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Synthesis and Characterization of North Aceh CEC Bentonite Determination with Methylene Blue Method and Increased D-Spacing after Addition of Surfactants CTAB-SDS

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Abstract. Bentonite is not susceptible to polymers because it is organophilic and has low basal spacing. The main objective of this study is to increase bason spacing of bentonite and change the properties of bentonite to hydrophobic by modifying bentonite with cationic and anionic surfactants using Cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS). Surfactant with different CEC concentration, namely CTAB 1 CEC, 2 CEC and 3 CEC while SDS 0.5 CEC, 1 CEC and 1.5 CEC where the CEC is generated by halometric methods. From the results of the analysis with CEC bentonite value through the halometric method obtained 95.2 meq/ 100 grams clay, while the basal spacing of interlayer bentonite with modification of cationic and anionic surfactants using X-Ray Diffraction (XRD) obtained an increase in basal spacing from 14. 18393 Å to 25.08971 Å on CTAB 3 CEC and SDS 1.5 CEC. This research can produce bentonite from northern Aceh with the largest basal spacing so that it can be intercalated by other additives.

1. Introduction

Bentonite is a rock term and is part of a group of smectite minerals containing montmorillonite. The main content of bentonite is mineral montmorillonite. Bentonite application has been widely used for fillers, pellets, drilling mud, catalysts and as adsorbents. Currently, it has also been made into several high value products such as nano materials, drugs and chemicals. Bentonite is widely used for the treatment of esophagitis, gastritis, and colitis and so on. Bentonite is also used as a raw material for cosmetics due to decontamination, detoxification, as a moisturizer. In addition, with chemical adsorption and stability, bentonite has been widely used in food processing industries which are closely related to human health and life [1].

Bentonite usually contains a negative charge which allows a cation exchange reaction. This charge comes from one or more of several different reactions [2]. The main contribution of the negative charge is the isomorphic substitute and the dissociation of the open hydroxyl group. The ions that can be exchanged are different ions around the alumina silica clay minerals.

Ion exchange reactions are stoichiometric and different from absorption or sorption and desorption. Ion exchange is a process whereby the cations usually found in the crystal layer are replaced by cations from



the solution. In water, the cations on the surface of the layer become more easily replaced by other cations contained in the solution, known as exchangeable cations [3].

The absorption ability is stated in milliequivalent per 100 gram dry clays called Cation Exchange Capacity (CEC). The price of clay mineral CEC varies according to the type and amount of colloids in the clay [4]. Breaking the bond around the angle of the silica-alumina unit in montmorillonite will cause an imbalance of surface charge. Al^{3+} substitution replaces Si^{4+} in tetrahedral sheets and substitution of more refined valence ions, especially Mg^{2+} replacing Al^{3+} in octahedral sheets produces an unbalanced charge in the montmorillonite structure unit.

The use of bentonite as an adsorbent for inorganic compounds such as heavy metal ions because bentonite has cation exchange capacity and has hydrophilic properties on the surface. The chemical properties of the bentonite pore structure generally determine its adsorptive capacity [5]. Because of the ineffective hydrophilic nature of bentonite to absorb organic compounds, to increase its capacity. One of the deficiencies of clay is its hydrophilic nature which can cause agglomeration of clay minerals in a hydrophobic polymer matrix. This deficiency can be overcome by intercalating organic cations such as amino acids or alkyl ammonium to form organoclays that are hydrophobic.

Increasing the basal spacing after the intercalation process can also increase the diffusion capability of the polymer or polymer coating into clay interlayer. Intercalation is based on the exchange of cations found in the layers of clay, such as Na^{+} , K^{+} and Ca^{2+} . Intercalation into the clay structure resulted in an increase in surface area, basal spacing (spacing of montmorillonite silicate layer) and surface acidity which affected the adsorption power [6].

This intercalation process can cause clay pores to become larger and homogeneous and the layers become more stable than before being intercalated [7]. The purpose of intercalation is to: expand the interlayer distance, reduce solid-solid interactions between clays and increase the interaction between clay and matrix.

