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The Influence of pH System on Adsorption Magnesium (II) by Bentonite.

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ABSTRACT

The objective of this research was to determine the Bentonite-Signa ((B-S) and pillaring Al bentonite (B-Al/400°C) characters that can be used to adsorb Mg^{2+} ions. Laboratory experimental study consist of two stages, characterization phase of B-S and B-Al using *Spectrophotometer IR* Buck Scientific – 500, *X-Ray Diffraction X'PERT* Phillips, *Gas Sorption Analyzer* Quantachrome NovaWin2, *Scanning Electron Microscope*, and *Atomic Absorption Spectrometer (AAS)* Perkin Elmer AA-100 to showed adsorption capacity for two adsorbents. The result of this research showed: 1). B-S and B-Al have different of interlayer as 12,4374 Å (B-S) and 9,3047 Å (B-Al); surface area 24,78 m^2/g (B-S) and 217,021 m^2/g ; total pore volume of radii which smaller than 1001,9 Å (B-S) and 1273,1 Å (B-Al), respectively. 2) The difference in the number of active sites of two adsorbents, cause the adsorption capacity of B-S is greater than that of B - Al. 3). At the system of pH 5, 6, 7, and 9 the adsorption capacities of B-S is greater than B-Al for Mg^{2+} , respectively.

Keywords: bentonite, adsorption capacity, magnesium ion.

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INTRODUCTION

Silicate clay minerals consist of two groups, namely crystalline and amorphous. Crystalline group consists of three types, namely: two-layer type or 1: 1 (eg, kaolinite: composed one layer of silica tetrahedrons and one layer alumina octahedrons); three-layer types or 2: 1 (eg montmorillonite: composed two layers of silica tetrahedrons and one central layer alumina octahedrons), and mixed layer types or 2: 1: 1 (eg, clinochlore). Three-layer types as well as bentonite / montmorillonite is composed of crystals that do not expanding and expanding (swelling). Among the mentioned type, which can be easily to modified is three-layer types expanding, as is the case of Indonesia and Wyoming bentonite. Both have major components montmorillonite and are easily expands when interact with water so that it can be applied as adsorbents and catalysts.

Indonesia's natural bentonite containing sodium or calcium ions thus known as the Na-bentonite or Ca-bentonite. Some areas such as in the area of East Java which contains bentonite is Ponorogo, Pacitan, Trenggalek, Tulungagung, Ngawi, and Malang. Among the areas that had been mined in the production of 212 900 m³/year at Ponorogo and Pacitan with production of 1080 tons / year (www. Mining EastJava, 2008). Wyoming bentonite containing ions of Na⁺ and Ca²⁺, Mg²⁺ ions and beidellit. (Smart & Moore, 2005). The bentonite type when used as an adsorbent will be able to adsorb metal ions and organic compounds through ion exchange, both cations and anions in the interlayer position (Grim, 1968).

In order to be used as a good adsorbent, modifications have been carried out in various ways. Modification can be done by reducing the swelling properties and increase surface area, both physically and chemically. Chemical activation efforts are being developed to improve the ability of bentonite as an adsorbent is the addition of an acid or base, for example HCl or NaOH, and pillaring interlayer bentonite.

The ability of bentonite to adsorb cation cause bentonite initially have a neutral charge, can turn into a negative charge in the presence of substitution isomorphous, that is change of Si from tetrahedral by Al³⁺ or Al from octahedral replaced by Mg²⁺, but it fixed the pH and structures (Tan, 1982). The charge can change because of all the hydroxyl group is located in side below the surface area covered by a network of oxygen atoms. Isomorphous substitution causes a neutral charge become negative charge that distributed on the oxygen of the surface layer and is balanced by adsorbed cations. Cations can be adsorbed bentonite is: Na⁺ as bentonite - Na⁺, Ca²⁺ as bentonite - Ca²⁺, and Mg²⁺ as bentonite-Mg²⁺

