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Abstract. The cation exchange capacity (CEC)measurement has been carried out in natural zeolite by percolation method. The natural zeolite samples used for cation exchange capacity measurement were activated beforehand with physical activation and chemical activation. The physically activated zeolite was done by calcination process at 600 °C for 4 hours. The natural zeolite was activated chemically by using sodium hydroxide by refluxing process at 60-80 °C for 3 hours. In summary, cation exchange capacity (CEC) determination was performed by percolation, distillation and titration processes. Based on the measurement that has been done, the exchange rate results from physical activated and chemical activated of natural zeolite were 181.90cmol (+)/kg and901.49cmol (+)/kg respectively.

INTRODUCTION

Zeolite (*Zeinlithos*) or boiling rocks, in chemical research has long been the center of attention. Every year, research journals around the world always contain zeolite utilization for various applications, especially those aimed at improving the effectiveness and efficiency of industrial processes and environmental pollution [1]. These rocks are widespread in some parts of Indonesia such as Java and Sumatra. In agriculture, zeolites are used to neutralize soil acidity, increase soil aeration, support mineral resources in soil fertilizers and also as effective controls in the release of ammonium, nitrogen and potassium ions. In livestock, zeolites serve to improve nitrogen efficiency, while their applications in chemistry and industry include zeolites as catalysts, as panels of solar energy development and phenol adsorption. Other zeolite applications are used as fillers in the paper, cement, concrete, plywood, adsorbent industries in the textile and palm oil industries as well as ceramic raw materials.

Directly, the use of zeolites can't be used due to the zeolites are generally still a mixture so it is necessary to process or modify the zeolite. Modification of zeolites aims to improve the function of zeolites in particular as adsorbents [2]. Some commonly used methods are modifying the surface properties of zeolites and washing using acid [3]. Washing using acid will remove the impurities present in the zeolite pore so that the zeolite pore surface will become wider [4]. In addition, natural zeolite modification can also be done physically. The activation of natural zeolite is physically done by heating. Natural zeolite heating process is done at 200-400 °C for 2-3 hours in vacuum system, whereas if in open space about 5-6 hours [5]. The heating process aims to evaporate water trapped in the pores of the zeolite crystals so that the number of pores and surface area is specifically increased. The modified natural zeolite can improve cation exchange ability, so it can be more optimal if used in the agricultural needs.

The determination of cation exchange capacity (CEC) becomes an important parameter on the soil. High exchange rate capabilities reflect the value of soil fertility. Soil is a component of the entire ecosystem and cannot be separated from the health of the ecosystem. In the field of agriculture, healthy soils become optimal physical, chemical and biological conditions for crop production and have a capacity to maintain plant health and the quality of ecosystems that include the availability of nutrients especially nitrogen [6]. The ability of cation exchange on

natural zeolite plays an important role in maintaining fertility and ecosystems in the soil so it is very important to measure the cation exchange capacity.

The determination of CEC in natural zeolite can be measured by percolation method based on standard method found on Indonesian Standard Method or known as SNI 13-3494-1994. A certain amount of zeolite was fed by an ammonium acetate solution. The ammonium acetate replacing the ions in the zeolite is converted again with a solution of potassium chloride and the resulting solution is distilled. Furthermore, the amount of ammonium present was determined by means of titration. According to the journal on testing the efficiency of modified nano porous zeolite catalysts as a mixture of urea, the cation exchange rate and natural zeolite characteristics can also be determined using UV-Visible and Fourier Transform Infrared Spectroscopy (FTIR) methods [7]. The principle of determining the CEC is the extraction using the principle of washing of elemental elements with salt in the column of soil (percolation). The natural zeolite in this research was conducted by activation both physical and chemical processes. The physical activation was conducted by calcination process at 600℃ for 4 hours and for chemical activation by refluxing process using sodium hydroxide solution at 60-80℃ for 3 hours. The result of the determined value of cation exchange capacity was each compared with the exchange rate of cation from natural zeolite without activation. During the process of determining the exchange capacity from natural zeolite both physical and chemical activation, also measured the water content as correction factor and standardization of sulfuric acid as titrant.

MATERIALS AND METHOD

Materials

The reagent used all were analytical grades such as natural zeolite, sodium hydroxide solution, distilled water, methyl orange indicator, quartz sand, NH_4-acetate solution pH 7, sodium chloride solution, 96% ethanol, sulfuric acid solution and Conway indicator.

Instrumentations

The equipment used is a set of reflux equipment, distillation apparatus, glassware, porcelain cup, analytical balances (Ohaus), magnetic stirrer, pestle and mortar, percolation column, oven (Memmert), furnace and desiccator.

