Nano-bentonite as a low-cost adsorbent for removal of mercury from aqueous solution

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Abstract. Study of the adoptive of mercury removal (Hg II) from aqueous solution was investigated by low-cost nanoparticle bentonite. Nanoparticle bentonite was prepared by the heating method at a temperature of 400 °C. The activation was carried out by immersed of natural bentonite in sodium hydroxide. The resulting powder was heating in the present of nitrogen gas as an activator agent. The bentonite sample was characterized by means of Scanning Electron Microscopy (SEM) and Brunai Emmet Teller (BET). The prepared bentonite had a heterogeneous surface with a particle size of 100-300 nm. The nano-bentonite was then tested in the absorption of Hg2+ synthetic were varied of the initial concentration (Co) from 5 to 400 ppm with 0.2 gram absorbent and 100 ml solution. The Hg2+ absorption amount was analysed using Atomic Absorption Spectroscopy (AAS). The adsorption capacities were fully fit with Freundlich isotherm models. It was found that the adsorption process followed the Freundlich isotherm model with n value of 1.9577 and Kf of 8.3985. Therefore, using the low-cost nano-bentonite is a potential adsorbent for removal of mercury from water solution.

1. Introduction
The rapid increasing of industrial development has an impact on increasing of heavy metal ions to be disposed of as waste in the water body. Some hazardous heavy metal in the water body includes mercury (Hg), chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd), and nickel (Ni). This pollutant could seriously effect on the environment cause if it existence the threshold and will cause serious illness for humans when accumulates in the body [1-3]. The industries that produce waste of metal ion are quite diverse in Indonesia, especially iron ore processing industry, gold, steel, electroplating, mining, petroleum, battery, automotive and chemical industries [4-6]. Some chemical and biological methods have been tried to extract heavy metal ions contained in waste, including adsorption, ion exchange, sedimentation, filtration, membrane separation, and others. The adsorption process is more widely used in industry because it is more suitable for absorbing ions dissolved in water.

Since 2016, mercury pollution in the river bodies, located in Calang area, Aceh Province of Indonesia has been reported by the mass media. The existence of Hg ion in the water body could endanger health ecosystem due to it’s the toxic heavy metal. To overcome this serious problem, it is necessary for the reduction methods for Hg ions removal. The precise way for reducing Hg ions in water solution is adsorption by utilizing adsorbents that can absorb heavy metals. The adsorbent materials that are widely used in the adsorption proses are activated carbon, silica gel, and zeolite. In this study, the activated
bentonite was used for the reduction of Hg ions from water solution. The use of bentonite to reduce Hg metal ions is still very limited in the literature \[3,7,8\].

\( \text{Al}_2\text{O}_3 \) It has a high specific surface area and is mechanically and chemically stable \[9\]. Bentonite is widely used in various industrial applications such as adsorbents, pesticide carriers, bactericidal agents, catalysts and color removal agents in the oil refining process, as well as in the pharmaceutical industry. The structure of bentonite/montmorillonite has an interlayer area filled with water and cations (Ca\(^{2+}\) and Na\(^+\)). Bentonite can be applied as an adsorbent due to its have high surface area, porous and an active site which the comply properties of an adsorbent \[10,11\].

To increase the adsorption ability of bentonite, the activation process was carried out by using strong acids such as \( \text{H}_2\text{SO}_4 \) and HCL to increase adsorption its ability. Activation of bentonite using acid will produce bentonite with a larger active site and surface acidity: those it could have a higher adsorption ability than the non-activated one. Activation aims to remove impurities that accompany in natural clay. The clay activation process refers to zeolite activation and the process consists of two types, namely chemical activation, and physical activation. Chemical activation is a process that includes chemical reactions or reagents while physical activation is carried out by the heating process.

