Electrokinetic of red mud

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Abstract. Red mud - a bauxite residue, is a by-product of the Bayer Process for refining bauxite to alumina. Red mud is highly alkaline, due to the sodium hydroxide utilization to purify bauxite from silicate and other impurities. In order to produce one ton of aluminium, it will be yielded 0.8 to 1.5 tons of red mud is produced as by-product. Red mud has unique characteristics such as acidity (pH) of 10.88, Electrical Conductivity (EC) of 22.3 dS m⁻¹ and Na⁺ level of 49.91 cmol(+) kg⁻¹. Safe storage of the red mud requires a specified impoundments with leachate collection and treatment to prevent contamination of soil and groundwater. This study investigated the feasibility of electrokinetic treatment for reclamation of red mud. A set of laboratory electrokinetic tests was carried out in order to identify the main parameters and processes affecting the removal of ions from red mud. Experiments were conducted using 30 and 45 volts direct current and was compared to washing method by using aquadest 1:25. After 30 days of electrokinetic, a zone of pH (8.6) was detected close to the anode, lower than the washing results (pH 9.17). Among the various cations, the highest removal efficiency was achieved for Na⁺ 98.01% close to the anode with 45 volts current, higher than washing result 67.2%. The result of this study provided evidence that the application of electrokinetics endorsing its validity as a viable red mud remediation technology.

1. Introduction

Red mud – a bauxite residue, is a by-product of the Bayer Process for refining bauxite to alumina. Bayer process uses sodium hydroxide (NaOH) to refining alumina from other impurity like silica (Si). The Government Regulation No. 4 year 2009 concerning Mineral and Coal Mining and Regulation of Minister of Energy and Mineral Resources No. 7 year 2012 concerning the mineral value increasing through mineral processing and refining, confirm that the exporting mineral bauxite in ore form must be stopped and the ore should be processed in the domestic industrial raw materials industry. Exporting as finished or semi-finished products benefit Indonesian economy. Under the regulation, bauxite ores processing or refining smelter has been established.

PT Indonesia Chemical Alumina since 2014 produces chemical grade alumina, and has production capacity of 300.000 ton every year. Red mud amount ranges from 40-50% of the weight of bauxite ores processed through the Bayer Process, or from 1 ton of bauxite ores produce 0.8 to 1.5 ton of red mud.

Various attempts to reuse red mud have been carried out in various countries having alumina industry. Red mud in Australia has been disposed to the dessert and used as planting media. Whereas in China, red mud dispose it into the sea [1]. This waste management method cannot be applied in Indonesia because Indonesia does not have a desert and to disposing waste into the sea is prohibited,
based on the regulation of the Minister of Environment No. 1 of year 2010 concerning waste management installation.

In Indonesia, several studies of red mud utilization have also been carried out, for example [2], washed the red mud with water with ratio 1:25. The result showed that red mud washing reduce pH from 11.91 to 10.55, EC from 2.68 to 1.93 dS m$^{-1}$ and Na$^+$ from 149.38 to 66.74 cmol(+)/kg$^{-1}$. Washing the red mud with water with ratio 1:70 [3] neutralized acid mine drainage and the remaining red mud can be used to improve the peat land. The data of these studies are not satisfy yet, because the pH was still alkaline to very alkaline and the Na content was still very high. Therefore, it is necessary to find other way to reuse red mud safely. One method that is expected to improve the quality of red mud is the electrokinetic method.

Electrokinetic is a method often used in soil remediation. This process uses the concept of direct current (DC) in the resistor through electrodes (anode and cathode) with low voltage. This concept is used to move the cations or anions towards the opposite poles, accordingly that cations buildup will be found in the anode and anions buildup in cathode. This method has been widely used in various fields such as agriculture and environment. The electrokinetic method eliminate some metals (Fe, Cu, Pb and Mn) up to 6-90% from the original content in the mine overburden [4]. Electrokinetic treatment might be used to reclaim the saline soil, which indicated by a decrease in EC values from 4.5 to 1.5 dS m$^{-1}$. In the salt industry, pure sodium from salt grosok using an electrolysis method with potential difference of 12 V and commercial polyvinyl acetal blocke. The result shows that this method obtained 44-48% more sodium compared to electrolysis using mercury cells. Based on the result of these studies, the electrokinetic method needs to be investigate in order to improve the chemical characteristics of red mud as well as to study its efficiency compared to washing method.

2. Materials and Methods

The experiment was carried out from January until June 2019 at teaching laboratories of the Department of Soil Science and Land Resources, Institute Pertanian Bogor University in Bogor, West Java, Indonesia.

2.1. Materials

The materials used in the experiment were aquadest, ammonium acetate pH 7, HCl 0.1 N, red mud which managed by PT. Indonesia Chemical Alumina, Sanggau Regency, West Kalimantan, direct current adapter with voltage 30 and 45 volts and copper electrodes.