Methods

Activation of natural zeolite

The physical activated was prepared by weighing as much as 10-20 grams of natural zeolite and then heated at 600 °C for 4 hours. The chemical activated prepared by weighing 20 grams of natural zeolite then refluxed using 2M of sodium hydroxide solution at 60-80 °C for 3 hours. The obtained product of chemical activation washed using distilled water until neutral (pH 7), then dried in oven at 110 °C to get constant weight. The activated zeolite was then heated at 500 °C for 10 hours.

Determination of water content

The determination of water content was conducted by weighing the empty porcelain cup then recorded the mass. A total of 2.5 grams of natural zeolite was weighed and put into a porcelain cup. The zeolite was then stirred for 3 hours at 105 °C, cooled and weighed again until a constant mass sample was obtained.

Standardization of H_2SO_4 solution

Standardization of H_2SO_4 solution was carried out by dissolving 0.106 grams of Na_2CO_3 in 25 mL distilled water and then titrated with 0.05N of H_2SO_4 solution. The titration was repeated 3 times and recorded the average volume and calculated the concentration of H_2SO_4 solution.

The determination of the cation exchange capacity began by weighing as much as 2.5 grams of physical activated zeolite sample and inserted in a 50 mL column glass. Samples were added 5-7.5 grams of quartz sand, stirred until homogeneous. The percolation column was prepared by closing the bottom of the column using a pulp filter, then put about 5 grams of quartz sand. Subsequently, there was a mixture of zeolite samples with quartz sand and about 5 grams of quartz sand into a prepared percolation column. Each material is flattened in a percolation column. A total of 2 x 25 mL of ammonium acetate solution (pH 7) was added to the percolation column and the percolation process-ready. The sample and sand in percolation column washed with 100 mL of ethanol. The sodium chloride solution was added for the percolation process, and the percolate was presented in a beaker glass for CEC determination. The resulted percolate was put into the round bottom flask then added with distilled water, sodium hydroxide solution and boiling stone. A boric acid put into erlenmeyer flask spiked with 3 drops of Conway indicator as a distillate container and then distillation process was carried out. The distillation was terminated when the volume of the distillate was sufficiently used for the determination of cation exchange capacity. The distillate titrated with H_2SO_4 standard solutions until the solution color was exactly changed from orange to pink. The acceleration of the chemical activated zeolite and natural zeolite were worked out. The formula for determining the value of cation exchange capacity was shown as below:

$$CEC = (V_s - V_b)\ x\frac{N}{10}x\ \frac{Volume\ of\ percolate}{Volume\ of\ percolation\ taken}\ \frac{1000\ g}{Sample\ mass\ (g)}\ x\ df\ x\ cf$$

whereV_s is the titration volume of sample, V_b is the titration volume of blank, dfis dilution factor and cfis correction factor.

RESULTS AND DISCUSSION

Zeolite is crystalline aluminosilicate with open 3D framework structures built of SiO_4 and AlO_4 tetrahedral linked to each other by sharing all the oxygen atoms to form regular intracrystalline cavities and channels of molecular dimensions. The natural zeolite structure is shown in Fig. 1. Zeolite frameworks are made up of four coordinated atoms forming tetrahedral, which are linked by their corners. This feature makes a rich variety of beautiful structures of zeolite. The framework structure of zeolite contains channels, cages, and cavities. These are linked and big enough to allow easy drift of the resident ions and molecules into and out of the structure.Zeolite's low specific density is the result of the system of large voids, which are interconnected and form long wide channels of various sizes depending on the compound. This ability puts zeolites in the class of materials known as molecular sieves.
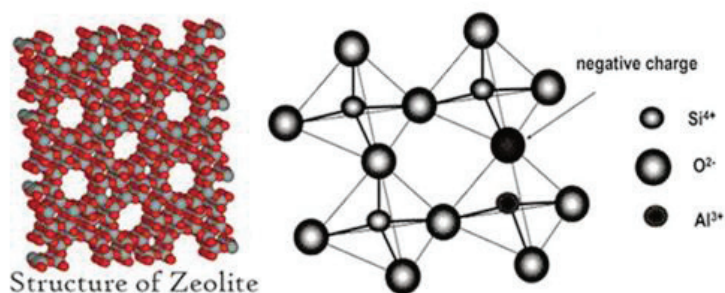
FIGURE 1.The structure of zeolite[8]

The empirical formula of zeolite chemistry was shown as $M_{x/n}.[(AlO_2)_x.(SiO_2)_y].wH_2O$,where the M notation was the alkali or alkaline earth metal cations, x, y, and w were the particular numbers whereas n was the charge of the metal ions. From the above formula zeolite can be seen the existence of three components that are part of zeolite, that wasaluminosilicate frame $[(AlO_2)_x.(SiO_2)_y]$, alkali metal ($M_{x/n}$) (Be,Mg,Ca,Sr,Ba,Ra) and water (H_2O)[9].

