Preparation Nature Nano-Bentonite as Adsorbent Heavy Metal Cd and Hg

Makmur Sirait*, Profita DS Manalu
Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Medan, Jl. Willem Iskandar Pasar V, Medan 20221, Indonesia
e-mail: maksir@unimed.ac.id

Abstract. The results of natural bentonite from South Tapanuli (Pahae) were synthesized by coprecipitation method using HCL solvent into nano-bentonite. The nano-bentonite is characterized by X-Ray Diffraction, Scanning Electron Microscope- Energy Dispertion, and Surface Area Analyzer. Nano-bentonite applications as metal adsorbents were characterized by Atomic Adsorption Spectrofotometric. Characterization results from X-Ray Diffraction showed that the diameter size of crystalline nano-bentonite of HCL solvent, 19.17 nm with crystalline structure form was hexagonal. From the results of the characterization obtained a single phase, SiO$_2$ with the field $d_{hkl}$ highest at millier index (011) with $2\theta$ is 26,58°. The results of the Scanning Electron Microscope-Energy Dispertion characterization of nano-bentonite showed that there was a reduction in agglomeration and finer nano-bentonite surfaces. The results of the Surface Area Analyzer show the $S_{BET}$ nano-bentonite is 608,6 m$^2$/g. Results of analysis of Atomic Adsorption Test Spectrofotometric showed that the absorption of metal content using nano-bentonite with adsorption power of 99,03% for Cd and 99,18% for Hg.

Keywords : Adsorbent, Cd, Hg, Nano-bentonite

1. Introduction
Industrial development is increasingly rapidly causing more and more heavy metal ions are discharged as waste [1]. This waste will cause serious pollution to the environment if the heavy metal ion contained in it exceeds the threshold and will cause serious illness for humans when accumulated in the body. Cadmium (Cd) affects humans in the long term and can accumulate in the body, especially the liver and kidneys. These heavy metal ions combine with lead (Pb) and mercury (Hg) as the big three heavy metal which has the highest level of danger in human health [2]. Several chemical and biological methods have been tried to extract heavy metal ions contained in waste, including adsorption, ion exchange, separation with membranes. The technique most often used for effective handling of heavy metal wastewater is nanoparticle-based adsorption [3].

Adsorbent is a solid substance that acts as an adsorbent for liquid and gas-like molecules. There are many compounds that can be used as heavy metal adsorption, including zeolite, activated charcoal, bentonite and magnetite [4]. Bentonite can be used as an alternative adsorbent, because the cost is cheap, and abundant in nature. The main constituents of bentonite are montmorillonite minerals[5]. Montmorillonite has a 3-layered structure with a 2: 1 configuration consisting of 2 layers of tetrahedral silica and 1 octahedral layer as a central. The existence of isomorphic substitution in the basic structure causes the formation of negative charges on the surface of the montmorillonite constituent of bentonite. This part is called the active site which can be used as an adsorbent to bind cations and organic and metallic compounds through electrostatic bonds. The process of natural bentonite synthesis can be done by several methods, which one is coprecipitation method[6]. Coprecipitation is a chemical process that begins with the presence of a solute that precipitates to produce the desired
precipitate. Precipitation occurs as a result of the formation of mixed crystals. After the sediment has formed, then increasing the purity of the sediment by filtering the sediment, dissolving it again and repeating it again repeatedly. This is done so that decomposition of ions is bound by a binding solution or alkaline solution.

Research on the use of bentonite as heavy metal adsorbent was absorb 50-200 ppm Cd metal solution using nano-bentonite with a weight of 2.5g with the amount of Cd metal absorbed by 82.4%[7]. The adsorbent of Hg heavy metal ion with nano-bentonite where activated adsorption capacity of Pb²⁺ bentonite and Cu²⁺ metal ion was 185.50 mg/g and 30.00 mg/g[8]. In other results of AAS test analysis showed that the optimum absorption of metal content was using HCl bentonite variation conclude the smaller the particle size, the greater the surface area of the material area[9].

