The utilization of hydroxylsodalite synthesized from coal fly ash for zinc removal in acid mine drainage

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Abstract. One of the alternative solution to reduce ash waste in landfills is by utilizing coal fly ash for the removal of metal ion in wastewater, especially acid mine drainage (AMD). In this study, zeolite was synthesized from coal fly ash using a two-step method, hydrothermal and fusion method. The coal fly ash and the zeolite product were characterized physically and were used for the removal of Zn$^{2+}$ in AMD. The adsorption experiment was carried out using batch method in synthetic AMD solution to study the influential parameters such as adsorbent dosage, contact time, adsorbent isotherms and kinetics. The zeolite synthesized in this study resulting hydroxylsodalite zeolite type, which increases the surface area. It was revealed from the adsorption experiment that the removal efficiency of Zn$^{2+}$ was 93.47% under the conditions of pH ± 3, initial concentration Zn$^{2+}$ 100 ppm, optimum contact time 120 minutes, and adsorbent dose 6 g/L. Furthermore, the Langmuir isotherm model and the kinetics model of pseudo-second-order fitted the adsorption data better, with the maximum sorption capacity of 27.32 mg/g. The result of this study indicate hydroxylsodalite synthesized from coal fly ash has great potential as an economical and sustainable material for the removal of metal ion Zn$^{2+}$ in wastewater.

1. Introduction

Indonesia is one of the largest coal producing countries in the world. Coal mining is considered an industrial sector that has a dominant position in socio-economic development. The Ministry of Energy and Mineral Resources of Indonesia stated that coal demand in Indonesia in 2018 is 92 million tons and predicted coal demand in 2027 will reach 162 million tons. The massive coal consumption in coal-fired power plants will result a large number of fly ash production and its solid waste disposal problem. Therefore, it is necessary to develop the handling and utilizing the fly ash waste. One of the utilizing of fly ash waste is as a raw material for synthetic zeolite [1-2].

On the other hand, acid mine drainage (AMD) resulting from the oxidation of pyrite in coal mining location can cause serious threats for the environment due to its low pH and high concentration of heavy metal. Metal elements, such as Zn, Cu, Cr, Ni, Cd on a certain concentration is considered toxic to humans and animals [3-4]. One of the polluting heavy metal ion with high concentration in AMD is Zn$^{2+}$ [5]. Thus, heavy metal removal from AMD is priorities in its management. Adsorption method is quite popular for the removal of heavy metals in wastewater and is more preferred due its simplicity.
and efficient mechanism. The adsorption process become more viable when the adsorbents are easily available and economically feasible, materials, certain industrial waste products, or by-products of agricultural activities [6-7]. One of the adsorbent that is gaining a lot of attention these days is coal fly ash, because it is the most abundant waste material produced from the coal-fired thermal power plants [8]. This aims to provide the value and price of the waste, and to extend its life cycle. However, raw fly ash shows low adsorption capacity than synthetic product. One solution in enhancing the effectiveness of fly ash is through modification or used as a raw material for zeolite synthesis [9-10]. The high content of metal oxides (SiO$_2$ and Al$_2$O$_3$) in fly ash, makes it potentially developed as a zeolite so that it can be used as an alternative adsorbent at a more economical price [11].

Using coal fly ash as raw material to produce synthetic product such as zeolite, has been widely study, especially for its various synthesis method and its application for heavy metal removal [12-14]. Among others, researchers had studied about the use of fly ash as raw material for the synthesized of modified fly ash, NaP, hydroxyl sodalite zeolite, zeolite X, and zeolite A [12-16]. From these previous studies, the most common process used to synthesize zeolite from fly ash is the two-step process proposed by Shigemoto et al. [17], in which combines alkali and hydrothermal fusion processes resulting the increased of silicate and alumina extraction from fly ash to increase the purity of the zeolite. Thus, a two-step method was used for the zeolite synthesis in this study.

The aim of this study is to investigate the possibility of applying synthesized zeolite from coal fly ash as an economical adsorbent for the removal of Zn$^{2+}$ in acid mine drainage. The synthesis was conducted using a two-step method, hydrothermal and fusion method. The product zeolite and the coal fly ash were characterized physically and were used for the removal of Zn$^{2+}$ in acid mine drainage. The adsorption experiment was carried out using batch method in synthetic acid mine drainage solution to study the influential parameters such as adsorbent dosage, contact time, adsorbent isotherms and kinetics.