In general, natural zeolite still contains organic and inorganic impurities that cover the pore, so to increase the ability of natural zeolite absorption must be done activation first [10]. Physical activation was carried out by heating at a temperature of 300-400 °C with hot air or a vacuum system to release water molecules or alkaline hydrates. Zeolite heating process or commonly called calc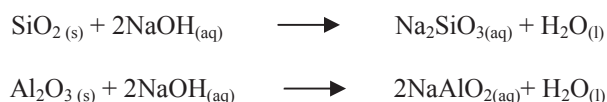ination must be controlled, meaning that the temperature and time should be properly guarded. The excessive warming will cause damage to the zeolite structure. Reduction of water content in natural zeolite after heating will be proportional to the temperature used during the calcination process. The water content of natural zeolite will decrease as the temperature of heating increases. The loss of this water molecule can increase the volume or empty cavity in the pores of the natural zeolite.

Chemical activation was the activation by using chemicals, either acid or base. The function of acid or base was to wash the cation that contaminated the zeolite surface. Chemicals that can be used for natural zeolite activation process are acidic solutions (H_2SO_4, HCl, HNO_3) and basic solutions (NaOH, KOH). The purpose of chemical activation to clean the pore surface, dissolve the impurity oxides including silica and free aluminum and rearrange the location of the atoms and dissolve some alkaline and alkaline earth metals so as to form zeolite-H^+ or zeolite-Na^+ [11].

In this research, treatment of natural zeolite with sodium hydroxide solution went to significant changes of SiO_2 content or known as desalination process. The change in chemical composition may be attributed to that alkali impact on zeolite material in Na^+ being exchanged for H^+ ions of hydroxyl groups bond to silicon atoms at the boundaries of the silicon-oxygen layer as described below:

$$\equiv Si\text{-}OH + NaOH \longrightarrow \equiv Si\text{-}ONa + H_2O$$
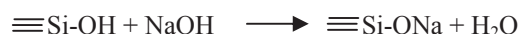
During alkaline treatment, dissolution of aluminum silicate takes place yielding sodium silicate and sodium aluminate with the following scheme [12]:

$$SiO_{2\,(s)} + 2NaOH_{(aq)} \longrightarrow Na_2SiO_{3(aq)} + H_2O_{(l)}$$

$$Al_2O_{3\,(s)} + 2NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O_{(l)}$$

After the activation, the sample of natural zeolite was determined its water content.Determination of moisture content was done by gravimetric method with oven drying that evaporating water present in a material by heating. Then weigh the material up to a constant weight which means all water has been evaporated. This method was relatively easy and cheap. The pre-determined water content is used to determine the water content correction factor. The water content correction factor is used to calculate the CEC content in the natural zeolite. Water content was not the only parameter determining differences in nature zeolite properties, but there was still testing of CEC levels.

The determination of cation exchange capacity in natural zeolite passes through three main steps, namely percolation, distillation and titration process. The percolation was done to separate the other nutrients and metallic elements present in the natural zeolite. The principle of percolation processwas on the washing of the basic elements by a salt in a column of soil (percolation). Percolation is a process of extracting simplicia by passing a suitable solvent for a long time on a simplicia in a percolator or a cold method of extraction using a newly flowing solvent. Percolation widely used for the extraction of secondary metabolites from natural materials, especially for heat-resistant compounds. The extraction was done in a vessel equipped with a tap to remove the solvent on the bottom. At percolation process, the bottom of the polishing tube was given glass wool then inserted quartz sand followed by mixed samples of natural zeolite and quartz sand. The percolation process is principally on the washing of the basic elements by a salt in a column of soil (percolation). The percolation process is initiated by using ammonium acetate salt pH 7. Furthermore, to remove or clean the ammonium ion in the soil solution, the colon should be rinsed using technical ethanol. The rinsing bunch was removed because it was not used in the determination of CEC. After the removal of cationic bases, the subsequent ammonium absorbed is replaced by sodium from a 10% sodium chloride solution and accommodated for further processing. The next process is distillation to determine the level of ammonium in the percolate. The distillation was carried out by taking 20 mL of the percolate and inserted into the boilers of round bottom flask, added 80 mL of distilled water and boiling stone. Boiling stones are added to prevent major outbreaks during heating. Then 10 mL of 40% sodium hydroxide was added to assist the breakdown of the ammonium compound at the time of distillation. The reaction was described as below:

$$NH_4Cl_{(aq)} + NaOH_{(aq)} \longrightarrow NH_{3(aq)} + H_2O_{(l)} + NaCl_{(aq)}$$