2. Experimental Method

Bentonite used is bentonite nanoparticles that have been made using the coprecipitation method. Sifted 20 grams of bentonite powder were dissolved in HCl 12 M 100 ml then heated in a magnetic stirrer at around 70°C for 120 minutes at a speed of 350 rpm. Wash the solution with distilled water repeatedly until the pH is neutral. Oven solution for 5 hours with a temperature of 100°C. After drying, crushed with mortar to produce powder. Bentonite powder is calcined in the furnace at 600°C. Powder bentonite at a ball mill with a speed of 100 rpm for 30 minutes and then sieved. Nano-bentonite with HCl solvents was tested with SEM, XRD, and SAA test. For testing as heavy metal adsorbents, 0.2 grams of heavy metal Cd and Hg were dissolved with 1200 mL of distilled water and then sterilized with 300 rpm rotation. Each solution was poured as much as 300 mL into a glass beaker which contained nano-bentonite and 1 cup of beaker without nano-bentonite as an indicator. The distilled solution at room temperature with a 300 rpm rotation for 1 hour is then filtered to separate the adsorbent solution and material. The filter results of heavy metal solutions were carried out by Atomic Adsorption Spectrofotometric (AAS) analysis.

3. Result and Discussion

3.1. XRD Analysis (X-Ray Diffraction)

Characterization of XRD using the Shimadzu type XRD device with a Kα wavelength of 1.541862 Å and a scan speed of 2.0000 deg/min. XRD characterization results as shown below.

![Figure 1. The result of X-Ray Diffraction Patterns: (a) natural bentonite, (b) nano-bentonite with HCl.](image-url)
From Figure 1 it can be seen that the main peak of the Miller index (011) with an angle of $\theta = 26.58^\circ$ with the SiO$_2$ phase. Besides that it is also strengthened by the appearance of several peaks in the other special clusters with the miller index (100) and (112). The crystalline structure for bentonite milling and nano-bentonite with HCl addition is hexagonal. From the picture above, it indicates that the widening of the diffraction peak is the smaller particle size. As seen in Table 1, nano-bentonite with HCl has a crystalline diameter size of 19.17 nm.

**Table 1.** Estimation measurement of crystalline diameter size of XRD analysis

| No | Samples                          | Size of the crystalline diameter (nm) |
|----|----------------------------------|--------------------------------------|
| 1  | Powder Bentonite Milling         | 72.43                                |
| 2  | Nano-bentonite with HCl          | 19.17                                |

3.2. **SEM-EDX Analysis (Scanning Electron Microscope)**

SEM is used to determine the morphological structure of a material. Through SEM analysis can be known the particle size of the sample with a certain magnification, besides the composition of the material can be determined through EDX devices that are integrated with the device.

![SEM-EDX Analysis](image-url)

**Figure 2.** The result of SEM with magnification 5000X: (a) natural bentonite, (b) nano-bentonite with HCl.

From Figures 2, shows that bentonite milling is agglomerated and has a rough surface indicating that there are still many impurities attached to the surface so that it looks rough, while nano-bentonite with HCl in the figure shows that there is a decrease in agglomeration and has a smoother and cleaner surface. Solvents that are soluble due to acid reactions cause the pores to be more open so that the surface area of the nano-bentonite area becomes larger [10]. As the adsorbent must show pores. The smaller the size of the adsorbent pores, the higher the surface area so that the number of molecules increased [11]. Preferably, in the SEM study, pore size is shown because in the application as an adsorbent, the pore is a requirement of adsorption. Bentonite particles using HCl coprecipitation method are optimal in reducing the particle diameter. The diameter size of the shrinking particles is caused by the reaction of acid (HCl), because in addition to cleaning impurities in bentonite particles it is also destroying particles so that the particle size becomes smaller.
Table 2. Estimation of particle diameter size of SEM analysis

| No | Samples                      | Particle size (nm) |
|----|------------------------------|--------------------|
| 1  | Powder Bentonite milling     | 19.231             |
| 2  | nano-bentonite/HCl           | 12.879             |

The chemical composition of bentonite nanoparticles samples was analyzed by Energy Dispersive X-ray Analyzer (EDX). In this analysis, a shooting was carried out at a point. EDX characterization results are shown in Figure 3.

Figure 3. EDX Analysis of nano-bentonite with HCl

Table 3. Composition of compounds from EDX analysis particles

| Chemical Element | Natural Nano-bentonite (%wt) | Nano-bentonite with HCl (%wt) |
|------------------|------------------------------|------------------------------|
| O                | 48.10                        | 50.00                        |
| Si               | 29.17                        | 29.88                        |
| Al               | 21.14                        | 13.94                        |
| C                | 1.60                         | 4.30                         |
| F                | -                            | 1.35                         |
| Mg               | -                            | 0.53                         |

From the results of EDX analysis in the table, the chemical elements that are most contained in natural nano-bentonite are O, Si, Al, and C. Bentonite with HCl solvent increases the content of elements O, Si and C in nano-bentonite. In addition, the activation process of bentonite using HCl solution activates elements of F and Mg. Bentonite is divided into several types, Na-bentonite and Ca-bentonite [12]. If the sodium content is more dominant, the bentonite is Na-bentonite, and vice versa.

