Determination of CEC value (Cation Exchange Capacity) of Bentonites from North Aceh and Bener Meriah, Aceh Province, Indonesia using three methods

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Abstract. Research on determination of value CEC (Cation Exchange Capacity) Bentonite North Aceh and Bener Meriah with three methods has been studied. The purpose of this study was to determine the value of CEC bentonite North Aceh and Bener Meriah. The methods used in this research were pH equilibrium, BaCl2/MgSO4 and the adsorption of methylene blue. These three methods used to determine, compare, and calculation of the CEC value and determine the effect of particle size of bentonite on the value of the CEC. Bentonite North Aceh and Bener Meriah sieved with particle sizes of 80, 100, 150, 200, 250 mesh. The results showed that determination of the value of CEC bentonite North Aceh using BaCl2/MgSO4 with a particle size of 250 mesh is the value of the highest, reaching 79.09 meq/ 100 g.

1. Introduction
Application of bentonite has been widely used for filler, pellet, drilling mud, a catalyst and as adsorbent. Currently it has also been made into several high value products such as nanomaterial materials, medicines and chemicals. Bentonite is widely used for the treatment of esophagitis, gastritis, colitis and so on. Bentonite is also used as a raw material for cosmetics because of its decontamination, detoxification, as a moisturizer. In addition, with its chemical adsorption and stability, bentonite has been widely used in food processing industries that are closely related to health and human life [8].

The use of bentonite as an inorganic compound adsorbent for example such as heavy metal ions because bentonite has a cation exchange capacity and has a hydrophilic property on the surface. The chemical nature of the bentonite pore structure generally determines its adsorptive capacity. Due to the ineffective hydrophilic nature of bentonite to absorb organic compounds, to increase its capacity to

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organic compounds, bentonite is intercalated with surfactants which can interact with the negative charge present on the interlayer surface. Bentonite has a surface chemical complex and arises from its ability to form a water gel thixotropic, high water absorption, high surface area, the layered structure and the ability of the cation exchange high, and contains quartz crystal, cristobalite, feldspar, or other compounds [10]. Mineralogical composition will have an effect on the value of CEC obtained. The analytical problem appear from the CEC determination method result of specific interaction between the bentonite component and cation exchange mode which may cause an increase or decrease in the concentration of cation index [4].

Indonesia is one of the exporting countries of natural materials in form of bentonite which is quite calculated in the world. Indonesia's bentonite reserves are abundant, amounting to approximately 380 million tons spread over several islands, mainly Java and Sumatra. Bentonite contained in Sumatra, especially in North Aceh and Bener Meriah abundance and most of its kind that is Na-bentonite.

Smectite is a group of naturally-coated silica minerals formed naturally. These minerals are included in secondary minerals that can be formed from a hydrothermal alteration process. This mineral group is a very distinctive group, which will expand in wet and shrink at the time of water loss. This is due to the crystal lattice properties that can expand because cations and water molecules easily enter in the cavity between mineral crystal units. An important member of the smectite group is montmorillonite and mineral composition consisting of dust quartz, calcite, accessories, feldspar, mica and illite. The presence of such minerals can reduce the value of CEC bentonite. So most of the low grade bentonite is not suitable for industrial applications, such as water purification [6] commodities [2] and food industry [9].

The nature of smectite is to absorb kinds of cationic from solution by exchange between the balance of cation charged negative layers and cations in solution is referred to as capacity cation exchange (CEC), and the values of CEC can be expressed in centimole of positive charge per kilogram of mineral clay to dry the same with miliequivalent per 100 g of clay (meq/100 g) [1].

There are various methods for determining CEC values. Most of the methods involve natural cation exchange with the clay minerals include cationic species such as ammonium, K⁺, N⁺ methylene blue, Co (III) hexamine complex, Ba, Mg, Ag thiourea complex, Cu (II) complex of ethylenediamine and so on others, followed by the removal of their excess species [7].

The determination of CEC values depends on the method used. However, the determination of CEC values is sometimes difficult and time consuming in the process to achieve a perfect cation exchange. Researchers determined the value of the CEC Bentonite North Aceh and Bener Meriah by three different methods, namely: pH balance method, the method BaCl₂/ MgSO₄ and methylene blue adsorption method.

Bentonite were then characterized using X-Ray Diffraction (XRD) to determine the content of element/compound (qualitative analysis) and determination of the composition (quantitative analysis), a phase change as a function of temperature and time on bentonite by using Thermogravimetric analysis (TGA) (Rihayat, 2010)

2. Materials and Method

2.1 Materials
Bentonite is collected from nature, North Aceh and Bener Meriah, sodium hexametaphosphate (NaPO₄)₆, glacial acetic acid (poison, Germany) distilled water, triethanolamine, barium chloride dihydride (BaCl₂.2H₂O), magnesium sulphate heptahydrate (MgSO₄.7H₂O), ammonium chloride, ammonia, erichrome black, ethanol, hydrochloric acid (HCL), Di-sodium EDTA, methylene blue (Merck, Germany).

2.2 Determination of CEC
Bentonite was modified by prearing and purifying before determination with three methods. Each 100 grams of bentonite is weighed and then pounded with pestle. Performed sizing of 80, 100, 150,
200, 250 mesh. The sieved bentonite was introduced into 1,250 ml of aquades and added 1.24 g of CTAB surfactant then dispersed with a magnetic stirrer for 2 hours. The dispersion result is then centrifugated for 2 minutes at a rate of 700 rpm to be separated from the liquid. Bentonite is dried in an oven with a temperature of ± 105 °C to dry. The process can be seen in Figure 1.

