

Article

Determination of Cation Exchange Capacity of Napa Soil in 50 Kota Regency using Atomic Absorption Spectrophotometer

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Abstract. This research discuss about the cation exchange capacity of napa soil from Limo Situjuah Nagari District and Sarilamak District, 50 Kota Regency by using an atomic absorption spectrophotometer. The purpose of this reserach are to optimize the saturation and replacement by certain cations on determination of cation exchange napa soil which the results is a value of the cation exchange capacity (CEC) and to review the differences of napa soil value and its influence on early treatment in the form of purification and treatment by using barium chloride method. According to the research that has been done, obtained the optimum concentration of BaCl₂ is 0.15 M and 0.15 M for MgSO₄. Determination of CEC in optimum condition showed that napa soil that has been purified have higher CEC value, CEC value of napa soil in Situjuah Limo Nagari District is 1.7 meq/g and CEC value of napa soil in Sarilamak District is 1.2 meq/g. The CEC value of napa soil in Situjuah Limo Nagari District and Sarilamak District which has been given treatment with peroxide are 0.3 meq/g and 0.7 meq/g.

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Email : mawardianwar@fmipa.unp.ac.id**1. Introduction**

Indonesia is a country which is rich in natural resources, such as plants, animals, and minerals that contained in the bowels of earth. One of these resources is natural zeolite that is widely around in the mount of fire [1].

There are many natural minerals around the mount of fire in West Sumatra. One of them is napa soil that contained in most areas of West Sumatra. Napa soil is popular name by the people in West Sumatra to the soil that rather hard, it has large pores and usually has grayish white colour. During this time, napa soil is used as traditional medicine which can treat various diseases in the body, for example in West Sumatra, Solok, napa soil is used to upset stomach. But now napa soil is not used as a treatment because nowadays there are so many practical modern cure.

Mawardi, Hary Sanjaya, and Desi Kurniawati (2013) have reported the chemical composition of napa soil from West Sumatra in generally were aluminosilicate minerals with group comparison of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ranges between 1.25 to 3.43. Napa soil which has been reported their chemical composition have canescent and big pores physical characteristics [2]

One type of aluminosilika minerals is zeolite. Natural zeolites are commonly in volcanic areas, riverside, sea, and sediment natural mineral lake, usually present in an amount megatons. Aluminosilika mineral types in some areas of the world such as in the USA, Japan, Cuba, the Soviet Union, Italy, Mexico, and Korea have been categorized including alumina silica minerals natural zeolite group. In Indonesia there are also some mineral group of aluminosilika into natural zeolite as found in Central Java, Klaten, Jawa Barat, Bogor, Tasikmalaya, and Sukabumi [3].

Ion exchange is a process that ions are in the pores of insoluble solids that can be exchanged with ion carried by the solution during contact with the solids. Characteristic of Ion exchange for clays and zeolites have been identified and studied for more than a century [4]. The result of research also shows that the napa soil has major components such as SiO_2 , Al_2O_3 , K_2O , Fe_2O_3 and CaO . These results show that napa soil contains cation exchange components, those are K and Ca_2 . Therefore, it is very useful conducted research to determine the cation exchange capacity (CEC) of the napa soil.

Ion exchange has limited application, usually used in the softening process and water demineralization. Nowadays cation exchange is used in a large scale and the most important part in industrial processes, example: uranium and thorium extraction in natural sample [5], radioactive isotopes separation such as ^{238}Pu , ^{239}Pu , and ^{240}Pu [6], magnesium isotope separation and other isotopes [7], and separation of metals from metal plating wastes [8].

Several methods have been done to measure the CEC of soil, such as ammonium acetate method and barium chloride method. The most commonly used method is barium chloride method based on soil cation exchange with salt solution of known concentration and contain cation which are not contained in the soil and also cation detection by standard techniques such as, spectrophotometry and titration [9]. In this research CEC determination was done by barium chloride (BaCl_2) method. This method was used and accepted as an international standard (ISO 11620) [10]. By seeing the usefulness of the above, it is useful conducted the research materials of cation exchange that have cation exchange characteristics such as napa soil.

This purpose of this research were to deteremine the optimum condition determination of napa soil CEC variable concentration of barium chloride solution and determine the consentration of magnesium sulfate and determine the effect of purification and treatment with acid to the CEC napa soil. Expected later it can be developed in the provision of napa soil as cation exchange material to

overcome the heavy metal pollution both in the laboratory and in industrial scale. It is also known that the mineral reserves of napa soil is quite abundant in many regions (districts) in West Sumatra, such as Tanah Datar District, 50 Kota District, Solok District and Pesisir Selatan District [11]. So it becomes a great opportunity to commercialize product of napa soil.

a. Napa Soil

Napa soil is a term by people of West Sumatra to the type of natural material and used as stomachache cure and diarrhea. After doing research by Mawardi and Bahrizal, et al (2021) napa soil from West Sumatra generally were aluminosilicate minerals with a comparison group of $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ranges between 1.25 to 3.43. The result shows that napa soil has a major component such as SiO_2 , Al_2O_3 , K_2O , Fe_2O_3 , and CaO . These results indicate that the napa soil contain cation exchange components of K^+ and Ca^{2+} [2].