The liberated ammonium is subsequently captured by a standard acid solution. The standard acid used is 1% boric acid solution with the excess amount. The boric acid solution was added in the erlenmeyerflaskas a distillate reservoir and the Conway indicator was added as a marker of the reaction occurring between ammonium and boric acid solution. Ammonium that reacts with boric acid will form a reaction:

$$NH_{3\ (g)} + H_3BO_{3(aq)} \longrightarrow NH_4^+{}_{(aq)} + H_2BO_3^-{}_{(aq)}$$

The next step was distillation to determine the ammonium content in the percolate. The distillation process stopped until a sufficient volume of distillate was obtained for use of CEC determination using titration. The distillates were titrated using a standard of H_2SO_4 solution that had previously been standardized with sodium carbonate.

$$Na_2CO_{3(s)} + H_2SO_{4(aq)} \longrightarrow Na_2SO_{4(aq)} + H_2O_{(l)} + CO_{2(g)}$$

The sulfuric acid solution acts as a standard titrant aiming at the treatment of a sulfuric acid solution and knowing the true concentration because in generally the secondary standard solution is unstable.The titration end point was marked by the color change of the orange solution to pink. The titration used was the same as acid-base titration or neutralization in general. The distillates containing alkaline ammonium will react with H_2SO_4 until a solution of the orange color changes to pink. The reaction that occurs during the titration describes as below.

$$2NH_4^+{}_{(aq)} + H_2BO_3^-{}_{(aq)} + H_2SO_{4(aq)} \longrightarrow (NH_4)_2SO_{4(aq)} + H_3BO_{3(aq)} + H^+{}_{(aq)}$$

The titration volume was then recorded and used to determine the natural zeolite cation exchange capacity.

At the time of measuring the value of cation exchange capacity in the natural zeolite, blank testing was also done. The blank test was performed similarly to the working procedure on the measurement of cation exchange capacity, but in the test was done without using the sample. The results of blank testing are shown in Table 1. Blank testing is used as a comparison in the analysis of natural zeolite cation capacity measurement.

TABLE 1. The result of blank titration

Distillate volume (mL)	Titration volume (mL)	The End Point titration
25 mL	0.54	
25 mL	0.57	Orange-pink
Average	0.55	

The determination value of cation exchange capacity in natural zeolite was performed on each of the already activated samples. The measurement result of natural zeolite exchange rate is listed in Table 2. From Table 2 express significant difference of cationexchange rate both physical and chemical activated of zeolite.

TABLE2. The CEC value of activated natural zeolite

Sample	Distillate volume (mL)	Average titration volume (mL)	CEC value (cmol(+)/kg)
Physicalactivated zeolite	25 25	5.37	181.90
Chemical activated zeolite	25 25	26.99	901.49

Untreated natural zeolite has been done in previous research, and the value of cation exchange capacity produced was 41.30 cmol(+)/kg, physical activated 1 zeolite was 181.90 cmol (+)/kg and chemical activated zeolite was 901.49 cmol(+)/kg. Based on Fig.2 it was clear that chemical activated zeolite has the highest value than untreated and physical activated zeolite. The higher concentrations of alkaline used for natural zeolite activation means higher cation exchange capacity and lower the number of H^+ ions present in the soil complex.

901.495

181.903

41.304

Natural zeolite   Physical acivated natural zeolite   Chemical activated natural zeolite
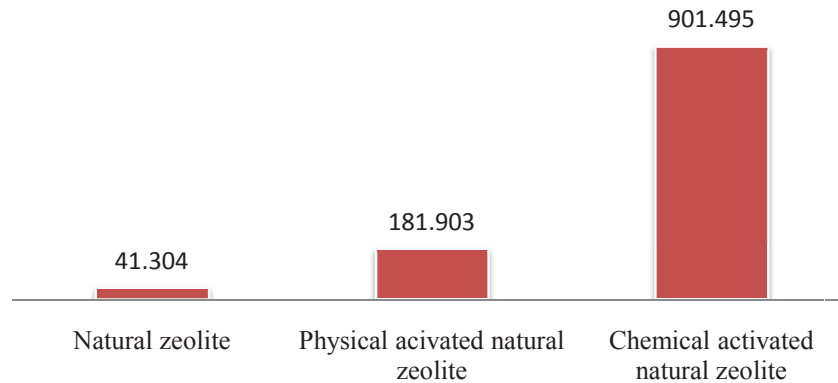
FIGURE 2. The CEC Value of Treated Zeolite

