Removal of mercury ion from wastewater using natural zeolite: effect of humic acid to adsorption isotherm

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Abstract. As Indonesia possessed a considerable amount of gold deposit, many golds mining activities, including the small-scale one, is commonly found. A simple mining technique (amalgamation) that utilizes mercury (Hg) will generate mercury-containing wastewater. One of the prospective Hg removal methods from wastewater is adsorption. In addition, it is also possible that metal contained in the wastewater interacts with other substances, such as humic acid. This experiment was aimed to examine the adsorption process of Hg$^{2+}$ ions in the wastewater using natural zeolite. The effect of the presence of humic acid, which might be found in sewage, toward the adsorption capacity of Hg$^{2+}$ onto natural zeolite was investigated. The natural zeolite, which contained several types of minerals, was obtained from Klaten, Central Java. The experiment was conducted using ten mg/L HgCl$_2$ as the initial concentration and ten mg/L humic acids. A comprehensive study that includes isotherm and the kinetic study was carried out. Experimental results showed that the presence of humic acid was found to reduce the capacity of Hg$^{2+}$ adsorption on natural zeolite. Freundlich isotherm model was found to be more suitable to represent equilibrium adsorption data. Kinetic examination revealed that the pseudo-second-order model was able to produce a better agreement with experimental data.

1. Introduction
Due to its geological condition, Indonesia possesses various mineral deposits, including gold deposits [1]. This condition has pushed many golds mining establishments, including small-scale gold mining. Small-scale gold mining, also known as amalgamation, was practiced by utilizing mercury [2,3]. As these activities usually meander around the river [3], the likelihood of mercury contamination (in the form of Hg$^{2+}$) from amalgamation wastewater in the river is high. Mercury in water is harmful to the local people as they usually still depend on river water [4]. From this viewpoint, it is imperative that mercury treatment in water needs to be conducted. One of the applicable removal methods for components from the water is through adsorption [5].

Zeolite is an aluminosilicate material that has been widely known as a material with good adsorption performance for a wide spectrum of purposes [6][7]. This is due to its crystalline structure, which has relatively high porosity (0.4 – 1 nm) [6]. The application of zeolite to remove metal contamination in water has also been extensively studied [7]. The zeolite’s capability to be utilized as adsorbent correlates with its characteristics, including hydrophobicity/hydrophilicity and structural features [8].

In an aquatic environment such as a river, a complex interaction of organic and inorganic substances commonly occurs. One organic compound usually presents in the water is humic acid (HA) [9]. Humic acid, also called humic substance, is a complex-large molecule organic compound containing aromatic
rings and many -OH and -COOH functional groups [9]. Its effect on the adsorption process of metal was previously studied [7,9].

Even though removing metal using the adsorption method has been previously studied, a study that explicitly targets mercury using zeolite in the presence of humic acid has not been found. This study is expected to provide insight into mercury removal process optimization, especially using the adsorption process in HA. Furthermore, to acquire a more comprehensive result, adsorption isotherm and kinetic are needed to be performed. In this experiment, Hg-containing wastewater will be prepared using synthetic wastewater.

2. Materials and Methodology

2.1. Materials
In this experiment, mercury-containing wastewater was prepared artificially using HgCl₂ (analytical grade by Merck with CAS number 7487-94-7) and distilled water. Humic acid (technical grade, Merck) was also used. The adsorption process was performed using natural zeolite obtained from Klaten, Central Java, Indonesia. The natural zeolite was then characterized using Energy Dispersive X-ray Fluorescence Spectrometer EDX-8000 from Shimadzu, Japan. The result of this analysis was presented in Figure 1 and Table 1 [10]. The research revealed that the natural zeolite contained several types of minerals, including mordenite, mesolite, gibbsite, quartz, stilbite, and hematite. Moreover, Table 1 reported that the zeolite used had a Si/Al ratio of 7. The Si/Al ratio of zeolite will affect the acidity of zeolite, thus also influencing its ability to adsorb cation [11].

![Zirconalia](image)

Figure 1. XRD analysis result of the natural zeolite.

Before adsorption, it was also essential to characterize the surface area of the adsorbent material. For this experiment, the natural zeolite was then analyzed using Quantachrome NovaWin analyzer by Quantachrome, Florida, USA [10]. The result showed that this zeolite had a surface area of 30.101 m²/g with a pore radius of 46.088 Å.
2.2. Methodology

2.2.1. Research Procedure. Solution of HgCl$_2$ having a concentration of 10 mg/L was prepared by dissolving 10 mg of HgCl$_2$ in 1 L distilled water. This solution was then designed for the practical step to study the adsorption isotherm model. Isotherm study was conducted by adding different amounts of zeolite (1.25; 2.5; 3.75; 5.00; 6.25; 7.5; 8.75; 10.00 gram), and the process was run for 24 hours. After completion, the sample was then filtered and analyzed using a mercury analyzer. Next, a kinetic study was performed using the same initial concentration of 10 mg/L in a shaker water bath. This step was then made using different time increments, which were 0, 10, 15, 30, 45, 60, 120, 180 minutes. Concentration determination was done using a mercury analyzer. In both isotherm and kinetic studies, the concentration of HA used was ten mg/L.