Mawardi and Bahrizal, et al (2021) has conducted research on napa soil that obtained from Solok district, West Sumatra. Based on the chemical composition data obtained the result that napa soil from X Koto sub-district, Solok district are aluminosilicate minerals have big pores and grayish white physical characteristics [2]. The Comparison of the chemical composition of natural zeolite Clinoptilolite produced by Gravis Mining Co industry can be seen in Table 1.

Table 1. Composition of Napa Soil in Solok Regency and *Natural Zeolit Clinoptilolit*

| Location without Napa | SiO_2 (%) | Al_2O_3 (%) | Fe_3O_3 (%) | TiO_2 (%) | CaO (%) | K_2O (%) | Na_2O (%) | $\text{SiO}_2/\text{Al}_2\text{O}_3$ |
|-----------------------------------|-----------------------|--------------------------------|--------------------------------|-----------------------|---------------------|-----------------------------|------------------------------|--------------------------------------|
| Kec.X Kab.Solok | 70.43 | 20.52 | 3.67 | 0.40 | 2.70 | 1.26 | <100ppm | 3.23 |
| Natural zeolite clinoptilolite | 65-72 | 10-12 | 0.8-1.9 | 2.5- 3.7 | 2.3- 3.5 | <100ppm | <100ppm | 3.40 |

The same type of soil also found in Sarilamak sub-district and Limo Situjuh Nagari sub-district, 50 Kota regency. This soil has the same physical shape with soil in Solok regency and local communities there also call as napa soil. The result of research by Mawardi and Bahrizal, et al (2021) was obtained composition of napa soil in 50 Kota regency [2], West Sumatra using XRF analysis can be seen in Table 2.

Table 2. Content Analysis of Napa Soil by XRF

| Location without Napa | SiO_2 (%) | Al_2O_3 (%) | Fe_3O_3 (%) | TiO_2 (%) | CaO (%) | K_2O (%) | Na_2O (%) | $\text{SiO}_2/\text{Al}_2\text{O}_3$ |
|---|-----------------------|--------------------------------|--------------------------------|-----------------------|---------------------|-----------------------------|------------------------------|--------------------------------------|
| Kec.Sarilamak Kab.50 Kota | 66.21 | 19.42 | 2.982 | 0.913 | <100ppm | 19.832 | <100ppm | 3.40 |
| Kec. Situjuh Limo Nagari Kab. 50 Kota | 68.70 | 21.24 | 2.168 | 0.734 | <100ppm | 6.832 | <100ppm | 3.23 |

This soil was located almost in the entire areas of West Sumatra, such in the hills where located in Solok regency, 50 Kota regency, Pesisir Selatan, and Tanah Datar regency. These soils derived from rocks *feldspatik* weathering which move away from its host rock because of exogenous force crust.

Mawardi, Hary Sanjaya, and Rini Sundari (2014) has conducted the research on characteristics of napa soil in 50 Kota regency with FT-IR instrument. FT-IR spectra of napa soil in Situjuh Limo Nagari district, 50 Kota regency can be seen in Figure 2. Based on data of FT-IR spectra in Figure 2 can be determined functional groups of napa soil. At the peak area of 3619.16 cm^{-1} occurs stretching

vibration group -OH that bound to the octahedral Al atoms on the surface or in between layers of silicate. In the area of 693.74 cm^{-1} occurs stretching vibration of Si-O and 911.18 cm^{-1} are Al --- OH stretching vibration. In the area of absorption peaks 828.59 and 999.54 cm^{-1} occurs symmetric and asymmetric stretch of O-Si-O or O-Al-O.

Minerals that contain silicate ions $[\text{SiO}_4]^{4-}$ called silicate minerals which are the dominant mineral in the earth's crust. Zeolites are aluminosilicate with framework structure are has pores contain large cations (Ca^{2+} , Na^+ , K^+) and has water molecules [12].

