Comparison of copper adsorption effectivity in acid mine drainage using natural zeolite and synthesized zeolite

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Abstract. Acid mine drainage (AMD) contains a high concentration of various heavy metals and have low pH levels. In this study, the comparison between the use of natural zeolite and synthesized zeolite for Cu²⁺ removal in AMD was conducted. The adsorbent of natural zeolite was prepared through a chemical activating method by adding NaOH. While, synthesized zeolite was made from coal fly ash using a two-step method, fusion, and hydrothermal process. The AMD used in this study was artificially designed with the concentration of Cu²⁺ 100 ppm and pH ± 3. The adsorption experiment was carried out using a batch method to observe the influential parameters such as adsorbent dosage, contact time, adsorbent isotherms, and kinetics. The result show that the removal efficiency of Cu²⁺ for natural zeolite and synthesized zeolite was 98.16% and 93.98% with optimum adsorbent dose 1.5 g/l and 21 g/l, respectively. The optimum contact time for both adsorbents was 120 minutes. The Langmuir isotherm model fitted the adsorption for synthesized zeolite and natural zeolite, with the maximum sorption capacity of 23.8 mg/g and 30.03 mg/g, and the kinetics model of pseudo-second-order and pseudo-first-order. The result of this study that the good adsorption effectivity synthesized zeolite. Furthermore, both natural zeolite and synthesized zeolite have great potential as a sustainable and economical material for heavy metal removal ion Cu²⁺ in wastewater.

1. Introduction

Acid mine drainage (AMD) is a severe problem in the mining sector. AMD resulting from the oxidation of pyrite in mining locations can cause threats for the human health and environment due to its low pH heavy metal [1,2]. One of pollutant heavy metal ions with a high concentration in AMD is Cu²⁺ [1–3]. The heavy metal removal becomes one of the concerns of the wastewater treatment management sector. Generally, there are two methods for treating acid mine drainage which is the passive method and the active method. The passive way uses technology that utilizes chemical and biological reactions which occur naturally in a controlled environment for acid mine drainage treatment with minimal operational and maintenance costs [4]. Passive processing that is commonly used is aerobic and anaerobic wetlands, anoxic limestone drains (ALD), and open limestone channels (OLC).

This treatment needs regular maintenance which can reduce long-term costs. One of the existing methods which are often used for heavy metal removal in wastewater is the adsorption method. Natural material and residual waste used as adsorbents. It can set aside high heavy metals from the economic aspect, the materials that are cheap and easily found in the natural ecology. Example include dead biomass, furnace slag, fly ash, clay, and natural zeolite. The material can be adsorbent is natural
zeolite and fly ash. In this research, fly ash and natural zeolite was used as adsorbent for copper removal in AMD. Natural zeolite exhibit high performance in adsorption of cations in an aqueous solution such as ammonium and heavy metals [5,6]. In research Panaya conducted a series of experiments using a Bulgarian natural zeolite and modifies form for removal of several metal ions included Cu$^{2+}$ [7]. The zeolite used in research without activated, the uptake process obeys the first-order irreversible kinetics [7]. The uptake equilibrium is the best described by the Langmuir adsorption isotherm. The natural with activated can increase adsorption for heavy metals [8]. Fly ash can be modified to zeolite because of the high content metal oxides (SiO$_2$ and Al$_2$O$_3$) [9]. The content of (SiO$_2$ and Al$_2$O$_3$) can heavy removal metal like a copper. After modified fly ash become synthesized zeolite, it can use in adsorption method.

The natural zeolite can used as adsorbents in the adsorption process. Before applying to the adsorption process, natural zeolite had to activate in order can increase removal capacity heavy metal. In this research using a chemical is NaOH. Activated using NaOH causes the value of the adsorption capacity to be caused by Na$^+$ base ions to be significant in dissolving Si to make sodium silicate so that the zeolite structure becomes more negative [8]. Modified the fly ash can be synthesized zeolite has been widely studied. One step to modified is a synthesis method. There are researchers had considered about synthesis method, the most common process used to synthesis method is two-step process. The process in which combines alkali and hydrothermal fusion processes resulting in the increased of silica and alumina extraction from fly ash to increase the purity of the zeolite [10,11].

The aim of this study is to the comparison of copper adsorption effectiveness in acid mine drainage using natural zeolite and synthesized zeolite. Besides, to investigate the possibilities of applying synthesized zeolite from coal fly ash and natural zeolite as an economical adsorbent for the removal Cu$^{2+}$. The adsorption experiment was carried out using a batch method in synthetic acid mine drainage with concentrations Cu$^{2+}$ solution to study the influential parameters such as contact time, adsorbents dosage, isotherms model, and kinetics.