Adsorption is a concentration process of gas or liquid molecules on a solid surface. In the adsorption process, there are two types of adsorption isotherms which commonly used to describe solid-liquid adsorption phenomena, namely Langmuir, and Freundlich isotherm types. The Langmuir isotherm consists of a monolayer layer while the Freundlich isotherm consists of multilayers of adsorbate molecules on the surface of the adsorbent. The adsorption process is influenced by the characteristics of the adsorbent, the characteristics of the adsorbate, the shaking time.

This study aims application as an adsorbent of mercury metal ions (Hg\(^{2+}\)). Several factors that influence the adsorption process such as pH, optimum time and initial concentration of the mercury metal ions have been studied. The effects of activation by using a hydrochloric acid and heating process have been investigated. In addition, the determination of adsorption capacity through Langmuir and Freundlich models were also evaluated. Bentonite is chemically activated using HCL followed by physical activation through heating in the furnace with air flow. The bentonite samples were characterized using scanning electron microscopy (SEM) and EDX.

2. Experimental procedure

2.1. Material

This research was carried out in several ways such as bentonite preparation and activation, Hg sample preparation, adsorption process and characterization of bentonite. The natural bentonite was collected from North Aceh, Sumatra Island, Indonesia. \( \text{HCl} \), \( \text{HgCl}_2 \), \( \text{NaOH} \), and \( \text{HNO}_3 \) were purchased from Merck (Germany, AR grade). Filter paper and distilled water were obtained from Chemical Company Banda Aceh, Indonesia. The equipment used is a 400 mesh sieve, magnetic stirrer, orbital shaker, analytical balance, and pH-meter. In addition, the AA-7000 Shimadzu AAS atomic absorption spectrophotometer was used for the analysis of mercury ion in the solution.

2.2. Preparation of bentonite

Natural bentonite used in this work was obtained from bentonite source located Lhoekseumawe, North Aceh Indonesia. Bentonite was washed with distilled water to remove impurities. The bentonite was crushed using a ball mill for 20 h. The bentonite powder was weighed of 20 grams was then heated in an oven at 110 °C, then cool down at room temperature. The powder was soaked in \( \text{HCl} \) 1.0 M during 12 h with continuous stirring. The bentonite was then washed using distilled water until the neutral pH. The dried bentonite was heated at 110 °C for 8 h to remove water until the weight constant. The non-activated and activated bentonite were denoted of NAc-B and Ac-B. To investigate the morphology of the structure, a scanning electron microscope (SEM) images of both bentonite were recorded by an LEQ 1450VP SEM apparatus. The specific surface areas of catalysts were measured by the BET method using Altamira Instruments 200, Inc.
2.3. Mercury (II) ions determination

The dissolved mercury (II) ions in water were detected using a UV-vis Spectrophotometer (DR5000, Hach Lange). Percent reduction in mercury (II) ions from solution is calculated as:

\[
\% \, R = \frac{C_0 - C}{C_0} \times 100\%
\] (1)

Where, \(C_0\) and \(C\) are the initial concentration and balance of mercury (II) ions in solution.

3. Results and discussions

3.1. Scanning Electron Microscopy (SEM) images

In SEM recording, it can be seen that the bentonite particles are not uniform. As seen in Fig. 1, the activated bentonite is found to be agglomerated. The average particle sizes of the bentonite are ranging between 100-300 nm with some particle less than 100 nm. Bentonite has a layered structure with the swelling ability and has the cations exchange [8,12]. It is expected that the adsorption capacity of adsorbent will be improved by an activation process.

Figure 1. (SEM) images on activated bentonite.

The specific surface area of the non-activated bentonite is 100.5 m\(^2\).g\(^{-1}\). The activated bentonite has the highest surface area of 151.2 m\(^2\).g\(^{-1}\). The activated bentonite has a relatively high specific surface area. The specific surface area of the adsorbent increases with an activated process. In addition, the increase in specific surface area of both bentonites is probably caused by the decrease in particle size of material by the milling process.