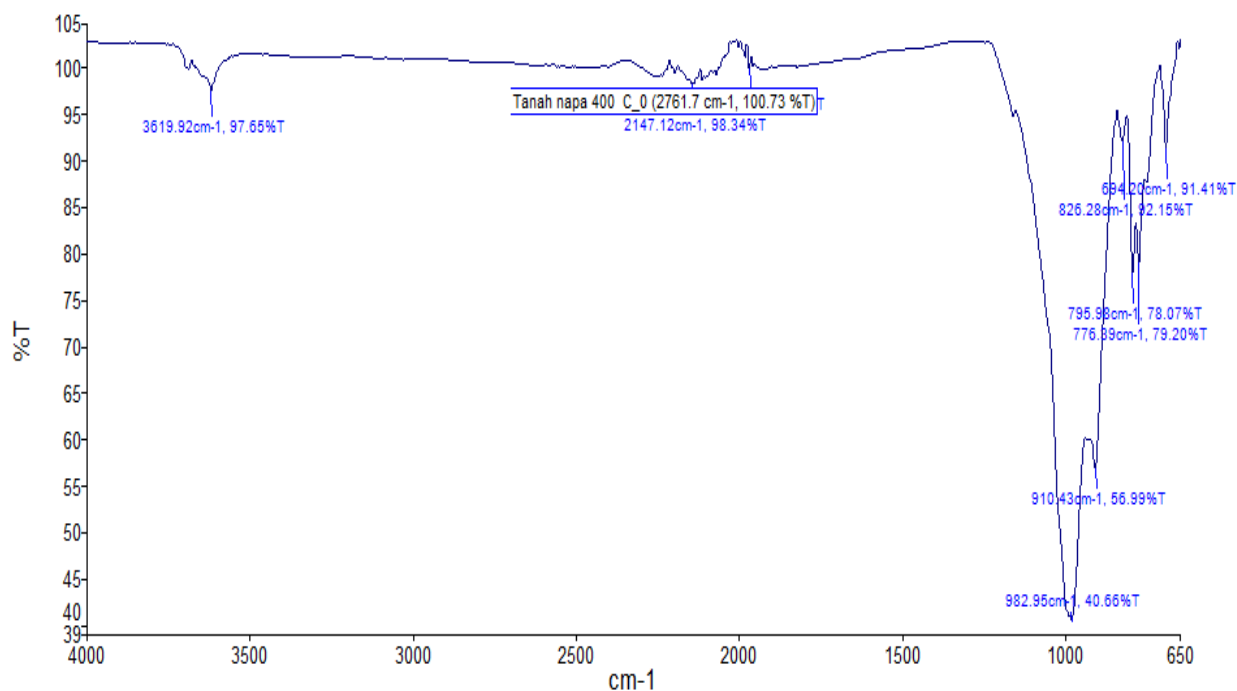


Figure 1. FT-IR Spectra of Napa Soil in Situjuh Limo Nagari District, 50 Kota Regency

According to Martin (2011) the structures with functional groups that may be contained in the zeolite are: various hydroxyl functional groups and acidic zeolites. (A) Bronsted acid-hydroxyl group; (B) silanol functional groups; (C) aluminum group in the extra frame; (D) Lewis acid groups in the framework of the defects seen in Figure 2.

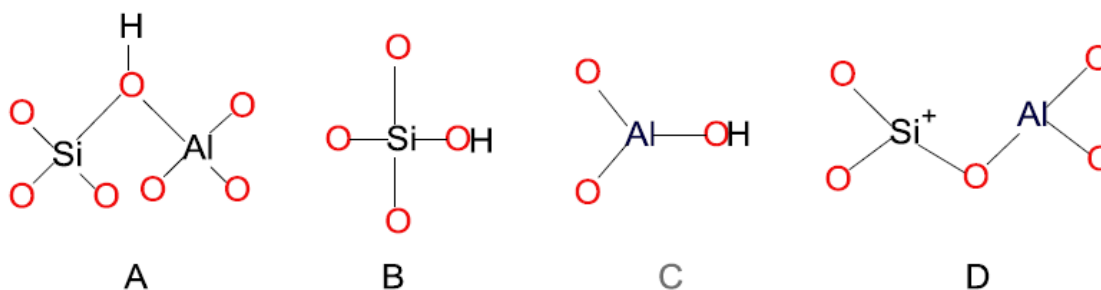
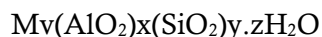


Figure 2. Chemical Structures of Zeolit

Based on the chemical composition and functional groups of absorption peaks in napa soil can be classified to the aluminosilicate minerals. One of aluminosilicate minerals is zeolite, a mineral found in rocks from natural sedimentation processes that have conducted research for use as a cation

exchange material. Zeolite firstly discovered in 1756 by Axel Freiherr Fredrick Cronstedt, a mineralogy from Sweden. According to the Greek word "zein" means boil and "lithos" means stone, to describe a group of silicate minerals that removes water when heated and looks like boiling, and can melt become a white glass [13]. Zeolites have the following general formula.



Where M is an alkali or alkaline earth cation, $v=x$ for monovalent cations 1 and $v = 2 \frac{1}{2}$ for monovalent cations 2.

Based on zeolite formation process can be divided into two, they are natural zeolite and synthetic zeolite. Natural zeolites are formed over thousands of years in the form of sediment that occurs due to volcanic with rain water, ground water, or sea water [14]. Based on the chemical composition and functional groups of peaks that found in the soil absorption of napa soil then it can be classified to the zeolite. Zeolites are generally used as an ion exchange in wastewater treatment for the purpose of separation of ammonium ions, heavy metals and radioactive waste.

b. Adsorption

Adsorption is the process of absorption particles on a surface. Adsorbed substance called the adsorbate and adsorbent substance called adsorb or substrate. Behind the process of adsorption is called desorption [15]. Adsorbent generally is solid, such as zeolites [16].

