STUDY OF ADSORPTION OF GROWTH REGULATORS NAPHTHALENE ACETIC ACID (NAA) ONTO NATURAL BENTONITE

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Abstract

The study of adsorption of plant growth regulators naphthalene acetic acid (NAA) by using natural bentonite aims to investigate the purification process of bentonite, determine the parameters that affect the ability of optimum adsorption and adsorption interactions of bentonite to NAA. Bentonite purification process is done by adding 30% H_2O_2 to oxidize organic compounds in the pores of the bentonite. Adsorption parameters in this study include the influence of the mass of adsorbent, contact time and adsorption capacity of bentonite nature of the NAA. Characteristics conducted in this study include analysis using UV-Vis spectrophotometer, infrared spectrophotometry (FTIR) and X-ray Diffraction (XRD). Bentonite adsorption capacity was determined using the model of Langmuir isotherm and Freundlich isotherm models.

This study was showed that the amount of NAA more adsorbed byincrease the mass of adsorbent in the adsorption process. The optimum contact time between NAA with natural bentonite is 4 hours on the condition of the masses as much as 0.5 grams of bentonite, pH 4.5 and in room temperature ($\pm$ 29^{0}C) with adsorption capacity of 1.502×10^{-6}mol/g. The optimum adsorption capacity of bentonite to the NAA at 1.712×10^{-6}mol/g. NAA adsorption isotherms with natural bentonite included in the Freundlichisotherm adsorption which assumes the Van der Waals bonds so that the interaction between NAA with bentonite was physically and heterogeneous on the multilayer surface.

Keyword : adsorption, plant growth regulators, *Naphthalene Acetic Acid* (NAA), bentonite

Introduction

Utilization of carrier material which is used as aimobilization matrix in agriculture can improve the effectiveness of growth regulator.As the example gibberellin acid is alternative to chemical fertilizers which more sustainable to enviroment[1]. Immobilization through physical adsorption method is the cheapets method, in this method, the style of interaction that occurs between the carrier material and the compound can be hydrogen bonds, Van Der Waals force and interaction hidrifobik[2].

Auxin is involved in many physiological processes such plants induces cell elongation, phototropism, gravitropism, apical dominance, root initiation, ethylene production, fruit development, sexual expression and weeds control[3]. IBA (*Indole-3-Butyric Acid*) and NAA (*Naphthalene Acetic Acid*) are the two kindsofthe synthesis of auxin that affect rooting and used commercially to stimulate adventive rooting[4]. NAA has properties more resilient, more stable, not easily oxidized by enzymes, not degraded and cheaper[5].

In the adsorption technique, the carrier material which is commonly used as adsorbents include activated charcoal, bottom ash, zeolite, and clay minerals. Clay minerals commonly found in some large groups, such as kaolinite, mica, montmorillonite (bentonite), chlorite, illite and vermikulit[5]. Montmorillonite group most attracted attention because it has the ability to inflate montmorillonite (swelling) when in water or organic solvents and has a high capacity ion exchange so as to accommodate the amount of cations in antarlapisnya besar[6].

Materials andMethods

Material

Materials used in this study is a NA bentonite with Driling Mud A3 brands obtained from Semarang, crystal of NAA (Naphthalene Acetic Acid) (brans), NaOH (p.a), H_2O_2 30% (technical), HCl (technical), akuabides and distilled water ,

Purification Samples

A total of 100g of Na-Bentonite passes a sieve with a diameter of 106 microns put into 1000 mL of distilled water while stirring with a magnetic stirrer for approximately 3 hours. A number of $\pm$ 700 ml 30% H2O2 solution is inserted slowly into the mix. The mixture was stirred overnight and allowed to stand so that the bentonite settles, then top part isdekantired.

Dekantir product was added by back distilled water and stirred for 1 hour, allowed to stand back and then dried in an oven at a temperature of 100^0C till dry. The treatment was repeated 3 times to remove H_2O_2residual. After the 3rd repetition, the top of the solution is taken with *sifoning*methods and then centrifuge of 4000 rpm of speed for 10 minutes. Furthermore, the solids are dried in an oven at a temperature of 100^0C for about 4 hours, in order to obtain Na-bentonite dry solids. Na-Bentonitesolids then analyzed using FTIR with 300-4000 $cm^{-1}$of range of wave number and analyzed using XRD.

Optimization of Adsorption NAA with Bentonite

Varying ContactTime

Bentonite samples prepared as much as 0.5 gram respectively used to adsorb 25 ml NAA sulution at 25 ppm of concentration. Adsorption process is carried out with stirring using a magnetic stirrer on the variation of contact time 30 minutes, 60 minutes, 90 minutes, 2 hours, 4 hours, 6 hours, 8 hours, 16 hours and 24 hours. at 29ºCof room temperatureand filtered through Millipore filter paper with the 0.4 microns ofsize. The number of NAA solution that is not adsorbed absorbance was measured using a UV-Vis spectrophotometer at the maximumwave-length.