Organic compounds, bentonite is intercalated with surfactants that can interact with the negative charge present on the surface of the interlayer. Bentonite has a complex chemical surface and arises from its ability to form thixotropic water gels, high water absorption, high surface area, layered structure and high cation exchange capability, and contains crystals of quartz, cristobalite, feldspar, or other compounds [8]. Mineralogical composition will affect the CEC values obtained. Analytical problems arise from the method of determining CEC resulting from specific interactions between bentonite components and cation exchange modes which can cause an increase or decrease in the concentration of the cation index [9].

The nature of smectite is to absorb the cationic type of solution with the exchange between the cation equilibrium that is charged with a negative layer and the cation in solution is called the cation capacity exchange (CEC) and the CEC value can be expressed in centimole positive charge. per kilogram of mineral clay to dry is equal to milliequivalent per 100 g of clay (meq / 100 g) [10].

Determination of CEC value depends on the method used. However, determining the value of CEC is sometimes difficult and time consuming in the process of achieving perfect cation exchange. The researcher determined the value of Bentonite CEC in north Aceh and Kabupaten Bener Meriah with one method namely the methylene blue method.

The purpose of this study was to increase the basal spacing of north Aceh bentonite which was then characterized using X-ray Diffraction (XRD) to determine the element or compound content (qualitative analysis) and composition determination (quantitative analysis), phase change as a function of temperature and time in bentonite using Fourier Transform Infrared (FTIR) and Scanning Electron Analysis Microscope (SEM).

2. Methods

2.1 Materials

The materials used in this study were bentonite from Nisam, North Aceh, Methylene Blue (Merck, Germany), aquadest, aquabidest, Sodium Dodecyl Sulfate (SDS), Cetyltrimethylammonium Bromide (CTAB), $AgNO_3$ solution and sodium hexametaphosphate ($NaPO_3$)₆.

2.2 Determination of Cation Exchange Capacity (CEC)

Determination of CEC values by determining the specific surface of the bentonite analyzed. Bentonite is crushed first, then mashed and sieved with a size of 100 meshes. Weigh 1.25 grams of methylene blue and dissolve it with an aquadest of 125 ml of aquadest. Weigh 2.00 grams of bentonite and dissolve with distilled water 100 ml of water and stir the two solutions in a glass beaker with a stirring speed of 700 rpm for 5 minutes. Take 1 ml of the methylene solution and put it into a bentonite solution and stir it with a stirring speed of 400 rpm for 2 minutes. Note the methylene blue normality is 0.028 N. Then, drop the solution on the filter paper and then observe, if the droplets form is a blue halo, then that is the end of the titration and it hasn't formed like halo above. Then add 1 ml of methylene blue into the solution bentonite. Every change when titration is followed by dripping on filter paper, the aim is to see the blue halos around dark blue and this substitution between bentonite and methylene blue exists and continues to absorb. This is called the principle of the methylene blue method. The volume of methylene blue is added to the value of the bentonite CEC obtained where the CEC unit is milliequivalent per 100 grams of clay bentonite. This is a halometric method.

Measurement of CEC values using the following equation (1)

$$CEC \frac{meq}{100 \text{ gram}} = \frac{100}{F} \times V \times NMB \quad (1)$$

Where, F is the dry sample weight, the volume of methylene is blue during the titration process with 0.028 N methylene blue concentrations.

2.3 Purification of Bentonite with Cationic and Anionic Surfactant

Bentonite with a size of 100 meshes as much as 2 grams mixed with 98 ml of aquadest with 0.5 hours at 80°C. CTAB surfactants are added with various CEC concentrations, namely 0.7 CEC, 1.0 CEC and 1.3 CEC stirred for 2 hours at 80°C. After cationic surfactant is homogeneous with bentonite, then placed the anionic surfactant into bentonite solution which has been homogeneous with cationic surfactant. Next, stir until homogeneous for 1 hour at 80°C with varying CEC concentrations 0.1 CEC, 0.2 CEC and 0.3 CEC. Furthermore, the results of the resulting samples were analyzed using XRD to determine the basal spacing of bentonite after the addition of cationic and anionic surfactants.

2.4 X-Ray Diffraction (XRD)

XRD analysis was used to identify the magnification of bentonite basal spacing after the addition of cationic surfactants and anionic surfactants. Analysis results in the form of basal spacing data with Å units.