Type of adsorption that commonly known are chemical adsorption (kemisorpsi) and physical adsorption (fisorpsi). Chemical adsorption (kemisorpsi) is adsorption by the chemical force and followed by a chemical reaction. This adsorption cause formation of chemical bonds. Then adsorption of this type will produce a reaction product in a new compound. Chemical bonding that occurs in very strong kemisorpsi binding molecules of gas or liquid with the solid surface, so it is difficult to remove (irreversible). While the physical adsorption (fisorpsi) is adsorption that occurs because of the forces of physics. The molecules are adsorbed in physics are not fastened to the surface and usually occurs a rapid behind process (reversible), so it is easy to be replaced with another molecule. Adsorption of physics is based on the van der Waals forces and can occur on the polar and non-polar surface [17].

c. Ion Exchange Characteristics of Zeolites

Ion exchange is a process which ions are in the pores of insoluble solids that can be exchanged with ions which carried by the solution during contact with that solids. Ion exchange characteristics of clays and zeolites have been identified and studied for more than a century [4]. There are many types of ion exchange from aluminosilicate minerals such zeolite which have three-dimensional structure and clay minerals.

CEC is one of soil parameters that depend on the ability of the soil to attract and retain the exchangeable cations (K^+ , Na^+ , Mg^{2+} , Al^{3+} , etc.). Many factors affect CEC soil especially pH of soil, texture and organic matter content is an important parameter and correlated with CEC [18]. The increasing of pH, organic matter content, and clay/loam cause high CEC due to the increasing amount of negative charge on the surfaces that attract and retain cations.

The pure silicate zeolite framework are neutral. Negative charge occurs on aluminosilicate framework resulting from the substitution of Si (IV) by Al (III), this structure can be seen in Figure 4 [19]. This substitution is commonly called isomorphic substitution in the structure (permanent charge /stable). Isomorphic substitution is replacing one atom to another atom of the same size in the crystal lattice without disrupting or changing the crystal structure of the mineral. Negative charge is formed

when the cations is similar to the substitution of positive lower charge cation to a higher positive charge. Isomorphous substitution occurs only in cations with similar ionic radius.

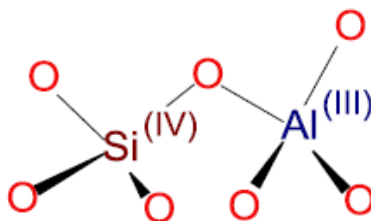


Figure 3. Si Substitution of Chemical Structure by Al.

CEC of zeolite refers to the total CEC, which is defined as the number of exchangeable cations in the unit of weight equivalent per unit weight of natural minerals. CEC indicates the number of cations that can be accommodated by zeolites [20].

d. Determination of CEC with Barium Chloride Method (BaCl_2)

Various methods have been conducted to measure the CEC and exchangeable cations. The most commonly used method is based on the soil cation exchange with saline solution containing a known concentration of cations that are not contained in the soil and detection of cations with standard techniques such as atomic absorption, spectrophotometry or titration [9]. In this research, the determination of CEC conducted use barium chloride (BaCl_2) method. This method was adopted and accepted as an international standard method. This method has advantage that it can be repeated and can directly measure the CEC [21]. This method was introduced firstly by Gilman in 1979. In 1986 Gillman and Sumpter made changes together. In 1994 has been tested and standardized so that it has a lot of implementation and the method becomes ISO 11260 [22]. While the deficiency of this method is take a long time, requires specific equipment, and produces toxic waste.

e. Complex Formation Based On Hard and Soft Acids (HSAB)

The strength interaction of adsorbate with the adsorbent is influenced by the characteristics of the adsorbate and adsorbent. Symptoms that commonly used to predict which components absorbed more strongly are polar adsorbent with its adsorbate. If its adsorbent is polar, so the polar component will attached more tightly than the less polar component. The strength interaction also influenced by the hard-soft of the adsorbate and adsorbent. The hard characteristics of cations are connected with the term *polarizing power cation*, the ability of a cation to polarize anions in a bond. Cations that have a large *polarizing power cation* tends to be hard. A high *polarizing power cation* characteristics owned by the metal ions with the size (radius) small but large charge. Otherwise low *polarizing power cation* characteristics owned by the metal ions with the big size but small charge, so they are classified as weak ion [23].

According to the Hard Soft Acid-Based (HSAB) principle, hard acid will interacts with hard alkali to form complex, as well as a soft acid with a soft alkali. Interaction of hard acid with hard alkali is ionic interactions, whereas the interaction of a soft acid with a hard alkali, it interactions is more covalent [24].

f. Atomic Absorbion Sphectrophotometer (AAS)

Atomic Absorption Spectrophotometry (AAS) is an analytical technique that is commonly used for determination of metal elements and metalloid based on the absorption of radiation by unpaired atoms of the metal element. The principle of SSA technique is the absorption of light by atoms. The atoms

absorb light at specific wavelengths, depend on the characteristics of the element. Absorbed light has enough energy to cause the atoms undergo electronic transitions from ground level to an excited level. Electronic energy levels of an element is specific, so that the energy absorbed cause transitions are also typical.

SSA technique is used for the determination of metals because it has a high degree of accuracy, precision, sensitivity and good selectivity, and low operating rates [25]. Monochromatic in SSA is a major requirement. SSA technique requires specific cathode lamp (*hallow cathode*). The concentration of the sample can be measured by extrapolating the absorbance values on the standard curve is a curve between the absorbance with concentration [26].