2. Methods

2.1. Materials and chemicals

The natural zeolite used in this study was from Padalarang, West Java. The fly ash used in this study collected from an electric power plant located in Pelabuhan Ratu, West Java, Indonesia. The chemicals used in this study are NaOH (Merck), Cu(II)SO$_4$.7H$_2$O (Merck), HNO$_3$ (Merck) and deionized water.

2.2. Preparation of adsorbent

Natural zeolite before being used for adsorption was activated. The activated method was added chemically using NaOH 1 M. First, natural zeolite 100 mesh put into a beaker glass. Next added NaOH with a ratio of 1:5 (w/v) then stirred. After stirring, the mixture filtered with filter paper. Later, filtered substantial put into the oven with heated at 105$^\circ$Celsius until dry. 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 7, then dried in an oven at 105$^\circ$Celsius overnight.

Synthesis of fly ash zeolite was carried out using a combination of two-stages synthesis method, and it’s fusion and hydrothermal process. First, fly ash and NaOH pellet with a ratio of 1:1.2 (w/w) were mixed.

After that, the mixture heated in a muffle furnace with a temperature of 550$^\circ$ Celsius for 60 minutes. The mixture cooled to room temperature, ground, 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 gave a hydrothermal treatment, which is heated at 105$^\circ$ Celsius 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$^\circ$ Celsius overnight.
2.3. Characterization method
Natural zeolite and the synthesized zeolite results were characterized for its mineralogical characteristics by X-ray Diffraction (XRD) Panalytical Epsilon 1.

2.4. Adsorption experiment
This research was conducted in batch mode and the adsorption process was performed in 250 ml Erlenmeyer flasks. The analysis was carried out with 100 ml of 100 ppm Cu\(^{2+}\) solution shaken in a shaking incubator at 150 rpm in room temperature. The pH of the solution was adjusted to correspond to AMD, which is pH ± 3. The effect of adsorbent dosage was examined in the range of 9 - 21 g/l for natural zeolite and 0.3 – 1.5 g/l for synthesized zeolite. The result of contact time observed in the field of 15-150 minutes of both zeolites. The pH of the solution also investigated in this experiment. The concentration was determined by Perkin Elmer – USA Analyst 800 Atomic Absorption Spectrophotometer (AAS).

First, determine the optimum time for effective copper metal removal. The calculation used for the kinetics of Cu\(^{2+}\) adsorption was analyzed the data result from the experiment with pseudo-first-order and pseudo-second-order models [8-9] shown in Equation (1) and (2).

\[
\frac{t}{q_t} = \frac{1}{k_1 q_e} + \frac{t}{q_e}
\]

From both equations above, \(q_e\) 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. To find the analysis of the isotherm model that fitted the data obtained from the experiment result using Langmuir and Freundlich isotherm models [14-15] shown in Equation (3) and (4).

\[
\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_mb}
\]

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

From both equations, \(q_m\) 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. Before using Langmuir and Freundlich isotherm, The adsorption percentage determined as 21

\[
\%A_e = \frac{A_e}{A_o} \times 100
\]

From the equations that, \(\%A_e\) is the final percentage adsorption, \(A_o\) is the initial concentration (mg/l), \(A_e\) is the final concentration after the adsorption process (mg/l). Besides, the amount \(q_e\) of Cu2+ adsorbed at equilibrium was calculated using the following equation

\[
q_e = \frac{(X_0 - X_e)V}{M}
\]

Where \(q_e\) is the mass capacity from adsorption (g), \(V\) is the volume of the solution (L), \(X_0\) and \(X_e\) are the initial and the final concentration solution (mg/l) respectively.
3. Result and discussion

3.1. Characterization analysis

The mineralogy of the activated natural zeolite and synthesized zeolite product was characterized by XRD. The diffraction pattern of XRD analysis on synthesized zeolite and natural zeolite showed in Figure 1. The diffraction pattern of natural zeolite and synthesized zeolite showed in Figure 1. The diffraction pattern of natural zeolite was identified by mineralogy (40.9%) and moganite (55.5%). From the results of tests that have been carried out for the synthesized zeolite position and peak intensity, which appears 10, 22, 26, 30.5°. This characterization was compared with the synthesized zeolite characterized in previous study mineral content in synthetic zeolites and natural zeolites contain silica. The results of the surface characterization of silica cause the presence of silanol (-SiOH) and siloxane (Si-O-Si) groups, which enables them to bind metal ions more selectively with specific mechanisms [7] Besides, the results of the characterization of the percentage of quartz are higher than cristobalite which causes the optimal adsorption metals in the synthesized zeolite.