2. Materials and method

2.1. Materials and chemicals

The fly ash used in this study was collected from an electricity power plant located in Pelabuhan Ratu, West Java, Indonesia. The fly ash used in this study is classified as Class F. The chemicals used in this study are NaOH pellet (Merck), Zn(II)SO$_4$.7H$_2$O (Merck), and deionized water.

2.2. Preparation of adsorbent

Synthesis of fly ash zeolite was carried out using a combination of two-stages synthesis method, namely fusion and hydrothermal process. Firstly, fly ash and NaOH pellet with a ratio of 1:1.2 (w/w) were mixed together. After that, the mixture is heated in a muffle furnace with a temperature of 550 °C for 60 minutes. The mixture is then cooled to room temperature, grinded, then added with distilled water with a ratio (water: ash 8.5: 1) and stirred in a magnetic stirrer for 24 hours. The resulting slurry is then given a hydrothermal treatment, which is heated at 105 °C for 24 hours in the oven. After that, the product obtained is cooled at room temperature then filtered and washed with distilled water until the pH of the filtrate reaches pH 9-10, then dried in an oven at 105 °C overnight.

2.3. Characterization method

Fly ash samples and the synthesized zeolite results were characterized for its mineralogical characteristics by X-ray Diffraction (XRD) Panalytical Epsilon 1. The surface morphology of the sample was carried out by Hitachi SU-3500 Scanning Electron Microscopy (SEM), and Quantachrome Nova 4200e Brunauer Emmet Teller surface area (BET) was used to determine the specific surface area of the two sample sizes.
2.4. Adsorption experiment

This study was conducted in batch mode and the adsorption process was performed in 250 ml Erlenmeyer flasks. The experiment was carried out with 100 ml of 100 ppm Zn\textsuperscript{2+} solution shaken in a shaking incubator at 150 rpm in room temperature. The pH of the solution was adjusted to correspond acid mine drainage which is pH ± 3. The effect of adsorbent dosage was examined in the range of 1-6 g/L, while the effect of contact time was examined in the range of 15-150 minutes. The pH of the solution was also investigated in this experiment. The concentration of were determined by Perkin Elmer – USA Analyst 800 Atomic Absorption Spectrophotometer (AAS).

The kinetics of Zn\textsuperscript{2+} adsorption was analyzed by fitting the data result from the experiment with pseudo-first-order and pseudo-second-order models [18-19] shown in Equation (1) and (2), respectively.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]
\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

From both equation, \( q_e \) is adsorption capacity at equilibrium state, \( q_t \) is adsorption capacity at time \( t \), and \( k_1 \) and \( k_2 \) are constants of adsorption rate. Furthermore, the isotherm analysis was carried out by fitting the data with Langmuir and Freundlich isotherm models [20-21] shown in Equation (3) and (4), respectively.

\[
\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b}
\]
\[
\log q_e = \log k_f + \frac{1}{n} \log c_e
\]

The parameter from both equation meaning, \( q_m \) is the maximum adsorption capacity (mg/g), \( b \) is a constant related to the energy of adsorption (L/mg), \( k_f \) is the distribution coefficient which is a constant related to the adsorption capacity (mg/g), where the adsorption capacity of the adsorbent increases with the rising of \( k_f \) value.

3. Result and discussion

3.1. Characterization analysis

The fly ash used in this study was classified as Class F fly ash based on ASTM C618 due to its metal oxide composition which is more than 70%. While the mineralogy and morphology of the fly ash and the zeolite product were characterized by XRD and SEM. Characterization using XRD was conducted to investigate the change of crystal structure or crystalline compound from the synthesis process. The diffraction pattern of XRD analysis on fly ash and zeolite can be seen in Figure 1. The diffraction pattern of fly ash identified by its mineralogy as quartz and iron oxide, whereas after the diffraction pattern showed that the zeolite synthesized was hydroxylsodalite (SOD). The phase was identified by comparing the peaks’ position and intensity, in which appear at 14, 24, 35, 42.5°, with those in the database of The International Zeolite Association. The similar pattern was also confirmed in accordance with previous studies conducted [12,16].
Figure 1. Diffraction pattern of fly ash (up) and hydroxylsodalite (down) synthesized from coal fly ash