The change of the ion depends on the size and valence of ions (comparable sized ions). Can be noted that the Na⁺ and Ca²⁺ is almost the same size of Na⁺ = 97 pm and Ca²⁺ = 99 pm (Manku, 2002) and can substitute for each other in spite of the higher valence of Ca²⁺. While the size of aluminum ions are between Si⁴⁺ and Mg²⁺ or Fe³⁺ and can be replaced by the ions with varying ease. Among the earlier compounds, potential ionic Al³⁺ > Mg²⁺ > Na⁺; so in a period the polarization of Al³⁺ = 56/3; Mg²⁺ = 28/2; and the polarization of Na⁺ = 9. Therefore according Fayan, the size of ion Al³⁺ < Mg²⁺ < Na⁺ (Effendy, 2008).

In addition to the negative charge, bentonite can also have a positive charge. Positive charge comes from the addition of H^+ ions to hydroxyl groups and this mechanism depends on the pH and the valence of the metal ions. Based on the character of bentonite as an adsorbent, we conducted research on the adsorption capacity these materials to be used adsorbed magnesium ions that influence pH system. Magnesium ions to be used as ions adsorbed due to possible occurrence of a change that is isomorphic substitution of Al octahedral structure by magnesium ions without changing the structure of bentonite (Tan, 1982). Thus bentonite modified in this way is expected to be classified as microporous or mesoporous materials that are no swelling any more so that it can be used as an adsorbent.

METHODS

Characterization of adsorbents

Characterization was conducted to determine differences between the physico-chemical properties of bentonite Sigma (BS) and the result of the pillaring B-S namely B-Al. Using X-Ray Diffraction type Phillips X'Pert the difference of interlayer distance in BS and B-Al may be obtain. Gas sorption NovaWin2 Quantachrome Analyzer to find out the surface area, pore radius and pore volume of BS and B-Al is used. The spectrophotometer is used to find out similarity and difference of main functional groups and finger print in B-S with B-Al used Buck Scientific IR Spectrophotometer - 500, EDX Scanning Electron Microscope is used to see the surface and mass compoud in the crystal of BS and B-Al. Adsorbent B-Al made by adopting the method Tomul and Balci (2007) that calcined at a temperature of $400^{\circ}C$.

Adsorption process

The process of adsorption isotherms performed with adsorbent BS and B-Al. Adsorbate in this study are Mg^{2+} ions obtained from dilution of Mg^{2+} 200 mg / L. Dilution is done with the addition aquademineralisata to make the necessary concentration. To determine the initial concentration and the final concentration of the adsorbate used Atomic Absorption Spectrometer (AAS) Perkin Elmer AA-100.

The amount of substance adsorbed measured by AAS, and calculated by the equation:

$$q = \{(Co - Ce) V\} / M$$

with q = substance adsorbed mg / g, Co = initial concentration of the solution, Ce = equilibrium concentration in mg / L, M = g bentonite is used, V = vol. mL solution.

RESULTS AND DISCUSSION

Characterization of the adsorbent

Characterization to determine the value of *d-spacing* (basal spacing: distance between interlayer), I (relative intensity), and 2θ (diffraction angle); using X-ray diffraction instrument types with a Phillips X'Pert wavelength $K\alpha = 1.54056 \text{ \AA}$ of Cu metal. Data

obtained from X-ray diffraction was measured on a Phillips X'Pert type 2θ : $0^\circ - 100^\circ$. The resulting diffraction pattern can be seen in Figure 1.

Based on the data obtained from X-ray diffraction the difference of interlayer distance in B-S (12.4374 \AA) is longer than the B-Al (9.3047 \AA). Differences may occur due to the interlayer cause of different atomic positions in the structures. At the B-S position $2\theta = 7.1015^\circ$ with an intensity of 36.82% has 12.4374 \AA of distance between interlayer that characterize Na-bentonite; on B-Al positions diffraction $2\theta = 9.4972^\circ$ with an intensity of 7.55% has 9.3047 \AA of the distance between interlayer. The different of the positions diffraction between two bentonite indicate the influence of bentonite constituent atoms (atomic positions in the structure) is different and it affects the intensity of X-ray diffraction.