![Figure 1. Diffraction pattern of synthesized zeolite (up) and natural zeolite (down)](image)

3.2. Adsorption studies

3.2.1. Effect of adsorbent dosage. The adsorption use natural zeolite and synthesized zeolite was studied by varying on Cu²⁺ removal, doses of 9 -21 g/L of the adsorbent for natural zeolite, while synthesized zeolite 0.3-1.5 g/L. The initial concentration of Cu²⁺ 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 percentage of adsorption increased rapidly with increases for natural zeolite dose (1.5-3g/100 ml). While the synthesized zeolite in doses (0.3-0.6g/100 ml). The result shows that the synthesized zeolite presents significantly higher performance than did the natural zeolite. The removal efficiencies of Cu²⁺ and the adsorbent dosage shows a linear relationship. The natural zeolite experiment, the removal efficiency was increased from 48.47% to 93.98%. In achieving a high level of metal removal effectiveness need natural zeolite adsorbent of 21 g/L. While the increase of adsorbent dose synthesized zeolite from 0.3 – 1.5 g/L. The removal efficiency also increased from 34.09% to 98.16%. Therefore, the dosage of 1.5 g/L synthesized zeolite chosen as the optimum dose for further experiment.
As shown in Figure 3, the removal efficiency for synthesized zeolite and natural zeolite, natural zeolite need more adsorbent to achieve a high removal rate than synthesized zeolite. A significant increase in removal efficiency integrated caused by smaller particle size, more upper surface, and availability of adsorbent sites [12,13].

3.2.2. Effect of contact time. The result of contact time on adsorption capacity of natural zeolite and synthesized zeolite can determine with the equilibrium time of adsorption and study the kinetics of the adsorption process. In the experiment the operating parameter of pH, adsorbent dose, and initial concentration of adsorbate set to pH ± 3 and 100. The adsorbent dosage for synthesized zeolite is 1.2 g/L and natural zeolite 15 g/L. 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. In 15 minutes reaction time, the removal efficiency reached 61.32%, and increased to 88.39% in 120 minutes for synthesized zeolite and remain constant after that. While of natural zeolite, the removal efficiency reached 55.48% and increased 88.45% in 120 minutes. Thus, the optimum contact time taken was 120 minutes for both. When at 60 minutes, more than 70% Cu$^{2+}$ adsorbed. It indicates that the rapid adsorption rates 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 [14].

3.2.3. Adsorption isotherm model. The isotherm of the adsorption was fitted, two isotherm models. The isotherm models were Langmuir model and Freundlich model. The Langmuir model is applicable for homogeneous and monolayer adsorption [15]. As seen in figure 4, the isotherm Langmuir model for synthesized zeolite and natural zeolite. While the Freundlich model was more suitable for
heterogeneous and multilayer adsorption, [16] The isotherm models for the adsorption of Cu²⁺ by synthesized zeolite and natural zeolite researched.

**Figure 4.** Adsorption isotherm Langmuir model Cu²⁺ on (a) natural zeolite and (b) synthesized zeolite.

**Figure 5.** Adsorption isotherm Freundlich model Cu²⁺ on (a) natural zeolite and (b) natural zeolite.

Figure 4 presents the plot of isotherm Langmuir models and Figure 5 Freundlich models for both zeolites. The parameters contained in Table 1 and Table 2. These models were able to give proper fit to experimental data, with correlation, $R^2$, in a range from 0.9 – 1 [5-7]. The result has shown that the isotherm Langmuir model fitted the experimental data better than the Freundlich model. It indicates that monolayer and homogeneous adsorption of Cu²⁺. Therefore, the adsorption capacity of synthesized zeolite and natural zeolite is 23.8 mg/g and 30.03 mg/g.