The surface morphology of both the fly ash and the zeolite product, in this case, hydroxylsodalite, were analyzed through SEM. Figure 2 presents the morphological of both samples, which can be seen that the fly ash particles shaped like a sphere with a relatively smooth surface. Whereas after the synthesis process, the shaped of the zeolite product, hydroxylsodalite, changed to having a crystallized surface with a slightly smaller particle size. Other than that, Brunauer Emmet Teller (BET) method was used to determine the change of specific surface areas of both fly ash and zeolite product. The specific surface area of the fly ash increased from 0.873 to 4.114 m$^2$/g after being synthesized to hydroxylsodalite. This is considered quite sufficient, although not as significant compared to previous studies [12-16]. It is possible that this result might be caused by the differences in specific characteristic of the raw material used or other specific condition in the process [15]. From these characterization, it can be concluded that synthesizing coal fly ash using two-step method, namely, fusion and hydrothermal method, produced hydroxylsodalite type of zeolite while increasing its specific surface area. This results can indicate the potential of enhancing the adsorption capacity for removing metal ion from aqueous solution.

Figure 2. SEM micrograph of (a) coal fly ash (raw) and (b) hydroxylsodalite synthesized from coal fly ash
3.2. Adsorption studies

3.2.1. Effect of contact time
To determine the equilibrium time of adsorption and study the kinetics of the adsorption process, the operating parameter of pH, adsorbent dose of hydroxysodalite, and initial concentration of adsorbate were set to pH ± 3, 6 g/L, and 100 ppm, respectively. The contact time of the adsorption varies from 15 to 150 minutes. As seen in Figure 3, the removal efficiency escalated with the increase of reaction time. It is shown that in reaction time of 15 minutes, the removal efficiency reached 79.47%, and increased to 94.37% in 120 minutes and remain constant after that. Thus, the optimum contact time taken was 120 minutes. Within 60 minutes, more than 85% Zn\(^{2+}\) was adsorbed. This indicates that the rapid adsorption rates were caused by the number of available reaction site for adsorption on the adsorbent surface. But after 60 minutes, the slow adsorption rate was due to the decrease of free reaction sites that were occupied by the metal ion [22].

![Figure 3. Effect of contact time on the removal of Zn\(^{2+}\) from adsorbate solution](image)

3.2.2. Effect of adsorbent dosage
To determine the effect of adsorbent dose on Zn\(^{2+}\) removal, doses of 1-6 g/L of adsorbent, both hydroxysodalite and fly ash were used. The initial concentration of Zn\(^{2+}\) was 100 ppm, and the initial pH was adjusted to resemble acid mine drainage which is pH ± 3. The adsorption contact time of this experiment was 120 minutes. The result shows that the hydroxysodalite presents significantly higher performance than did the fly ash. The removal efficiencies of Zn\(^{2+}\) and the adsorbent dosage shows a linear relationship. For instance, with the increase of adsorbent dose of hydroxysodalite from 1 to 6 g/L, the removal efficiency was also increased from 7.41 to 93.47%. In contrast, fly ash shows a much lower adsorption capacity than the hydroxysodalite did. As shown in Figure 4, the removal efficiency did not increase much, whereas, the increase of adsorbent dose of fly ash from 1 to 6 g/L, the removal efficiency only rose from 3.89 to 8.12%. Therefore, the dosage of 6 g/L hydroxysodalite was chosen as the optimum dose for further experiment. The significant enhancement of the removal efficiency by hydroxysodalite could be due to the larger surface area, the smaller particle size, and the availability of adsorbent sites [12-14,23]. For doses higher than 6 g/L, it can be predicted that under the same condition but with higher adsorbent concentration, the availability of reaction sites will increase, resulting the reduction of the adsorptive capacity of the hydroxysodalite [12]. Furthermore, Figure 4(b) shows that the pH of the solution increased with the adsorbent dose up, approaching a more neutral state. This may due to the basic nature of the adsorbent [14].
3.2.3. Adsorption isotherm models

The surface properties of an adsorbent can be determined from adsorption isotherms studies. The two classics isotherm models, Langmuir and Freundlich models, were used in this study. The Langmuir model is applicable for homogeneous and monolayer adsorption, while the Freundlich model more suitable for heterogeneous and multilayer adsorption. The isotherm models for the adsorption of Zn\textsuperscript{2+} by hydroxylsodalite was investigated in this study.

