 g/L to 4.65 g/L, respectively (Figure 3). Based on Figure 4, conductivity increased in electrolyte pH 3 from 7.01 mS/cm to 8.01 mS/cm. While in electrolyte pH 4, there was a fluctuation in the conductivity during the electrolysis process, and the conductivity decreased from 9.15 mS/cm to 9.09 mS/cm.

![Figure 2. Oxidation reactor](image)

![Figure 3. TDS values during electrolysis](image)
Figure 4. Conductivity values during electrolysis

The low decrease in TDS and conductivity during electrolysis revealed that the reactions at the electrodes producing hydrogen and oxygen gases were not optimum (Sequiera et al., 2013). The fluctuative TDS and conductivity values could have also been caused by the dissolved ions in one compartment at the electrolysis, so that the reduction and oxidation reactions occurred at the same time without any barrier. The high dissolved organic matter also resulted in the low ability of electrolysis to decrease TDS and conductivity (Sengupta and Prakash, 2002). The fluctuation of TDS and conductivity in the electrolyte also affected the weight of metals deposit at the cathode. The slight decrease of TDS and conductivity at the end of the electrolysis process resulted in the small amount of aluminum deposited at the cathode.

3.1.2 Deposition of Aluminium at Cathode

The deposited matter at the cathode was weighed at the end of electrolysis. The percentage of aluminum removal was calculated from the results of ICP measurement of the deposited matter at the cathode (Table 1). The highest weight of the deposited matter at the cathode (2661 mg) was gained at electrolyte pH 3 (Table 2).

| Electrolysis process | Metal concentration from ICP measurement results (a) [mg/L] | Total metal concentrations (b) [mg/L] | Metal compositions = ((a/b) x 100%) (c) [%] |
|----------------------|-------------------------------------------------------------|--------------------------------------|------------------------------------------|
|                      | Al   | Fe   | Pb   | Cr   | Cu   | Al   | Fe   | Pb   | Cr   | Cu   |
| Electrolyte pH 3     | 63.93| 0.53 | 0.57 | 0.39 | 0.60 | 66.01| 96.86| 0.80 | 0.86 | 0.59 | 0.90 |
| Electrolyte pH 4     | 52.31| 0.17 | 0.33 | 0.59 | 0.55 | 53.96| 96.95| 0.31 | 0.62 | 1.02 | 1.10 |

Table 2. Weight of deposited matter after electrolysis in initial pH 3 and 4

| Parameters                  | Units | Electrolysis process | Initial pH 3 | Initial pH 4 |
|-----------------------------|-------|----------------------|--------------|--------------|
| Al concentration in t-0 (c) | mg/L  | 3341.67              | 2721.60      |
| [ICP measurement results]   |       |                      |              |              |
| Weight of Al in t-0 (d)     | mg    | 3340                 | 2720         |
| [c x Vol. feed tank (1 L)]  |       |                      |              |              |
### Parameters

| Parameters                                      | Units | Electrolysis process |
|------------------------------------------------|-------|----------------------|
| Weight of deposited matter at cathode (e)      | mg    | 2611                 |
| [weighing results]                              |       | 2330                 |
| Al concentration at the cathode (c)            | mg/L  | 63.93                |
| [ICP measurement results]                      |       | 52.31                |
| Al composition at the cathode (g)              | %     | 96.86                |
| [(a/b) x 100%]                                  |       | 96.95                |
| Weight of Al deposits at cathode (f)           | mg    | 3.19                 |
| [g \times e]                                   |       | 2.61                 |

The highest weight of aluminum deposit at the cathode was 3.19 mg at electrolyte pH 3. Aluminum removal was low (3.19 mg), which was caused by the decay and redeposition of silver cathode in acidic electrolytes (Molleman and Hiemstra, 2017). The decay of silver cathode was caused by the high silver solubility at pH 3 solutions (Molleman and Hiemstra, 2017). While, redeposition of silver ions at the cathode surface occurred as Ag$_2$O$_3$ was formed from Ag$_2$O which was attached on the silver electrode. It was caused by the high current density in these processes (60 mA/cm$^2$), whereas redeposition of silver ions occurred at the current density of more than 15 µA/cm$^2$. In this range of current density, the oxygen evolution occurred beyond the reduction at cathode (Casey and Moroz, 1964).