**Table 1.** Isotherm Langmuir models parameters for Cu²⁺ adsorption.

| Isotherm Langmuir model | Parameter | Parameter values |
|------------------------|-----------|-----------------|
| Natural Zeolite        | $q_m$ (mg/g) | 30.03           |
|                        | $K_L$ (L/mg) | 2.586           |
|                        | $R^2$     | 0.9897          |
| Synthesized Zeolite    | $q_m$ (mg/g) | 23.8            |
|                        | $K_L$ (L/mg) | 0.14            |
|                        | $R^2$     | 0.8333          |
Table 2. Isotherm Freundlich models parameters for Cu$^{2+}$ adsorption.

| Isotherm Freundlich model | Parameter | Parameter values |
|--------------------------|-----------|-----------------|
| Natural Zeolite          | $K_f$     | 0.4158          |
|                          | $1/n$     | 0.0701          |
|                          | $R^2$     | 0.7086          |
| Synthesized Zeolite      | $K_f$     | 653.96          |
|                          | $1/n$     | 0.682           |
|                          | $R^2$     | 0.5869          |

3.2.4. Adsorption kinetics models. To find out the solution uptake rate adsorption of Cu$^{2+}$ by synthesized zeolite and natural zeolite. This research uses adsorption kinetics models such as pseudo-first-order, and pseudo-second-order was conducted.

![Figure 6. Pseudo-first-order kinetic model for Cu$^{2+}$ adsorption onto by synthesized zeolite.](image)

![Figure 7. Pseudo-second-order kinetic model for Cu$^{2+}$ adsorption onto by synthesized zeolite.](image)
Figure 8. Pseudo-first-order kinetic model for Cu$^{2+}$ adsorption onto by natural zeolite.

Figure 9. Pseudo-second-order kinetic model for Cu$^{2+}$ adsorption onto by natural zeolite.

Table 3. Kinetic adsorption parameters for Cu$^{2+}$ adsorption using synthesized zeolite and natural zeolite.

| Kinetic model     | Parameter       | Synthesized Zeolite | Natural Zeolite |
|-------------------|-----------------|---------------------|----------------|
|                   | $q_e$ (mg/g)    | 7.124               | 26.33          |
| Pseudo-first-order| $K_1$ (min$^{-1}$) | 0.0436              | 0.0124         |
|                   | $R^2$           | 0.4667              | 0.9638         |
|                   | $K_2$ (g/mg.min) | 0.000878            | 0.000234       |
| Pseudo-second-order| $q_e$ (mg/g)   | 87.18               | 49.01          |
|                   | $R^2$           | 0.9967              | 0.8186         |

Figure 6, Figure 7, and Table 2 represent synthesized zeolite, the plot and the equilibrium parameters from the experiment data. The plot shows that the linear correlation coefficient $R^2$ of the 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. Figure 8, Figure 9, and Table 2 present
for natural zeolite, the plot shows that pseudo-first-order model is higher than the pseudo-second-order.

4. Conclusion
Based on the results of the research, natural zeolite before use for adsorption activated with NaOH. The synthesized zeolite from coal fly ash using a two-step synthesis method. The physical characteristics of synthesized zeolite and natural zeolite produced proof that the synthesis process had changed and enhanced the mineralogy. The synthesized zeolite more efficient in removal metal heavy cause the content of silica was found in it. Synthesized zeolite and natural zeolite as an adsorbent for the removal of metal ion Cu$^{2+}$ from AMD. The highest removal efficiency synthesized zeolite, were at initial Cu$^{2+}$ concentration 100 mg/L, contact time 120 minutes, the adsorbent dosage of 1.5 g/L, pH ± 3, and room temperature. While for natural zeolite with the same concentration and contact time, need adsorbent dosage of 21 g/L. The research of isotherm adsorption showed that Cu$^{2+}$ synthesized zeolite and natural zeolite adsorption fitted the Langmuir isotherm model better. Based on the result, the monolayer sorption capacity Cu$^{2+}$ by synthesized zeolite and natural zeolite was 28.8 mg/g and 30.03 mg/g. The kinetics of the adsorption process for synthesized zeolite fitted the kinetics model of pseudo-second-order. The natural zeolite adsorption process provided the kinetics model of pseudo-first-order. The result from comparison the of copper adsorption effectivity using natural zeolite and synthesized zeolite has excellent effectiveness with high adsorption capacity of Cu$^{2+}$. The synthesized zeolite has a great potential as an economical and sustainable material for removing Cu$^{2+}$ metal ions in wastewater and can be considered a promising material for further development and applications in wastewater treatment.

Acknowledgments
This study received financial support from the Ministry of Research, Technology and Higher Education of the Republic of Indonesia based on agreement letter between Directorate of Research and Community Service and Universitas Indonesia No. NKB-1660/UN2.R3.1/HKP.05.00/2019.

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