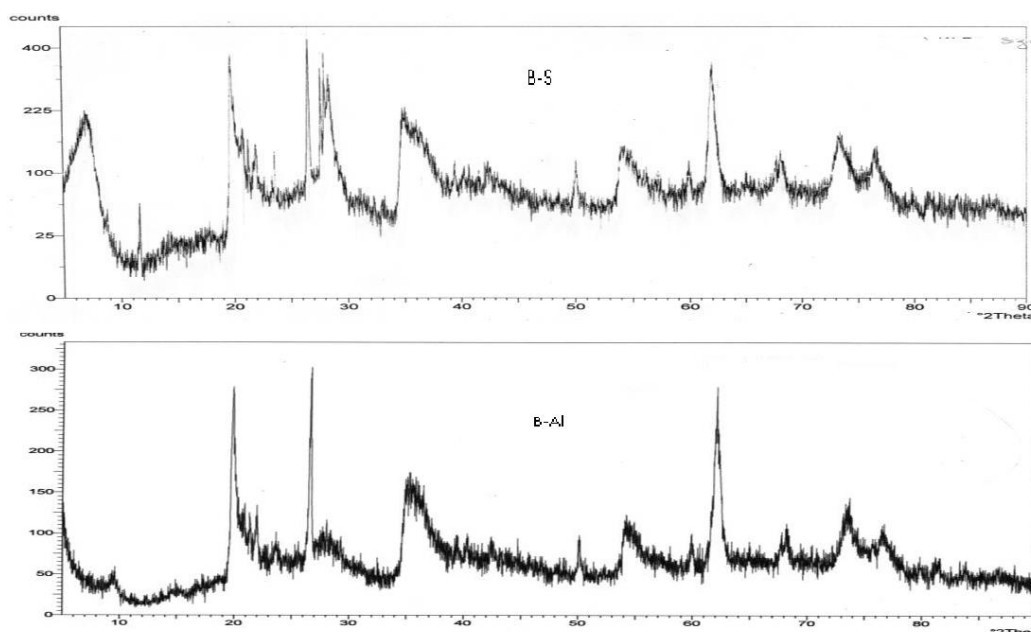


Figure 1: The Difraktograms of B-S and B-Al with 2θ (X) counts (Y).

At the B-S, the long distances between interlayer due to the presence of H_2O molecules. The data obtained in accordance with the statement of West (1988), that the difference between interlayer is affected by the number of atoms and atomic positions in the cell.

In the B-Al, addition of pillared element during pillarization causes the change of surface area and pore radii are different than the BS. Added pillared element Al result in decreased interlayer as proposed by Smart (2005), namely that the presence of isoelektron such Al^{3+} will result in a decrease of the radius corresponds to an increase of positive charge.

In the SiO_2 layer is seen that the distance interlayer for B-Al (4.4764 \AA) is smaller than the B-S (4.4834 \AA), whereas the intensity of X-ray diffraction BS is smaller than the B-Al. The intensity which is the inverse of the value d means that the number of electrons contained by B-Al is less than the number of electrons that are owned by the B-S, so that the distance interlayer of B-Al is smaller than the B-S. Reduced electron due to the substitution of Al pillaring on SiO_2 . This is in accordance with the opinion of Tomul and Balci (2007) which states that the number of species intercalated cause as across distances that affect

the surface area and the strength of the crystal structure. The crystal structure relates to the number of electrons contained at a certain point and is known as the intensity I (Ismunandar, 2006).

In Al_2O_3 structure shows that the distance on B-Al (2.5635 Å) is smaller than the BS (2.5743 Å), and the intensity value B-S is smaller than the B-Al. Based on the intensity value seen that the biggest d value B-S has a low intensity, which means that there is the effect of electrons in Al_2O_3 that causes great value of d . This possibility are due to the presence of water molecules on the structure of interlayer that prevents electrons to form strong bonds with SiO tetrahedra.