In the Fig. 2 was shown that untreated natural zeolite only has 41.304 cmol(+)/kg for CEC value which indicated that uptake process of ammonium ions during percolation was due to exchange reaction between ammonium ions and exchangeable cation in natural zeolite. Meanwhile an exchange interaction dominated between Na^+ and Ca^{2+} ions and ammonium ions after alkali treatment because there was a destruction process during alkaline treatment of silicon according to following scheme in Fig. 3 [12]:
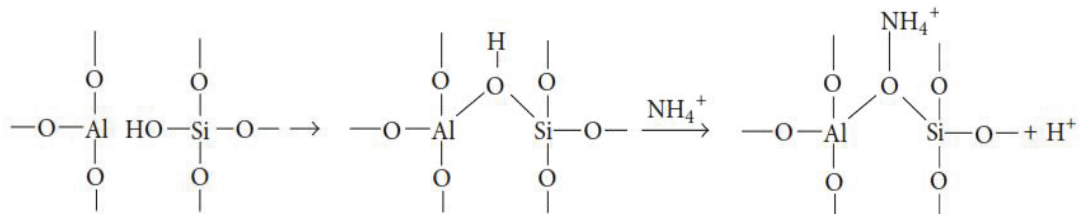
FIGURE 3. Destruction of silicon in alkali treatment

The cation exchange capacity was an important indicator of fertility testing and soil productivity potential. Affecting factor of cation exchange capacity is soil texture. Softer ground texture has the higher CEC value. Sand and clay sand contain little colloidal clay as well as poor organic and humus materials, rather than fine textured soils containing more clay. Thus, this fine soil has a higher CEC than the sand soil. The soil was very dynamic, so the equilibrium reaction will always occur on the ground according to the changing circumstances. In areas with high rainfall, many hydrogen ions enter the glacial complexes of the earth, while calcium ions come out of the complex, entering the soil solution. Calcification and fertilization will cause the reaction equilibrium to reverse, resulting in fewer hydrogen ions in the ground soil and an increase in pH value. Potassium derived from the fertilizer which is then absorbed is the nutrient available for the plant. Therefore, cation exchange is useful for the preparation of nutrients for plants. The exchange of cation in the soil occurs due to the negative charge of the soil colloids that absorbed the cation in the form of exchange. The exchange of cation in the soil occurs due to the negative charge of the soil colloids that absorbed the cation in the form of exchange. The cation exchange capacity is usually expressed in cmol(+)/kg soil or clay. These cations are positively charged ions in the soil, such as H^+, Al^{3+}, Ca^{2+}, and Mg^{2+}. These cations are absorbed in mineral and organic colloid surfaces with less strong electrostatic bonds, which can be removed or interchanged.

The most optimal natural zeolite testing for parameters including moisture content and cation exchange capacity needs to be done to determine the natural zeolite differences that have been reactivated physically and chemically. From the process it was obtained that the zeolite activated with base would become more polar when compared with acid-activated zeolites [13]. Treatment with acids on zeolite proved to cause the zeolite to be more hydrophobic so that its adsorption power to water will decrease [14]. The higher the acid concentration used, the zeolite adsorption power to water vapor becomes smaller [15]. Chemically activated zeolites are more optimal when applied to soil as

they are used to absorbed heavy metals in the soil, chemically activated zeolites are much more optimal than physically activated natural zeolites because when natural zeolites are activated using an alkaline, the natural zeolite pore surface becomes clean and impure oxides can be completely dissolved so as to reestablish zeolite H-zeolite or Na-zeolite and natural zeolite ability to exchange larger cation and increase soil fertility.

CONCLUSION

Based on the research that has been done can be concluded that there are differences of cation exchange rates in natural zeolites that have been activated both physically and chemically. Natural zeolites with chemical activation have higher cation exchange rates than natural zeolites with physical activation. The value of cation exchange capacity both chemically and physically respectively are 901.495 cmol (+)/kg and 181.9036 cmol (+)/kg. The chemical activated zeolites are more optimally applied to soils than physically activated zeolites to maintain soil fertility.

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