2. Experimental Section

2.1. Materials

Glass apparatus, vaporizer cup, sieves, a set of reflux tools, Shaker (180 rounds per minute), analytic Scales (250 gram capacity, resolution 0.01 g), Mortar and pestle, Magnetic stirrer, Oven, SSA SHIMADZHU type AA 660, aquades; $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$; ethanol 90%; $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; chief liquor magnesium 1000 mg/L.

2.2. Preparation of Napa Soil

2.2.1. Purification of Napa Soil

Napa soil sample in the form of lumps are crushed using a pestle and mortar until smooth and sieved using a 100 mesh sieve. Napa soil that has been prepared with a size of 100 mesh is taken as 150 grams, refluxed with 600 ml of aquades in the distillation flask (1000 mL) for 4 hours, then decanted. After that it is refluxed again with 600 ml of aquades for 4 hours and then decanted. Then dried it in an oven for 3 hours at a temperature of 105°C [2].

2.2.2. Napa Soil Treatment with Acid Peroxide (H_2O_2) 20% (v/v)

The activation process is done by the sedimentation method where the dry napa soil was smoothed using a muller porcelain and sieved to a certain size, as much as 100 g of napa soil passes 100 mesh sieve, put into 1000 mL of aquades while stirring with a magnetic stirrer for 3 to 4 hours. Some of H_2O_2 solution 20% was added gradually to the mixture to remove organic substances, it were characterized by there're no air bubbles formed. The mixture was stirred for 12 hours and allowed to stand until the napa soil settles, then top part is decanted. In the sediment is added back distilled water and stirred for 1 hour back, settling back and decanted. The above treatment was repeated 3 times to remove residual H_2O_2 then filtered and dried.

2.3. Determination of CEC Napa Soil in Optimum Condition

Put each 2 grams of pure napa soil into 8 pieces erlenmeyer then contacted with 20 mL of barium chloride at concentration of 0:05 M, 0.1 M, 0:15 M, and 0.2 M and shaken using a shaker for 120 minutes. Furthermore, decanted and then added 40 mL of barium chloride dihydrate 0:05 M and stir in the shaker and decanted again. Excess of barium from napa soil samples can be rinsed with ethanol 90% by adding 40 mL of ethanol and decanted, repeat twice. After rinsing, add magnesium sulfate hepta hydrate solution with 0.2 M concentration of 100 mL and stir on a magnetic stirrer to replace barium in napa soil at each erlenmeyer. Move the filtrate by filtering using Whatman filter paper No.1 or equivalent with it. Next, determined the concentration of Mg^{2+} which is not adsorbed by Atomic Absorption Spectrophotometer at a wavelength of 285.2 nm [27].

Put each 2 grams of pure napa soil into 8 pieces erlenmeyer then contacted with 20 mL of barium chloride dihydrate with optimum concentration and shaken using a shaker for 120 minutes. Then, decanted and then added 40 mL of barium chloride dihydrate 0:05 M and stir in the shaker and

decanted again. Excess of barium from napa soil samples can be rinsed with 90% ethanol by adding 40 mL of ethanol and decanted, repeat twice. After rinsing, add magnesium sulphate solution with a variation concentration, 0:05 M, 0.1 M, 0:15 M, and 0.2 M of 100 mL and stir on a magnetic stirrer to replace barium in napa soil at each erlenmeyer. Move the filtrate by filtering using Whatman filter paper No.1 or equivalent with it. Next, determined the concentration of Mg^{2+} which is not adsorbed by Atomic Absorption Spectrophotometer at a wavelength of 285.2 nm [27]. After obtained the optimum conditions, the results are compared both fresh napa soil and napa soil activation.

3. Results and Discussion

3.1 Optimization Concentration of Barium Chloride Solution

In this research, the variations concentration of barium chloride solution with a concentration of 0.05 M, 0.1 M, 0.15 M and 0.2 M was conducted. The influence of the concentration in the optimization concentration of $BaCl_2$ solution can be seen in Figure 4.

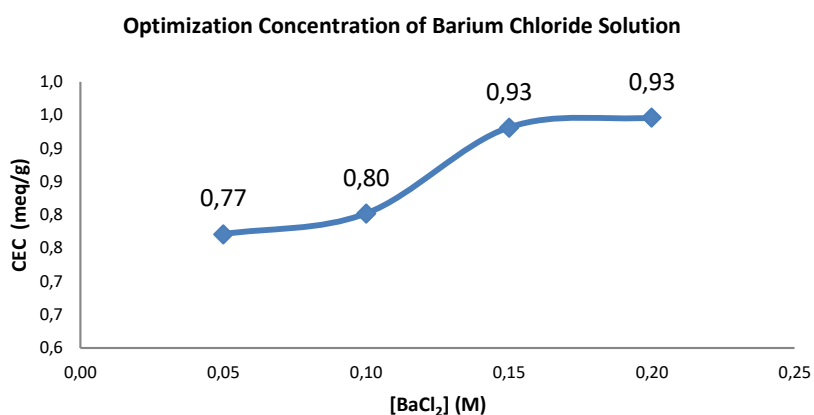


Figure 4. Concentration Effect of $BaCl_2$ Solution for CEC Value of Napa Soil

Based on data could be seen the increase value of CEC napa soil from barium chloride solution concentration of 0.05 M. The increase of barium chloride solution concentration show the tendency of napa soil CEC pattern which tends to rise and reaches the optimum value at a concentration of 0.15 M. This shows that the system has reached equilibrium.