The difference of interlayer due to pillarization will cause the size of the pore radius and surface area different from the BS and B- Al. To determine the nature of the two adsorbents, followed by studies using other instruments that Quantachrome Analyzer Gas sorption isotherms NovaWin2 by BET adsorption. Using the BET adsorption isotherm can be known surface area, pore radius, and pore volume.

The results showed that the highest relative pressure (P / P_0) 9.90338×10^{-1} atm and the maximum adsorption capacity of B-S = 77.5421 cc / g. After the achievement of these conditions the desorption was done and which resulted in hysteresis loops that occur in the relative pressure of 5.02498×10^{-1} atm up to 4.48912×10^{-1} atm with a gas volume of each desorption are 15.5011 cc / g and 11.6992 cc / g, respectively.

In total pore volume of 1.199×10^{-1} cc / g, an average pore size of B-S is 99.2186 Å with a surface area of 24.178 m² / g.

Analysis of the B-Al produces the maximum adsorption capacity = 112.3119 cc / g at the relative pressure = 9.9241×10^{-1} atm. After this condition, the desorption process produces hysteresis loops at relative pressures between 5.01630 to 4.00797 atm with the volume of 96.31215 to 77.8521 cc / g. In the total pore volume of 1.737×10^{-1} cc / g, an average pore size of B-Al is 16.0110 Å with a surface area of 217.021 m² / g.

Based on the adsorption desorption process can be noted that both types of bentonite has a pore group E of the classification of de Boer is a pore that has the form of an ink bottle (Oscik, 1982). When viewed from the pore size, the B-S has a pore size that can be classified as mesoporous; while the B-Al classified as micropores (Smart, 2005).

Characterization using infra red spectrophotometer instrument Buck Scientific type 500 is used to determine the main functional groups and fingerprints region on B-S and B-Al. Spectral data obtained for B-S and B-Al in Figure 2. shows that B-S has a spectral peak lies in the wave number (λ -1) 3622.6; 3430.3; 2364.4; 1638.4; 1149.7; 923.2; and 797.8 cm⁻¹. Characteristics of B-Al is located at the peak spectra with wave numbers: 3627.2; 3457.4; 1636.4; 1082.1; 918.5; and 794.3 cm⁻¹.

Using the data of infra red spectrophotometer can be analyzed that the B-S and B-Al have similarities and differences in functional group (wave number 4000-3000 cm⁻¹) and in the fingerprint region (wave numbers 1400-795 cm⁻¹). Similarities and differences in

functional groups showed areas associated with the number of HOH contained bentonite (Tan, 1982). In this region the structure of B-Al is more rigid than the B-S that is reinforced by the wave number 1635 cm^{-1} (deformation of the adsorbed water) which shows the amount of water on the stability of B-Al. Similarities and differences in the fingerprint region can be used to determine the structure of bentonite is related to the tetrahedral layers of SiO_2 and Al_2O_3 octahedral layers.

At the wave numbers $3600 - 3400\text{ cm}^{-1}$ indicates that the B-Al has a strong OH bond or OH due to the vibration of O-Al-OH, or because it has not happened substitution isomorfi on B-S. This is consistent with the statement of West (1988) which states that the peaks in the region $3000-3500\text{ cm}^{-1}$ shows the characteristics of the group OH is strong OH covalent bond, and the location information of the OH groups it depend of water molecules and hydrogen bonds.

In the fingerprint region that at wave numbers $1200 - 1000\text{ cm}^{-1}$ shows the difference in functional group of the octahedral O-Al-OH, or Si-O stretching, stretching Si-O-Si antisimetris owned B-Al and B-S. Changes in the wave numbers indicate a change in bond length O-Al-OH groups due to the substitution of Al on Si tetrahedra. In this area there is a difference of the wave numbers because no pillars in B-S.