2.2. Methods

Before the experiment carried out, red mud was chemically characterized to determine pH, EC, and cations (exchangeable-Na, -Ca, -Mg, -K, -Fe). There were two treatments each with two replications. First treatment was using water to washed red mud. 1 kg of red mud was placed inside the bucket and 5 liters water was poured into it. Red mud was then stirred manually and left until that the sediment settles. This washing processes were repeated 5 times and red mud was then chemically characterized. The second treatment was electrokinetic method with electrodes placed vertically. This experiment used a container with a height of 15 cm and diameter of 5 cm and red mud was placed inside. The anode was copper rods placed at the top of container while the cathode used copper-plate placed at the bottom.

3. Result & Discussion

The result of red mud chemical characterization can be seen in Table 1. It shows that the main problem of red mud is the very high of pH, EC and exchangeable-Na. These properties cause red mud classified as hazardous and toxic materials which cannot be utilized directly. Red mud washing using water with a ratio of 1:25 can reduce the pH from 10.88 to 9.17, EC from 22.3 to 1.93 dS m$^{-1}$, Na$^+$ from 93.16 to 30.5 cmol(+)/kg$^{-1}$. These can be caused by OH$^-$ ions and cations such as Na dissolved in water.
Table 1. Red mud chemical characteristics before and after washing

| Parameter     | Before washing | After washing |
|---------------|----------------|--------------|
|               | Extracted by   | Exchanged by |
|               | Aquades  pH 7  | HCl          |
| pH            | 10.88          | 9.17         | -            |
| EC (dS m⁻¹)   | 22.30          | -            | 1.95         |
| Na⁺ (cmol(+kg⁻¹)) | 49.91        | 19.41        | 30.50        |
| Mg²⁺ (cmol(+kg⁻¹)) | nd            | nd           | nd           |
| Ca²⁺ (cmol(+kg⁻¹)) | nd            | nd           | nd           |
| K⁺ (cmol(+kg⁻¹))  | nd            | nd           | nd           |
| Fe³⁺ (cmol(+kg⁻¹)) | -             | -            | nd           |

Note: nd= not detectable - = not conducted

Electrokinetic process is expected to improve the chemical properties of red mud. The result of this experiment showed that the pH, EC, and exchangeable-Na were decreased (Figure 1, 2, 3, 4, 5). The current strength in this study showed whether this electrokinetic process was running well or not. The current flows were steady at 5 mA until the 24th days (Fig 1.), which was about 5 mA which showed that electrokinetic process was not performed perfectly. When the current stabilized to near zero, experiment was stopped. During the experiment, 450 ml of water was needed to achieve a voltage of 45 V and 250 ml of water for a voltage 30 V.

![Figure 1. Graph of changes in electric current during electrokinetic experiment](image)

Changes in the value of electric conductivity (EC) during the experiment can be seen in Figure 2. The initial red mud EC was 22.3 dS m⁻¹ and decreased in the anode area at 30 V and 45 V to 5.4 to 4.23 dS m⁻¹, respectively or lowered about 76.45 to 78.8%. The decrease was related to the decrease in Na⁺ concentration in the red mud anode area.
The initial red mud pH was 10.88 and decrease in the anode area at 30 V and 45 V to 8.6 (Fig. 3). This showed the breakdown of water molecules produce H⁺, but the resulting H⁺ will be blocked because of the buffer capacity of red mud. The H⁺ will react with OH⁻ to produce H₂O.

The level of Na⁺ was decreased as much as 97.71-98.03% or from 93.16 to 1.83 to 2.13 cmol(+) kg⁻¹ (Fig. 4). The decreased in Na⁺ that occurs in this process was caused by Na⁺ undergoes electro-osmosis and electro-migration processes towards the cathode. The Na at the red mud will move ahead compare to the other cations. The decrease in Na also result in decreasing in the EC value because Na cations were getting less towards the anode.
The tendency of increasing Ca\(^{2+}\) buildup around the anode (Figure 5) was associated with a decrease in pH and increase in Eh. The electrokinetic process resulting the decrease in pH and increase in Eh to 22-70 mV in the area near anode. Acidification that occurs around the anode trigger the dissolution of Ca into an ionic form that’s migrates to the opposite electrode under the electric field. Changes in K\(^+\) and Mg\(^{2+}\) in this study were not significant hence they can be ignored.

**Figure 4.** Na red mud graph after electrokinetic experiment

**Figure 5.** Ca red mud graph after electrokinetic experiment

4. **Conclusion**

Washing of red mud using water with a ratio of 1:25 can reduce the pH from 10.88 to 9.17, EC from 22.3 to 1.93 dS m\(^{-1}\) and Na\(^+\) from 93.16 to 30.5 cmol(+)/kg\(^{-1}\). The electrokinetic method was better than washing method to improve the chemical characteristics of red mud, by reducing the pH from 10.88 to 8.6, lowering the EC up to 76.45 - 78.80% or from 22.93 to 4.23 to 5.4 dS m\(^{-1}\), and Na\(^+\) level up to 97.71 - 98.03% or from 93.16 to 1.83 to 2.13 cmol(+)/kg\(^{-1}\).
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