From the results of EDX bentonite milling analysis, it is known that the type of bentonite is Na-Bentonite. The most chemical elements are Si, Al, and O which are characteristic of the composition of bentonite compounds such as the [13] while F is the impurity.
3.3. SAA Analysis (Surface Area Analyzer)

Figure 4. Graph isotherm absorpsi-desorpsi nitrogen of nano-bentonite

Figure 4 shows a graph of desorption adsorption isotherm from a nano-bentonite sample. The experimentally observed adsorption isotherms can be classified according to IUPAC-recommendations in 6 different types I-VI [14]. Based on the shape of the hysteresis loop, nano-bentonite with HCl can be categorized as type V.

Figure 5. Pore size distribution of nano-bentonite

Figure 5 shows the pore distribution of nano-bentonite samples. From figure 5 it is clear the pore distribution of nano-bentonite samples is in the range of (0.4-2.8) nm with the majority of pore sizes being 0.75 nm. The result of SAA analysis shows the surface area is 69.2 m$^2$/g, pore volume is 0.1869 cc/g, and pore diameter of nano-bentonite is 5.04 nm. According to IUPAC the pore type of material
can be categorized into 3 types based on size or pore diameter, that’s micropore (<2nm), mesopore (2-50nm) dan macropore (>50 nm)[14]. With an average pore diameter of 5.04 nm, nano-bentonite can be categorized as mesopore.

\[
S = \frac{St}{W} \\
S = \frac{69.2}{0.1137} \\
S = 608.6 \text{ m}^2/\text{g}
\]

Where \( St \) = Surface area (m\(^2\)/g) \\
\( S \) = specific Surface area (m\(^2\)/g) \\
\( W \) = mass of material (g)

From the data obtained by BET analysis, the area of surface area of nano-bentonite is 69.2 m\(^2\)/g and the specific surface area \( (S_{BET}) \) is 608.6 m\(^2\)/g. This value is better compared with nano-bentonite reaches a \( S_{BET} \) surface area of 109.80 m\(^2\)/g[15].

3.4. AAS Analysis (Atomic Adsorption Spectrofotometric)

| Samples           | Cd (ppm) | Hg (ppm) | Method |
|-------------------|----------|----------|--------|
| Indicator         | 9.11     | 0.1872   | AAS    |
| Nano-bentonite    | 8.77     | 0.1522   | AAS    |

The results of the AAS analysis show that the metal solvent before being given nano-bentonite is 9.11 ppm for Cd and 0.1872 ppm for Hg. After being given nano-bentonite there is a reduction metal content of 8.77 ppm for Cd and 0.1522 for Hg. So that the percentage of metal absorption by nano-bentonite is 99.03% for Cd and 99.18% for Hg. From the results of the characterization obtained, almost all of each metal is absorbed by nano-bentonite. This is because the bentonite with HCl solvent has the highest silica and magnesium content compared to other solvent bentonite variations (H\(_2\)SO\(_4\) and HNO\(_3\)) [9] which are described in Table 3 of the composition of compounds from EDX analysis particles. Silica and magnesium function in the process of exchanging heavy metal cations that enter into thenano-bentoniteso that there is an element in the bentonite coming out which results in increased absorption of heavy metals. Weak ions in bentonite will decrease when strong ions (heavy metal ions) enter the bentonite described in Figure 6.
When exchanging heavy metal ions with bentonite will be exchanged with bentonite elements that have weak ionization, so that bentonite can absorb the metal ion. The second indicator that causes high absorption results is because the small particle size will increase the surface area of the area, thus causing the absorption properties to be higher. This is also supported by a small particle size of 12.879 nm and is supported by a surface area of 608.6 m$^2$/g.

The high absorption capacity of HCl solvent nano-bentonite is due to the large surface area. This indicates that the pore size is smaller, the absorption is high. The smaller the particle size and porous, the specific surface areas also greater. The AAS number reflects the number of pores of a material, the higher the AAS number, the more porous the material [16].

4. Conclusion
The result was shown, the crystal structure of natural bentonite and nano-bentonite is hexagonal; Bentonite before coprecipitation has a rough surface and agglomeration while bentonite which has been coprecipitation has a smooth-looking surface and less agglomeration; The nano-bentonite has a size of 19.17 nm as well as a nano-particle whose specific surface area is large compared to the others, namely 608.6 m$^2$/g; and The percentage of metal absorption by nano-bentonite is 99.03\% for Cd and 99.18\% for Hg.

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