At wave numbers $950-847\text{ cm}^{-1}$ represents a group of Al-OH and/or OH-cation deformation. The difference of wavenumber between B-S and B-Al indicate a active site of acid-base Bronsted / Lewis at B-Al. This statement is in accordance with the study by Tomul and Balci (2007) and the theory that the presence of the OH group is open from O-Al-OH causes a negative charge (Tan, 1996; Grim, 1968).

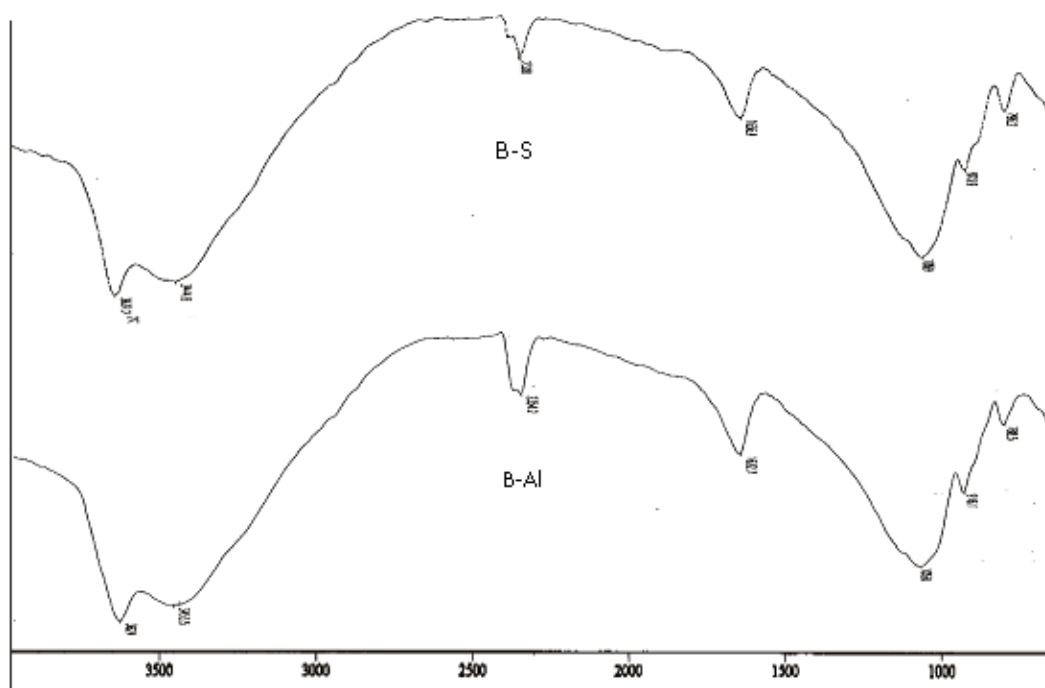


Figure 2. IR Spektra data of B-S and B-Al

At wave numbers $792\text{--}795\text{ cm}^{-1}$ shows the deformation of Si-O. In this area the wave numbers of the B-S smaller than the B-Al due to intercalation of cations pillar. Intercalation of pillar indicated by changes in the composition of the compound as seen in the SEM-EDX and the wavenumber changes in the fingerprint region, especially the changes in the functional group O-Al-OH. These changes occur due to the formation of pillar compound using AlCl_3 0,4 M and NaOH 0.4 M, with the result condensation reactions to form bonds Al-O-Al. The formation of this bond in accordance with Schubert (2000) which states that at a pH below 3 will be formed of metal complex cations $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$, whereas at pH above 3 water ligands will deprotonated.

Characterization is also performed using SEM-EDX instrument to determine the mass of constituent crystals. The data obtained from these instruments show that the B-S is composed of atomic mass O = 52.03%; Al atoms = 10.47%; Si atoms = 37.50%; and the masses in the form of the compound Al_2O_3 = 19.78%; SiO_2 = 80.22%; cation Al = 2.86 and Si = 9.85. Data constituent crystalline mass of B-Al consisting atomic mass O = 51.37%; Al atoms = 16.10%; Si atoms = 32.52%; and the masses in the form of the compound Al_2O_3 = 30.43%; SiO_2 = 69.57%; cations Al = 4.466 and Si = 8.65. Based on this data it can be seen that the difference between the two adsorbents, namely the increase of Al and decrease in O and Si.