3. Result and Discussion

3.1 Effect of Cation Exchange Capacity (CEC) Surfactant on the Bentonite Interlayer

CEC or called cation exchange capacity (CEC) is a soil component to absorb and exchange or rerelease soil solutions. One of the CEC tests is the methylene blue method. Methylene blue powder when mixed with water and identified with the chemical formula: $C_{16}H_{18}N_3SCl$. When mixed with clay (bentonite), the chloride ion in a solution of methylene blue is replaced with cation in clay. The amount of adsorbed methylene solution varies according to the number of minerals and types of clay [11].

Liao's research in 2016 stated that bentonite with the addition of cationic surfactants can improve the natural properties of bentonite itself (high hydrophobic) and with the addition of anionic surfactants can the cation driving force in the interlayer of bentonite. Where the linking of these two surfactants can increase the basal spacing of the interlayer bentonite, so that the cation can enter the interlayer of bentonite.

The mixture is made by adding 5 ml of methylene blue solution to the stirred clay solution to 200 rpm. After 1 minute, a number of mixtures is taken with a dropper pipette and dripped onto filter paper. Generally, on filter paper there is a circle but there is no blue shadow around it this means the test is negative. To get a positive test, repeat the previous step until you see the last drop has a bright blue circle around dark blue meaning the test is positive or this can be called as halometry.

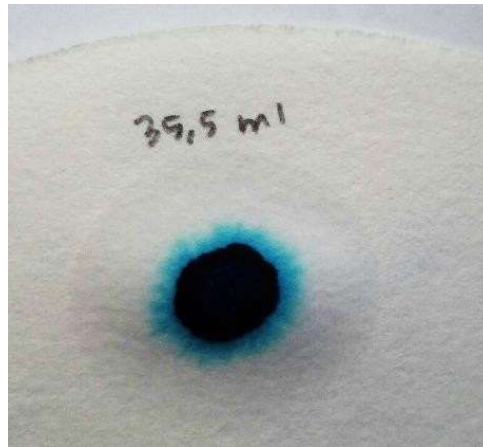


Figure 1. The acquisition of North Aceh bentonite CEC is marked by Halo metric formation on filter paper.

3.2 Bentonite Preparation with Addition of Cationic-Anionic Surfactants

Bentonite clay is widely used in paint. White Bentonite is the material of choice that is widely available around. In water-based paint, sodium or montmorillonite suspend and thicken substances. This montmorillonite is also used as an emulsifier in water and oil paint formulations. Organoclays can be made specifically with organic compounds to meet different vehicle requirements including varnishes, epoxy resins, and vinyl resins which are used in paint formulations. These organoclays improve pigment suspension, viscosity, and techotropic control and are very good in non-drip emulsion paints [12].

Bentonite used is from Nisam, north Aceh. This bentonite was previously ground and then sieved to a size of 100 meshes. Before being mixed with surfactant, raw bentonite was first analyzed using XRD to find out the spacing of the interlayer bentonite.

3.2.1 X-Ray Diffraction (XRD) Analysis. X-Ray Diffraction is one of the characterizations that use x-rays; x-ray scattering is produced if an electrous metal is fired by electrons at high speed in a vacuum tube. A crystal can be used to diffract x-ray beam due to the order of x-ray wavelengths almost the same or smaller with the order of distance between atoms in a crystal.