The low aluminum removal was also caused by the high organic content in the electrolytes. The high organic concentrations caused a decrease in electrolyte conductivity and electron transfer between the anode and cathode (Huitle et al., 2018). In addition, the low aluminum removal was caused by electrolysis which was carried out in one compartment, so that the oxidation and reduction reactions were not selective (Barazesh et al., 2016).

#### 3.1.3 Removal of Organic Contaminants using Carbon-Silver Electrodes

Organic contaminants in electrolyte were measured in the form of COD. COD decrease during electrolysis process with carbon-silver electrodes is shown in Figure 5. COD decreased from 3600 mg/L to 3200 mg/L and 4600 mg/L to 4400 mg/L in electrolyte pH 3 and 4, respectively (Figure 5). The highest COD removal of 11.11% was shown at the electrolyte pH 3.

![Figure 5. COD values during electrolysis](image-url)
The electrochemical process using carbon electrode as an anode is called electrosorption, where the carbon electrode can also remove the high organic concentrations in the electrolyte (Park and Kwak, 2014). The electrosorption process is the same as the process of absorbing dissolved organic contaminants by activated carbon on the surface of the carbon anode (Zou et al., 2008). However, the COD values at the end of the process still exceeded the effluent standards of the State Ministry for The Environment Decree of Republic Indonesia No. 5/2014, which was 100 mg/L. In addition, the surface reactions at the carbon anode would decrease in the oxidation process since it would have been covered by organic contaminants that had been absorbed by the anode. After electrolysis, the carbon anode that was saturated with organic matter would also be solid waste. Therefore, the organic contaminant in electrolyte should have been removed before the electrolysis or used the type of electrodes that has the ability for electrooxidation process should be used to remove the high organic concentrations in electrolytes.

3.2 Pre-Treatment for Decreasing Organic Matters

COD concentration in acidified filtrate pH 3 from alum sludge was 1733.33 mg/L (Table 3). The COD concentrations obtained after the oxidation process with addition of H$_2$O$_2$ and H$_2$O$_2$ + UV light exposure were 733.33 mg/L and 433.33 mg/L, respectively. The COD removal were 57.69% and 75%, respectively (Table 3).

| Oxidation Method                     | Initial [COD] (mg/L) | After Treatment [COD] (mg/L) | COD Removal (%) |
|--------------------------------------|----------------------|-----------------------------|-----------------|
| Addition of H$_2$O$_2$               | 1733.33              | 733.33                      | 57.69           |
| Addition of H$_2$O$_2$ + 254 nm UV light exposure | 1733.33              | 433.33                      | 75              |

After going through the oxidation process, the solution changed color from initially brown to clear yellow as shown in Figure 6.

![Filtrate before oxidation](image1.png) ![Oxidized filtrate with addition of H$_2$O$_2$](image2.png) ![Oxidized filtrate with addition of H$_2$O$_2$ + UV light exposure](image3.png)

**Figure 6.** Color differences before and after oxidation process

The pH of the acidified alum sludge filtrate increased after oxidation from 3 to 3.5. This was caused by oxidation with the addition of H$_2$O$_2$ could produce hydroxyl radicals (• OH) (Wulandari and
Soedjono, 2017). The hydroxyl radicals are a type of oxygen radicals which is an active agent to stop microbial activity in acid electrolyte (Mokudai et al., 2012). The highest COD removal was 75%, which occurred in the filtrate with addition of H$_2$O$_2$ + 254 nm UV light exposure for oxidation. According to Collivignarelli et al. (2017), the combined oxidation process of H$_2$O$_2$ and UV light exposure could activate H$_2$O$_2$, which could accelerate the formation of hydroxyl radicals ($\cdot$OH) due to an indirect photolysis reaction. Therefore, this method can be applied as pretreatment in aluminium removal using electrolysis in electrolyte with the high organic concentrations.

4. Conclusions
The conclusions achieved from this study were that the low removal efficiency of aluminium from alum sludge by electrolysis method was caused by an incompatible type of cathode for low pH and the high organic concentrations in the electrolyte. In addition, the electrolysis using carbon-silver electrodes resulted in a low removal efficiency of organic contaminants in the electrolyte. Therefore, H$_2$O$_2$ oxidation and UV light exposure could be applied as pretreatment before electrolysis for optimizing aluminium removal.

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