If the concentration is added so significant increase in the value of CEC did not happen again. This is because the Ba^{2+} ions have saturated all the negative charge of napa soil. The results show the value of CEC napa soil was 0.93 meq /g. According to Mumpton (1996) cation exchange reaction is not perfect if it is not used excessive concentration of the solution to force the equilibrium to the right. The increasing concentrations of $BaCl_2$ solution will increase the number of Ba^{2+} ions which will replace the cations in napa soil. Addition of concentration causes the dominant reaction towards the right, at concentrations approached the cation exchange capacity of the sample.

The increasing concentration that used, the higher value of CEC will get. This is due to the increasing concentration of barium chloride solution that used, so the number of Ba^{2+} ions which can saturate all the negative charge on the ground will increase. At low concentrations, amount of particles that collide with the particles are fewer particles, so that liquid-solid phase equilibrium will occur, thus the amount of cations which replaced by Ba^{2+} ions are less than ion exchange capacity of Ba^{2+} cations that located in soil samples. The concentration of exchanged ion will be massive because of the higher concentrations [28].

b. Optimization Concentration of Magnesium Sulfate Solution

Variations in the magnesium sulfate solution concentration that used was the concentration of 0:05 M, 0.1 M, and 0.2 M 0:15 M. From the data in Figure 7 can be seen the effect of magnesium chloride concentration of CEC napa soil. Generally, the higher concentration will affect the increasing of CEC value from 0.05 M.

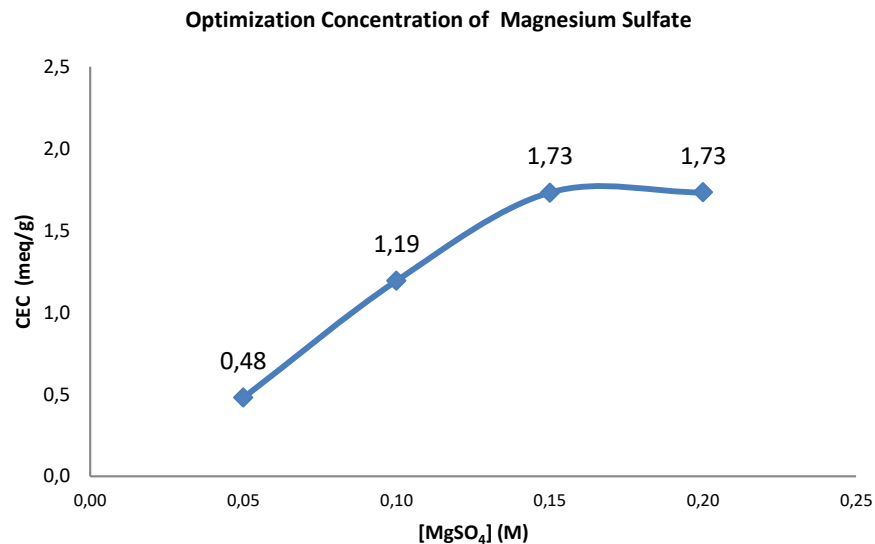


Figure 5. Concentration Effect of MgSO₄ Solution for CEC Value of Napa Soil

The increasing of magnesium sulfate solution concentrations showed the tendency of increasing CEC value that tends to rise and reach the optimum value in the magnesium sulfate solution concentration of 0.15 M. This is because the higher concentration, the more collisions will occur, so that Mg²⁺ ions replace Ba²⁺ ions in the napa soil and push the reaction equilibrium towards the right direction. If increased concentration of magnesium sulfate solution conducted then it was not give the increasing of CEC value significantly.

c. Determination of CEC Napa Soil in Optimum Condition

Determining the CEC value of napa soil from the Situjuh Limo Nagari District in optimum condition with fresh napa soil samples, purified samples, and given treatment samples with an acid as in Figure 6. From the results show that the CEC value of purified napa soil has a higher value than napa soil which given treatment with acid and fresh napa soil. It was because samples of napa soil which purified by refluxing purpose to remove polluter such as clay and salts are dissolved in water. Thus simplifying the exchangeable ions contained in napa soil to be exchanged.