![Figure 1. Research procedure.](image-url)

For the determination of CEC value has done with three methods of analysis were: equilibrium pH, BaCl₂/MgSO₄ and methylene blue adsorption. Equilibrium pH method described in the literature, the CEC values can be determined by measuring pH change with pH meters. Measurements and calculations of CEC values were performed in accordance with procedures from the Laboratory of Soil Chemical Analysis. The material used was 1 M acetic acid solution, bentonite sample was inserted into beaker glass and 25 ml of acetic acid added into beaker glass containing sample. The solution stirred for 1 hour using a magnetic stirrer. Then suspension is fall down during sedimentation. Then, supernatant pH is checked. In order to accurate data, three repetitions performed. Measurement of CEC value using the following equation (1)

CEC (meq per 100 g of clay) = (pH observed - pH acetic acid) x 22

Where, 22 is a derived conversion factor of the curve of Brown (1943).

BaCl₂/MgSO₄ method involves the substitution of interlayer cations by Ba, which in turn was replaced by Mg, followed by titration with EDTA in the presence of ammonia [9]. The substitution of the interlayer cation with Ba is accomplished by adding a barium buffer chloride solution made by mixing the same volume of barium chloride. Further substitution with Mg is done by adding a solution of MgSO₄ with centrifugation and discarding the supernatant. The result of the end of the supernatant centrifugation is used for titration. Then the aliquot pipette of supernatant solution is titrated with standard EDTA by adding buffer ammonia and EBT indicator. The titration was repeated three times. The CEC values are calculated by the equation (20)

CEC (meq per 100 g of clay) = 8 (B-A2)

Where, A2 is the end point is obtained from the equation [A1 x (100 + M2-M1)] / 100 ml, B is the endpoint solution of MgSO₄ (ml), A1 is the endpoint in the sample, M1 and M2 mass of bottle plus ...
Dry content, and bottle mass plus wet content (g). The detailed procedure based on the procedures of the Industrial Mineral Laboratory Guidelines: Bentonite [5].

Methylene blue adsorption method. Basically this procedure is performed by Pejon (1992), and gives a determination of the CEC value by determining the specific surface on the analyzed bentonite. This method is also easy and fast in analyzing a sample. Before the first analysis was diluted the solution of methylene blue with the need of 125 ml and stirred using a magnetic stirrer for all mixtures dispersed, for 1 minute. Please note the normality of methylene blue is 0.028 N. After the preparation of the material then the next sample is analyzed. Samples were inserted into beaker glass by adding 3 ml of methylene blue solution. Then stirred using a magnetic stirrer for 1 minute. After 1 minute titration with methylene blue solution. Any change at the time of the titration is followed by a dripped on filter paper, the goal is to see a light blue halo around dark blue and this is that the substitution between bentonite and methylene blue exists and continues to absorb this is called the principle of methylene blue method. This analysis is repeated three times to keep it accurate. The CEC values are calculated by the equation (3)

\[
\text{CEC (meq per 100 g of clay)} = \frac{100}{F} \times V \times NMB
\]

(3)

Where, F is the sample weight, V is the required methylene blue volume at the time of titration, NMB 0.028 N.

3. Results and Discussion

The determination of CEC (Cation Exchange Capacity) value of bentonite North Aceh and Bener Meriah using three methods to get different values.

The following results comparative data of CEC values with particle size of the pH equilibrium method.

Results of the data comparison of the CEC with a particle size of BaCl₂/MgSO₄ method.
Results of data comparing the CEC values with particle size of methylene blue adsorption method.

From the results of the three methods found that a higher CEC value by using methods BaCl₂/MgSO₄ at 250 mesh particle size reached 79.09 meq/100 g, this method is also the most efficient method in the analysis of determining the value of CEC in terms of ease of process and shorter time consumption rather than the pH balance method and the methylene blue adsorption method. This CEC value is greater than the value of CEC bentonite [3] which is 76.4 meq/100 g. Because with the smaller particle size/nano can easily exchange cations present in bentonite. After calculation of the CEC value, then characterized using XRD were done and report in diffractogram in Figure 5.
Figure 5 shows that the XRD peak of bentonite at highest CEC value results using a BaCl$_2$/MgSO$_4$ method. The X-RD graph plots data between the angle of reflection on the x-axis and the intensity on the y-axis to produce a bentonite d-spacing layer automatically. Using the peak 20 setting which yields data at the reflection angle from 2$^\circ$ to 10$^\circ$ indicates that the bentonite origin of Bentonite North Aceh has a maximum reflection angle peak at 4.2$^\circ$ with a d-spacing value of 3.281 nm, while bentonite Bener Meriah, it has found that the reflection angle peak at 6.7$^\circ$ with a d-spacing value of 2.415 nm. It seen there is a distinct bentonite diffraction of bentonite North Aceh is higher than Bener Meriah. The difference is caused by the condition where the bentonite located so that the Na$^+$ ion composition that affects the expanding properties may vary. Thus, from the results of this study can be said that the best swelling power that effect the CEC value shown by bentonite North Aceh. This also proves that the use of surfactant has succeeded in opening the d-spacing layer to make exchangeable higher in bentonite in the presence of organic compounds exchanging between the two cations (ammonium) of surfactants with ions in bentonite (Na$^+$).

4. Conclusion
The most efficient method from the results of determining CEC value of bentonite North Aceh and Bener Meriah by three methods is BaCl$_2$/MgSO$_4$ method. The particle size can affect the value of the CEC, and the maximum value of CEC found in North Aceh Bentonite obtained of 79.09 meq/100 g with particle size of 250 mesh. The size of interlayer bentonite found at reflection angle peak at 4.2$^\circ$ with a d-spacing value of 3.281 nm by XRD graph.

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