Adsorption Capacity of Bentonite to NAA Solution

NAA solution adsorption capacity assessment is done by varying the concentration of the solution. Making NAA solution in 10 ppmofconcentrations, 15 ppm, 20 ppm, 25 ppm, 30 ppm and 35 ppm at 25 ml, then added 0.5 grams of bentonite. Then stirred using a magnetic stirrer during the optimum time according to the results of the variation of contact time at 29ºC of room temperatureand filtered through Millipore filter paper with the 0.4 micronsof size. The number of NAA solution that is not adsorbed absorbance was measured using a UV-Vis spectrophotometer at the maximumwave-length. Results absorbance concentration calculated to determine the adsorption capacity of bentonite to the NAA and the reaction can be determined isotherms. Further characterization of bentonite which has been contacted by NAA using FTIR with 300-4000 cm^{-1}of range of wave number and analyzed using XRD

Results and Discussion

Sample Purification

The content of the bentonite is composed of quartz, pirofisit, kaolinite, with the main of content issmectite minerals (montmorillonite) as much as 85-95% which is plastic and high colloidal. Bentonite is purified by adding 30% H_2O_2 to remove organic substances which is marked absence of air bubbles formed in bentonite which has didissolved[7]

Purification method was conducted by sedimentation followed by siphoning based on Stokes's law. Siphoning method based on differences in density of the materials contained in bentonite, in which the material that has a greater specific gravity is relatively will settle more quickly than material that has a small specific gravity[8].

FTIR spectroscopic data of bentonite samples before and after purification provide information the of type of vibration functional group byobserving the absorbance clay-absorption that appeared in the area of wave numbers 4000-400 cm^{-1}. Based on Figure 1 we can see the important peaks to identify functional groups contained in bentonite.
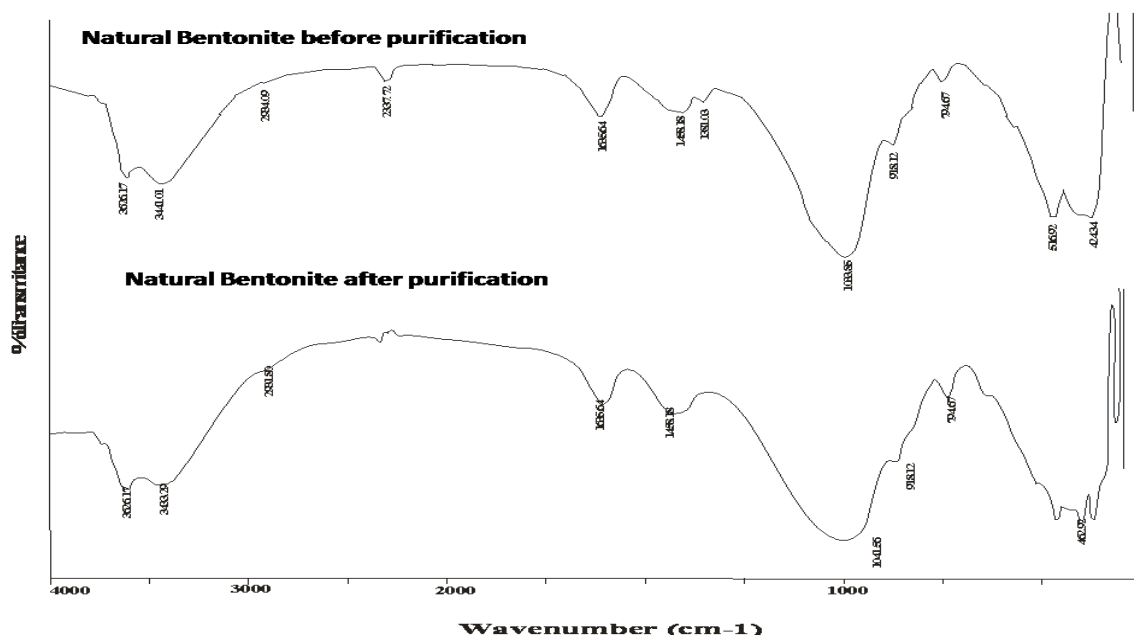
Figure 1. FTIR spectra of Natural Bentonite Before Purification (A) and Bentonite After Purification (B)

Table 1. IR absorption peak of Natural Bentonite Bentonite Before Purification and Natural After Purification

Wave Number (cm^{-1})		UptakeFunctional groups
Natural Bentonite before purification	Natural Bentonite after purification	
3626,17	3626,17	Stretching vibrationof OH (Al-OH inter oktahedral)
3441,01	3433,29	Strain vibration of OH fromoktahedraland or H$_2$O
2934,09	2931,80	Strain vibrationof CH alkana
2337,72	-	organicMaterial
1635,64	1635,64	Bucking vibrationof OH dari H$_2$O
1458,18	1458,18	Bucking vibrationof metilengroupCH$_2$
1381,03	-	Bucking vibration groupof C-H from CH$_3$ (organicmaterial)
1033,85	1041,56	Strain vibrationof Si-O-Si
918,12	918,12	Strain vibration ofAl-OH-Al
794,67	794,67	Symmetrical vibrationof Si-O-Si
516,92	-	vibrationof Si-O-Al octahedral
424,34	462,92	stretching vibrationof Si-O-Si