Thus both the structural differences relate to the nature of the adsorbent surface in the presence of Bronsted/Lewis acid site between B-S and B-Al. Both of these adsorbents can be classified as type II adsorbent that is specific positive adsorbent, because on the surface contain OH groups although the surface of B-Al more negative due to the presence of Al-pillared.

According to Kiselev (Ošcik, 1982) an adsorbent can be classified in type II cause at $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, H atoms on the surface of H_2O is protonated so strong that d- orbitals of Si are empty. Thus the negative surface of B-S only obtained from protonation of H_2O , while the B-Al surface charge was also obtained from surface at pillar that has four types of active sites, namely Al^{3+} ions (acid); O^{2-} ions (base); OH group is ionized (base); and defect proton (electron acceptor).

Adsorption Process

Adsorption capacity is affected by the amount of adsorbent used, the structure of adsorbents, chemical properties of the surface, the interaction between the adsorbent and adsorbate (Ošcik, 1982). In the adsorption isotherm is also worth noting the interaction time, pH of the system, as well as the chemical properties of the liquid phase is involved in the adsorption process (Barrow, 1973; Shaw, 1983; Alberty, 1982; Rouquerol, 1999).

To determine the ability of the two adsorbent, the adsorption process was undertaken for Mg^{2+} ions. Adsorption isotherm performed at pH 5, 6, 7, and 9 in 40 minutes and for a fixed concentration of $\pm 25\text{ mg/L}$, and the mass of adsorbent $\pm 0.1\text{ g}$. In this case the pH of the solution used for conditioning adsorbate is by adding 0.5 M NaOH solution in order to obtain a pH of 7 and 9; or the addition of 0.1 M HCl to pH 5; and at pH 6 without

adding NaOH or HCl solution. Concentration of the adsorbate before and after adsorption process was measured using AAS.

Results obtained from several different pH systems depicted in Figure 3 with a pH as abscissa and the adsorption capacity as ordinate.

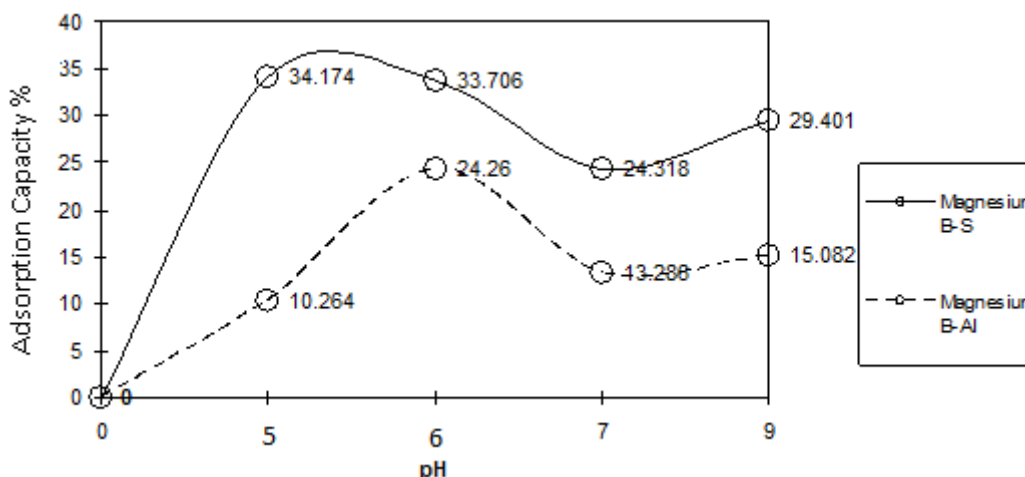


Figure 3. The Effect of pH on adsorption capacity of B-S and B-Al for Mg²⁺

Highest adsorption capacity of the adsorbent is owned by B-S at pH 5 is 34.174% otherwise the lowest adsorption capacity is owned by B-Al is 10.264%. Whereas at pH 6, 7, and 9 obtained the adsorption capacity for B-Al is also lower compared to the B-S. The adsorption capacity for B-S and B-Al at pH 6 was 33.71% and 24.26%; at pH 7 is 24.32% and 13.29%; at pH 9 was 29.40% and 15.08%, respectively.