2.2.2. Adsorption Isotherm and Kinetic Study. In this study, experimental data were then examined using an equilibrium adsorption model. The adsorption model can be necessary to reveal its adsorption phenomenon. Moreover, studying the adsorption equilibrium allows improving the adsorption pathway and process design [11]. There are several models that available to perform equilibrium study of adsorption [12]. However, the most commonly used adsorption equilibrium is Langmuir and Freundlich Isotherm [5,13–15]. Langmuir isotherm correlates the fraction vacant surface area with the adsorbed substance and occupied surface with desorption process [11]. In general, both Langmuir and Freundlich isotherm can be stated as follows [5,13]:

$$q_e = \frac{K_L q_m C_e}{1 + q_m C_e} \tag{1}$$

with:

- $C_e$: Concentration of adsorbate at equilibrium (mg/L)
- $K_L$: Langmuir constant that is related with adsorption capacity (mg/g)
- $q_m$: Langmuir constant
- $q_e$: amount of adsorbate at equilibrium (mg/g)

To determine its parameter values, Equations (1) usually can be linearized as follows [11].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{2}$$

In addition, Freundlich isotherm equation can be written as follows [5,13]:

$$q_e = K_F C_e^{1/n} \tag{3}$$

$K_F$: Freundlich capacity factor (mg adsorbate/g adsorbent) x (L solvent/mg adsorbate)$^{1/n}$

1/n: Freundlich intensity parameter

Again, determination of parameters constant can be performed through curve linearization as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

A kinetic study was also performed to analyze the experimental data. Upon evaluating kinetic behavior, two models were used, namely pseudo-first-order and pseudo-second-order models [16,17]. Those equations can be described as follows [16,18]:

- Pseudo-first order reaction
  $$q_t = q_e (1 - \exp(-k_1 t)) \tag{5}$$

  Determination of the constants was conducted using curve linearization. Equation (5) was then modified into:

  $$\ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{6}$$

- Pseudo-second order reaction
\[ q_t = q_e \frac{q_el}{1 + q_e k_2 t} \]  

(7)

Modification for linearization results in Equation (8).

\[ \frac{1}{q_t} = \frac{1}{k_2 t} + \frac{1}{q_e} \]  

(8)

In this experiment, the Hg concentration obtained after 24 hours of batch operation will be used for the “q_e” value in isotherm simulation. In addition, for kinetic study, Hg concentration sampled several times during the experiment was taken for “q_t” value.

3. Results and Discussion

The adsorption process of HgCl\textsubscript{2} in zeolite and zeolite combined with humic acid showed a different trend. Using the additional amount of adsorbent, the experimental data can be shown in Figure 2. Based on Figure 2, it is revealed that variation without HA produced a higher HgCl\textsubscript{2} removal percentage than its counterpart (Zeolite with HA). In the water, HgCl\textsubscript{2} will be dissociated into its ionic constituent (Hg\textsuperscript{2+} and Cl\textsuperscript{-}). It was possible that the ionic mercury would interact with the humic acid [19]. The reaction of humic acid and metal, which can be considered as ion charge neutralization process [19], would have the likelihood to hinder to adsorption process. The hindrance of Hg\textsuperscript{2+} was probably caused by complex formation [9,19] that led to size enlargement around the mercury, thus making it more challenging to enter the adsorbent pore. A previous study reported that the complexation of HA could also occur with various metals [9].

![Figure 2](image)

**Figure 2.** Removal percentage of mercury after adsorption process.

On the other hand, Pandey et al. [9] suggested that this HA - metal complex could immobilize the metal, thereby aiding metal detoxification in the water. Another study also revealed that at low pH, the presence of HA increased adsorption capacity [7]. The negatively charged HA can be sorbed by zeolite at low pH, which induces high complexation potential. This phenomenon that occurs on the zeolite surface will lead to an adsorption increase. On the other hand, high electrostatic repulsion occurs at high pH, which reduces the H.A. sorption on the zeolite surface. This condition leads to the formation of HA – metal complex in the liquid body.

This experiment also investigated the adsorption process of HgCl\textsubscript{2} in water in terms of equilibrium and kinetic aspects. The experimental data of both variables (Zeolite and Zeolite + HA) was then examined using Langmuir and Freundlich Isotherm. Even though the previous investigation reported that both models could be applied for adsorption [13–15], based on the curve linearization, comparison
for both isotherm models can be seen in Table 2. It was revealed that the calculated R-square of the Freundlich linearization was better for both variations. Based on that $R^2$ value comparison, it can then be concluded that the Freundlich model has a better fit with experimental data as represented with a higher $R^2$ value (Compared with Langmuir’s $R^2$ value). Similar results, in which Freundlich isotherm was more favorable, were presented in previous studies [5].