Figure 5 (a) and (b) presents the plot of both isotherm models, while the parameters are contained in Table 1. The suitable isotherm model was determined from the higher linear correlation coefficient R\textsuperscript{2}. It is shown that the Langmuir model fitted the experimental data better than the Freundlich model. This indicates that monolayer adsorption of Zn\textsuperscript{2+} occurs at specific homogeneous sites on the surface of the adsorbent, which confirms physisorption followed by chemisorption [20]. Therefore, the adsorption capacity of the adsorbent was found to be 27.32 mg/g.

\[ y = 0.0356x + 0.1784 \quad R^2 = 0.9842 \]

\[ y = 0.2112x + 1.0382 \quad R^2 = 0.8371 \]

**Figure 4.** (a) Effect of adsorbent dosage on Zn\textsuperscript{2+} removal from adsorbate solution; (b) Effect of adsorbent dosage on the pH of the adsorbate solution

**Figure 5.** (a) Adsorption isotherm Langmuir model of Zn\textsuperscript{2+} on hydroxylsodalite; (b) Adsorption isotherm Freundlich model of Zn\textsuperscript{2+} on hydroxylsodalite
Table 1. Isotherm parameters for Zn\textsuperscript{2+} adsorption using hydroxylsodalite synthesized from coal fly ash

| Isotherm model | Parameter          | Parameter values |
|---------------|-------------------|------------------|
| Langmuir      | $q_m$ (mg/g)      | 27.322           |
|               | $K_L$ (L/mg)      | 0.205            |
|               | $R^2$             | 0.9842           |
| Freundlich    | $K_f$             | 10.919           |
|               | $n$               | 4.735            |
|               | $R^2$             | 0.8371           |

3.2.4. Adsorption kinetics models

In order to investigate the solution uptake rate of Zn\textsuperscript{2+} adsorption by hydroxylsodalite, adsorption kinetics models, such as pseudo-first-order and pseudo-second-order was conducted.

![Figure 6](image-url) (a) Pseudo-first-order kinetic model for Zn\textsuperscript{2+} adsorption onto hydroxylsodalite synthesized from coal fly ash; (b) Pseudo-second-order kinetic model for Zn\textsuperscript{2+} adsorption onto hydroxylsodalite synthesized from coal fly ash

Table 2. Kinetic adsorption parameters for Zn\textsuperscript{2+} adsorption using hydroxylsodalite synthesized from coal fly ash

| Kinetic model       | Parameter          | Parameter values |
|---------------------|-------------------|------------------|
| Pseudo-first-order  | $q_e$ (mg/g)      | 8.44             |
|                     | $K_1$ (min\textsuperscript{-1}) | 0.046           |
|                     | $R^2$             | 0.9393           |
| Pseudo-second-order | $K_2$ (g/mg.min)  | 0.015            |
|                     | $q_e$ (mg/g)      | 14.006           |
|                     | $R^2$             | 0.9994           |
Figure 6 and Table 2 present the plot and the equilibrium parameters from the experiment data. The plot shows that the linear correlation coefficient $R^2$ of pseudo-second-order model is higher than the pseudo-first-order model. Which means that the pseudo-second-order kinetics model fitted the adsorption data better. This indicates the reaction occurred in the adsorption process is chemisorption and the adsorption capacity is proportional to the active sites on the surface of the adsorbent [19].

4. Conclusion
Based on the results of this study, hydroxylsodalite type zeolite was produced from coal fly ash using a two-step method synthesis. The physical characteristics of the hydroxylsodalite produced proven that the synthesis process had change and enhance the mineralogy, morphology, and specific surface area of the fly ash. This indicate the potential of hydroxylsodalite as an adsorbent for the removal of metal ion $\text{Zn}^{2+}$ from AMD. The highest removal efficiency was observed at initial $\text{Zn}^{2+}$ concentration of 100 mg/L, contact time of 120 minutes, adsorbent dosage of 8 g/L, pH ± 3, and room temperature. The result stated that the removal efficiency has a direct relationship with adsorbent dosage and contact time. The study of isotherm adsorption showed that $\text{Zn}^{2+}$ adsorption onto hydroxylsodalite fitted the Langmuir isotherm model better. Based on this result, the monolayer sorption capacity for $\text{Zn}^{2+}$ by hydroxylsodalite was found 27.32 mg/g. While the kinetics of the adsorption process fitted the kinetics model of pseudo-second-order. The result of this study indicate hydroxylsodalite synthesized from coal fly ash has great potential as an economical and sustainable material for the removal of metal ion such as $\text{Zn}^{2+}$ in wastewater and could be consider as a promising material for further development and application in wastewater treatment.

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