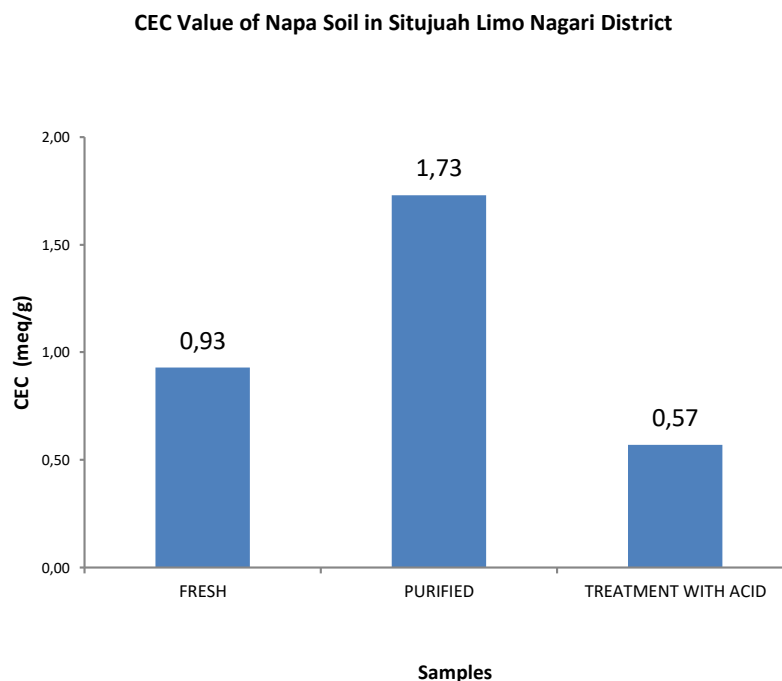


Figure 6. CEC Value of Napa Soil in Situjuh Limo Nagari District with Fresh Napa Soil Sample, Purified Sample, and Given Treatment with Acid in Optimum Condition

According Susetyaningsih (2009) CEC of a sample is strongly influenced by the simplicity of alkali metals to be exchanged, which the way to achieve it was purified. According Supandi (2010) one of the way that can be conducted for the purification is the reflux process. It can eliminate polluter in napa soil samples which caused the simplicity of alkali metals and alkaline moving and interchangeable. Polluters that had to be lost is the polluter materials such as clay material, felspar, and salts that mixed as other polluters so it can make cations can be exchanged easily.

Napa soil treatment with acid peroxide 20% can decrease the CEC of napa soil. According to Ross, D. S and Quirine Ketterings (2011) the CEC value of napa soil will decrease if occurs acidification on the ground. Treatment with acid will also increase the Si/Al ratio of silica alumina compounds as reported by Mawardi, Hary Sanjaya and Arwita PU (2014) that showed treatment with acid using H_2O_2 20% increase Si/Al ratio. After given a treatment with hydrogen peroxide, levels of alumina (Al_2O_3) fresh napa soil decreased to 23.313% and after given treatment with acid, the levels decreased to 19.37% cause of dealumination. The comparison of Si/Al fresh samples with given hydrogen peroxide treatment 20% increased from 3.01 to 3.84.

To reinforce the results, analysis is conducted using FT-IR analysis. Spectroscopically, aluminosilicate minerals can be observed at wave number 300-1300 cm^{-1} . That wavelength is a major area of uptake tetrahedral aluminosilicate constituent of the main components, SiO_4 and AlO_4 . While the results of FT-IR spectra analysis can be seen in Figure 7.

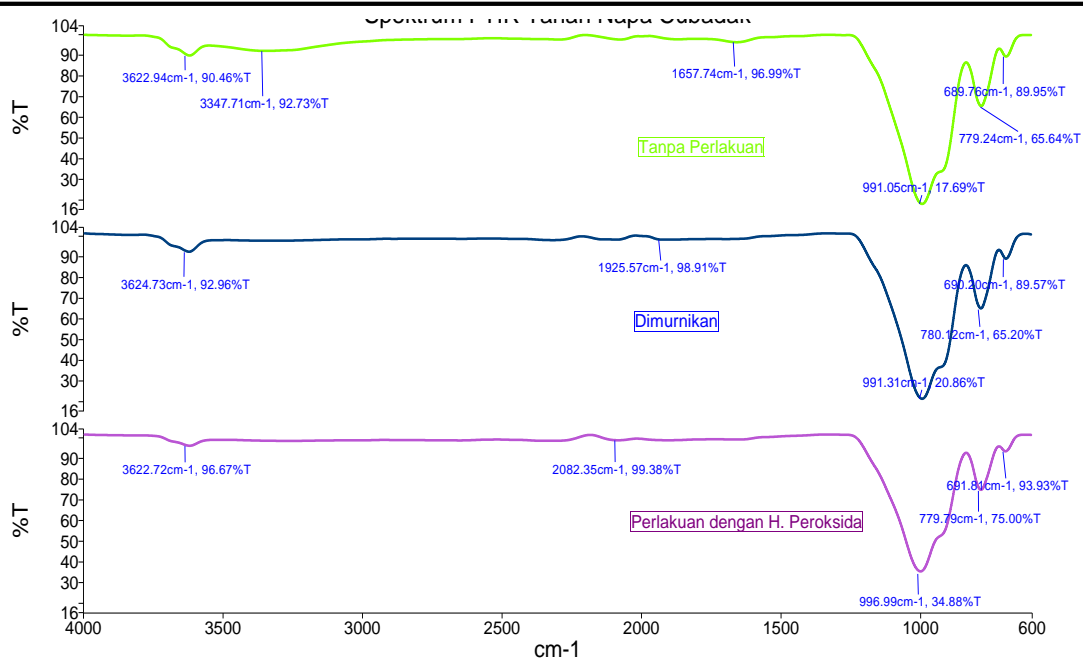


Figure 7. FT-IR Spectra of Napa Soil in Situjuh Limo Nagari District, 50 Kota Regency, Fresh Napa Soil, Purified Sample, and Given Treatment With Acid

According to Weitkamp, J. and Puppe, L, (1999) band at 300-420 cm^{-1} is an area to *pore opening* in *external linkage*, the span of symmetry O-Al-O or O-Si-O in the internal tetrahedral will appear at 650 -720 cm^{-1} , while for *external linkage* will appear in the 750-820 cm^{-1} , bending Si-O or Al-O will appear on the region 420-500 cm^{-1} and adsorbant in range asymmetry area. In the asymmetric stretch of napa soil shown on band 991 cm^{-1} for fresh napa soil samples and purified napa soil whereas napa soil which given treatment with an acid is shown on band 996 cm^{-1} .