3.2. Determination of equilibrium time

In an adsorption process, the process will continue until the equilibrium is reached. For the determination of equilibrium time, the experiment was carried out to determine the contact time required to reach the equilibrium between the solid phase (adsorbent) and the liquid phase (effluent). The results obtained for NAc-B are shown in Figure 2. The results showed that after 15 minutes, the efficiency of removing Hg (II) ions using NA-B and Ac-B is 50.3% and 75.7%, respectively. Adsorption of Hg (II) increases with a contact time of up to 60 minutes and then becomes almost constant. Therefore, to find the equilibrium distribution between the adsorbent and the adsorbate, an experiment was conducted by varying the
contact time. The efficiency of removing Hg (II) after 60 minutes are found of 74.2% and 96.7% for NA-B and Ac-B.

The amount of Hg (II) ions adsorbed at equilibrium reflects the maximum adsorption capacity of the adsorbent under certain conditions [13]. Because the adsorption of Hg (II) becomes almost constant at 60 minutes of contact time and above for all adsorbents, other batch experiments were carried out above 60 minutes contact time.

![Figure 2. Influence of contact time on adsorption of metal ions Hg (II) using non-activated and activated bentonite.](image)

3.3. Adsorption isotherms studies

Metal mercury adsorption isotherm in activated bentonite is obtained by making a curve of the relationship between the equilibrium concentration in the liquid phase (Cs) and the equilibrium concentration in the solid phase (log Qe). The logarithmic form of the Freundlich isotherm equation can be written as:

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e
\]

where \(K_f\) is Freundlich's isotherm constant which is related to adsorption capacity, \(1/n\) is a constant indicating the intensity of the adsorption process, and \(C_e\) is mercury concentration at the equilibrium (mg.L\(^{-1}\)).

![Figure 3. Freundlich isotherm and linearized curve of Hg (II) ions adsorption on activated bentonite.](image)
The adsorption capacity of Hg (II) metal ions on bentonite were determined using adsorption isotherms. The adsorption isotherm model used is the Freundlich adsorption isotherm model, as seen in Figures 3.

The slope of the curve is \(1/n\) and the intercept is \(\alpha\). The plot of the log \(C_s\) value versus log \(Q_e\) shows the absorption of Hg\(^{2+}\) metal by activated bentonite behaving according to the Freundlich isotherm as shown in Fig. 4.

The Freundlich isotherm is based on multilayer adsorption on the surface of heterogeneous adsorbents while the Langmuir isotherm assumes the coverage of monolayer sorbents on a homogeneous surface (Dong et al., 2010). The Langmuir isotherm curve is not shown in this study due to the results obtained for the adsorption of Hg (II) follow the Freundlich adsorption isotherm. The correlation coefficients \(R^2\) obtained from the Freundlich model are 0.977 for Hg (II) onto activated bentonite, as shown in Table 1.

| \(K_f\) | \(n\) | \(R^2\) |
|-------|------|-------|
| 8.3985 | 1.9577 | 0.977 |

The process of adsorption of Hg (II) metal ions by bentonite follows the Freundlich isotherm model. The suitability of the Freundlich equilibrium model on the research data shows that the adsorption process occurs on the surface of the heterogeneous bentonite. This is different from the Langmuir equilibrium model based on the assumption that absorption occurs on a homogeneous [14]. The Freundlich isotherm model also explains that the adsorption process on surface parts is heterogeneous where not all adsorbent surfaces have adsorption power [15, 16]. The surface heterogeneity of adsorption in the Freundlich isotherm model is expressed by the surface heterogeneity factor \(n\) constant which is 1.9577 and \(K_f\) of 8.3985 on activated bentonite.

4. Conclusion

From the description above, it can be concluded that the activation of bentonite with HCl solution follow by heating results in a larger surface area of non-activated bentonite. Activated bentonite was used as adsorbent of metal ion Hg (II) with an optimum contact time of 55 minutes. Adsorption isotherms of metal Hg (II) with activated bentonite followed the Freundlich isotherm model with an \(n\) value of 1.9577 and \(K_f\) of 8.3985.
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