The differences of physico-chemical between B-S and B-Al is laid on the surface area, pore radius, although both BS and B - Al has the similarities in the pore structure. This difference is caused by the distance interlayer between B-S with B-Al which is based on the atomic number and atomic positions in the structure/cell (West, 1988), namely the substitution pillar at the tetrahedral layer of B-Al . According to Smart (2005) , the existence isoelektron Al³⁺ as pillar causes a decreased the distance of interlayer or decreasing the size of the radius corresponding to the increase in positive charge . It is also stated by Tomul and Balci (2007) which states that the number of species intercalated cause interlayer distances and influence on the surface area and the strength of the crystal structure . The crystal structure is related to the number of electrons contained at a certain point and is known as the intensity I (Ismunandar , 2006). Thus the number of electrons in the tetrahedral layered more B-S than the B-Al . The number of electrons is also derived from the adsorbed water as proposed by Grim (1968) , causing the distance between fields B-S is longer than the B-Al.

Based on the chemical characteristic the difference of adsorbent relates to the nature of the adsorbent surface. Using IR Spectrophotometer data known to exist differences in the functional group of the octahedral O-Al-OH, or Si-O stretching, stretching Si-O-Si antisimetris owned B-Al and B-S. In the B-Al substitution of Al on Si tetrahedral while the B-S without substitution or no pillar. Structural differences between the two adsorbents showed active site acid-base Bronsted / Lewis at B-Al and B-S. The existence of adsorbed

water and the presence of O-Al-OH bonding due to substitution of Al on Si tetrahedral causes the difference between B-S and B-Al.

Active site of the adsorbent is located on the surface B-S and B - Al , so the number of active site is proportional to the surface area and pore radius of the two adsorbents . In terms of surface area , active site of surface B-S less than the B - Al . Therefore, the adsorption capacity reduced due to covered of the active site . Addition of HCl in the system will cause protonation on anionic group . The addition of NaOH to the system (ionization of NaOH) will cause Na⁺ occupy active sites on the adsorbent surface (O²⁻ ions) , while the OH⁻ will bind to Al³⁺ . At the B-S , OH⁻ ions into the charge off the system even though they have elektrostrostatis bond with Na⁺ and this is known as the Stern double layer (Shaw , 1983) . The charge of B-S from the Stern double layer increases , while the negative charge of the adsorbent B - Al will be reduced and this charge will vary according to the pH (Tan , 1996) . Thus the difference in the active sites of the two adsorbents, cause the adsorption capacity of B-S is greater than that of B - Al.

CONCLUSION

Based on the data obtained it can be concluded that:

- B-S has different physico-chemical with B-Al in terms of: the distance interlayer 12.4374 Å for BS and 9.3047 Å for B-Al; surface area is 24.78 m² / g for BS and 217.021 m² / g for B-Al; and total pore volume for pore radii smaller than 1001.9 Å (BS) and smaller than 1273.1 Å for B-Al; as well as the number of active site at surface.
- The difference in the number of active sites of two adsorbents, cause the adsorption capacity of B-S is greater than that of B - Al.
- 3)The interaction between the adsorbent and adsorbate is affected by the pH of the system caused by the addition of HCl or NaOH.
- 4)At the system of pH 5, 6, 7, and 9, the adsorption capacity of B-S is greater than that B-Al. The adsorption capacity of B-S and B-Al at pH 5 are 34.17% and 10.26%; at pH 6: 33.71% and 24.26%; at pH 7 24.32% and 13.29%; at pH 9: 29.40% and 15.08%, respectively.

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