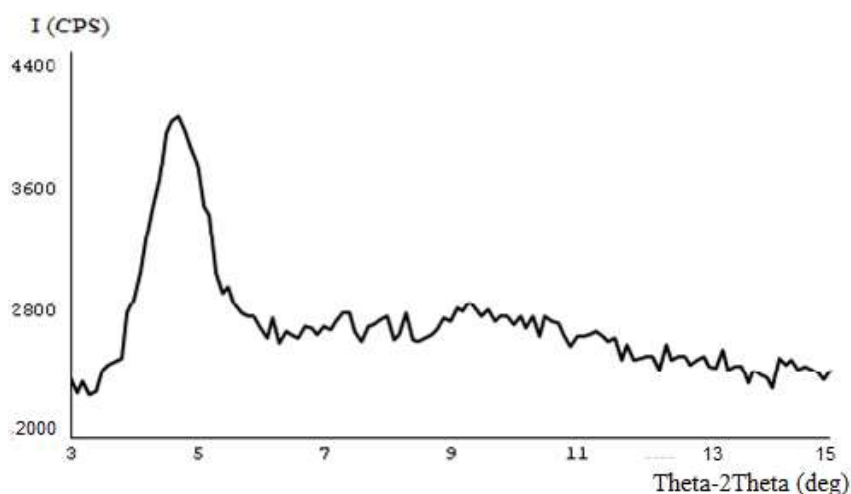


Figure 2. Graph XRD of bentonite sample without modification using surfactants

The basal spacing of raw bentonite is 14.18393 Å from figure 2. Then the raw bentonite was mixed with Cetyltrimethylammonium Bromide (CTAB) cationic surfactant stirred for 2 hours and then the mixture of Anionic Sodium Deodecyl Sulfate (SDS) surfactant was added for 1 hour. The results of these two types of surfactant were then washed to remove surfactants contained in the interlayer of bentonite using aquadest. To test whether the surfactant has been lost from the bentonite solution, AgNO_3 solution was used which was dripped into surfactant water. If the water turned gray then still contained surfactant, therefore it is necessary to re-wash with aquadest.

Then solid free from surfactants are filtered with a vacuum pump to separate solids with the remaining liquid. The solids are obtained then in the oven at 150°C until dry. Then it is crushed again until smooth and then re-analyzed with XRD to see the increase in d-spacing and SEM to observe the morphological structure of the bentonite obtained.

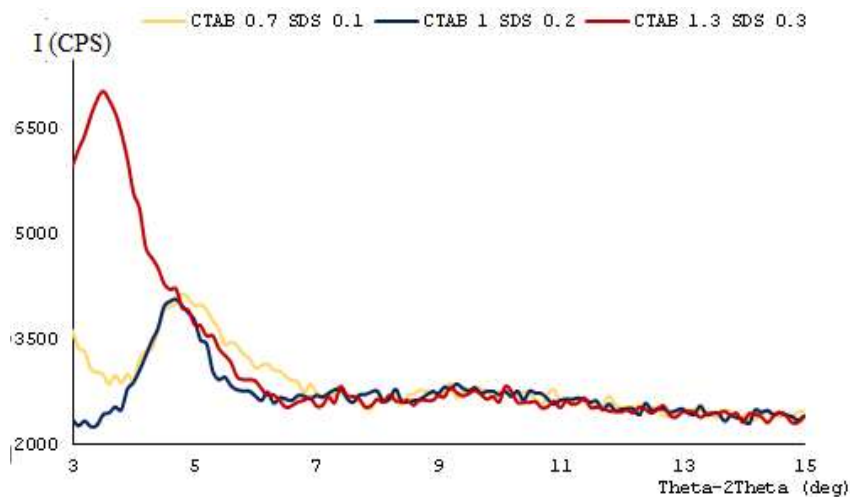


Figure 3. Graph XRD of bentonite samples after intercalation

The bentonite basal spacing has been modified using cationic and anionic surfactants on CTAB 0.7 CEC and SDS 0.1. CEC obtained spacing namely 15.11134 Å on CTAB 1 CEC and SDS 0.2 CEC obtained spacing for example 19.11531 Å on CTAB 1.3 CEC and SDS 0.3 CEC it is found that spacing is 23.00023 Å from figure 3. Thus, the highest d-spacing is the addition of CTAB 1.3 CEC and SDS 0.3. CEC surfactant which is 23.00023 Å. The intercalation mechanism between CTAB is positively charged and interlayer of negatively charged bentonite through cation exchange. When SDS is added, interlayer bentonite increases [6].

4. Conclusion

Bentonite is part of a group of smectite minerals containing montmorillonite. The application of bentonite has been widely used for fillers, pellets, drilling mud, catalysts and as adsorbents. This study has succeeded in determining the value of CEC using several methods. However, determining the value of CEC is sometimes difficult and time consuming in the process of achieving perfect cation each.

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