The dealumination can be observed from a friction in the vibrational spectra of internal and external. If dealumination process is happened, then there will be a friction of spectra towards higher wave numbers in the internal stretching vibration band of zeolite and friction of spectra towards lower wave numbers on external vibration. This is in a row with the decrease in the amount of Al in the structure [29]. From the results that suitable with the explanation, there was a friction in the internal vibration band of napa soil is 991 cm^{-1} becomes 996 cm^{-1} on the dealumination of napa soil. Dealumination of napa soil by hydrogen peroxide as reported by Mawardi, Hary Sanjaya, and Arwita PU (2014) cause napa soil loss the negative charges on the framework which is characterized by increasing Si/Al ratio and shows a low CEC values [30].

Ertan and Ozkan (2005) made modification with given acid treatment in natural zeolite from Gordes, Turkey [31]. That natural zeolite was rich of clinoptilolite and has a chemical composition (% heavy oxide) Al_2O_3 14.1, 64.2 SiO_2 , MgO 1.8, 1.7 Na_2O , K_2O 5.3, 1.0 CaO, Fe_2O_3 1.8, and 10.3 H_2O . Natural zeolite from Turkey rich in Clinoptilolite, when given treatment with acid by using HCl, H_3PO_4 , H_2SO_4 , and HNO_3 , decreased the amount of cations.

Activation by using acid can cause an increase in ratio of Si/Al cause of dealumination. Dealumination is a process of reduction both the aluminum in the zeolite and on the surface framework. Dealumination may occur because H^+ in acid will trigger the discharge aluminum from the zeolite [32].

In this research also conducted the CEC value of napa soil from Sarilamak district in optimum condition with fresh napa soil sample, purified, and given treatment with acid activation. CEC value of each sample is shown in Figure 8.

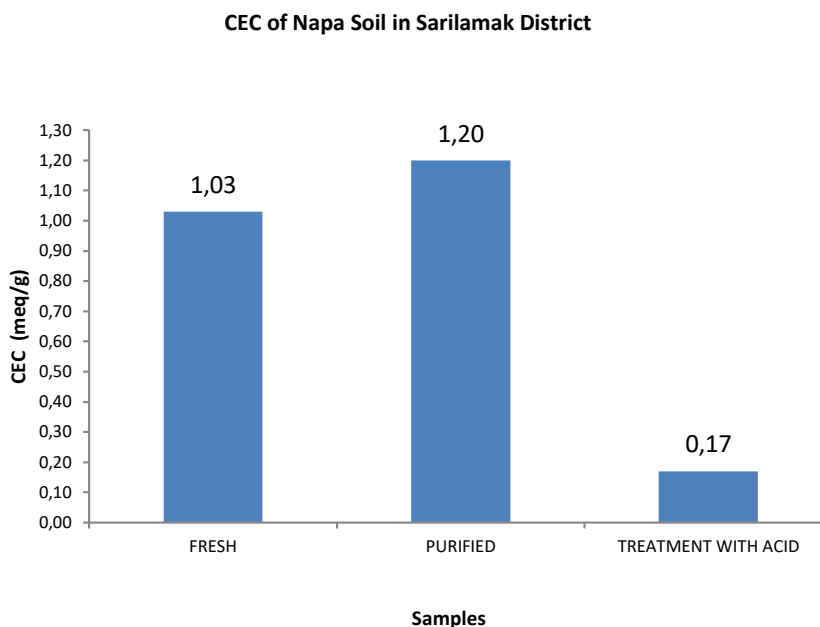


Figure 8. CEC Value of Napa Soil in Sarilamak District with Fresh Napa Soil Sample, Purified Sample, and Given Treatment with Acid in Optimum Condition

From the data it can be seen that the CEC value of napa soil from Sarilamak district have the same pattern with napa soil from the Situjuah Limo Nagari district. Purified napa soil has a high CEC values than fresh napa soil and given treatment with acid. That is because purification can remove pollutants in napa soil, making it easier for exchangeable cations of napa soil to be exchanged. Treatment with acid decreased the CEC value of napa soil cause of dealumination.

4. Conclusion

Based on the results dan discussion that have been conducted, can be concluded some point, they are concentration of Barium chloride as saturated ion and magnesium sulfate as a substitute ions affect the CEC value and the optimum conditions obtained barium chloride at concentration of 0.15 M and the optimum conditions of magnesium sulfate at concentration of 0.15 M. Napa soil that had been purified have highest CEC values. CEC values of purified napa soil from Situjuah Limo Nagari district and Sarilamak district were 1.73 meq/g and 1.2 meq/g.

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