Since Langmuir isotherm assumes that the adsorption occurs in the homogeneous condition in the adsorbent sites [13], the dealt state might deviate the experimental data with the Langmuir model. A previous study suggested that Freundlich isotherm was more applicable on heterogeneous adsorption site [13]. Moreover, the Freundlich isotherm equation is usually used to describe a heterogeneous system without monolayer coverage restriction [15]. In this experiment, although both Langmuir and Freundlich presented a similar agreement with experimental data, Freundlich was slightly more favorable due to its nature to account for the heterogeneity of adsorption sites. This is also probably matched with natural zeolite’s characteristics used in this experiment. Based on the XRD analysis, it was found that the zeolite itself consisted of several crystal forms, which corresponds to the ability of zeolite to perform adsorption. Experimental data was then evaluated using the Freundlich isotherm adsorption model to determine its parameter. The result presented in Figure 3 illustrated that the Freundlich model produced a good agreement with experimental data. The Freundlich parameters were also calculated in Table 3.

As previously obtained that the absence of HA in the system provided better adsorption capacity, the kinetic study was then performed for this system. Figure 4 illustrates that a high adsorption rate was obtained during the experiment’s around 30-40 minutes. It is represented by the rapid decline of mercury concentration in water. Since the mass transfer rate was affected by the concentration gradient, a high speed was expected at the initial period. Kinetic models of the pseudo-first and second-order were used on the experimental data. At the beginning of the process, there is a significant $\text{Hg}^{2+}$ concentration difference between the liquid body and zeolite surface, allowing this driving force to push the process faster. A similar result was obtained from previous studies [16,17,20], in which a high adsorption rate was observed at the early period.

Further examination using the kinetic model of pseudo-first and second-order illustrated that the pseudo-second-order presented a good agreement with experimental data (Figure 5). This result is also in line with other studies that showed better suitability of pseudo-second-order model with data [16,17]. Kinetic parameters were also presented in Table 4.

![Figure 3. Freundlich Isotherm – Experimental Data Fitting for various Hg Concentration.](image-url)
Table 1. Oxide compounds of natural zeolite (XRF analysis).

| Component | Result (%) |
|-----------|------------|
| SiO₂      | 66.9365    |
| CaO       | 9.5650     |
| Fe₂O₃     | 8.3664     |
| Al₂O₃     | 9.3697     |
| K₂O       | 3.7562     |
| TiO₂      | 1.2802     |
| SrO       | 0.2602     |
| MnO       | 0.1765     |
| ZrO₂      | 0.1010     |
| CuO       | 0.0454     |
| V₂O₅      | 0.0610     |
| Rb₂O      | 0.0350     |
| ZnO       | 0.0286     |
| Y₂O₃      | 0.0183     |

Table 2. R-Square comparation for langmuir and freundlich isotherm model.

| Isotherm Model | R-square |
|----------------|----------|
| Zeolite        |          |
| Langmuir       | 0.7218   |
| Frendlich      | 0.9806   |
| Zeolite + H.A. |          |
| Langmuir       | 0.4411   |
| Frendlich      | 0.7232   |

Table 3. Freundlich Isotherm Parameters for Zeolite and Zeolite + H.A System.

| Parameter | Zeolite | Zeolite + H.A. |
|-----------|---------|----------------|
| Kf        | 0.006237| 0.053420       |
| n         | 0.494   | 1.601          |

Table 4. Kinetic parameters of Pseudo-First and Second Order Model

| Model               | Parameter | constant, (k) | qₑ, calc. | R-square |
|---------------------|-----------|---------------|-----------|----------|
| Pseudo-first-order  |           | 0.0494        | 0.997503  | 0.9883   |
| Pseudo-second order |           | 0.1449        | 1.021659  | 0.9998   |

Figure 4. Mercury Concentration Profile in Liquid Phase.

Figure 5 Kinetic Model Fitting on Experimental Data.

4. Conclusion

In this research, mercury adsorption using zeolite and the presence of humic acid (HA) were studied. Experimental resulted that zeolite was able to reduce mercury concentration in water. However, the presence of HA produced different data trends. Adsorption with the presence of HA was found to reduce the amount of mercury adsorbed in the zeolite. Operating conditions needed to be optimized to improve HA performance in enhancing the adsorption process. Adsorption isotherm was also employed to examine experimental data. It was concluded that Freundlich isotherm was more suitable to fit the data. In addition, a kinetic study for the adsorption process revealed that the pseudo-second-order model presented a better data fitting than pseudo-first-order.
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