Based on Figure 1, the absorption band between natural bentonite before purification with natural bentonite after purification have the difference. At bentonite purified with H$_2$O$_2$ can be seen that there has been a reduction of organic compounds contained in natural bentonite before purification indicated by the loss of wavenumber 2337.72 cm^{-1}. That is because H$_2$O$_2$ solution oxidize organic compounds that bind around the pores on bentonite. Oxidation of

organic compounds in the pores of the bentonite is characterized by the release of bubbles that bring CO_2 gas..We can also see the dealumination (releasing Al) in the octahedral layers which is characterized by the loss of absorption at 516.92 cm^{-1}wave numbers, which causes an increase in the ratio between Si and Al in the octahedral layers 9.X-ray diffraction analysis use to determine the type of bentonite clay mineral constituent indicated by the appearance of peaks at the region of2θ. Results of analysis of samples of natural bentonite with difraks X-ray is presented in Figure 2.
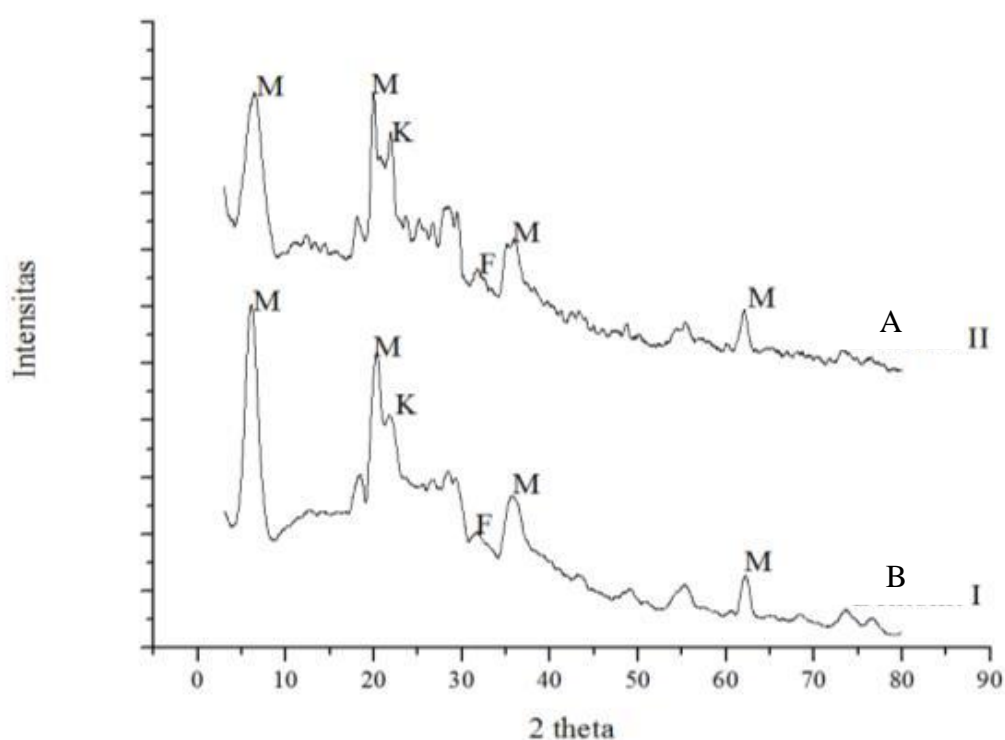

Figure 2. Diffractogram X-Ray Diffraction (XRD) of Natural Bentonite Before Purification (A) and Natural Bentonite After purification (B)

Based on Figure 2, we can observed the price change in 2Ө and basal spacing that occurs as a result of natural bentonite purified by adding a solution of 30% H_2O_2. XRD diffractogramof natural bentonite after purification showed at the peak 2Ө = 6.400 with basal spacing of 13.81 Å, 2Ө = 19.920 with basal spacing of 4.45 Å, 2Ө = 35.920 with basal spacing of 2.50 Å and 2Ө = 62.010 with basal spacing of 1.50 Å indicates a the existences of mineral montmorillonite. Furthermore, at the peak 2Ө = 21.890 with basal spacing of 4.06 Å indicates the mineral quartz, whereas at the height of the 2Ө = 31.750 Å basal spacing by 2.82 shows that it contains feldspar[10]. The content which is contained in bentonite nature before

purification and bentonite nature after purification has the same categorized, the differences is the intensity of the peak which indicates the purification method using $H_2O_2$to bentonite. does not damage the existing structures in the bentonite and the reactions that occur in the purification method using H_2O_2 only reduce levels of organic compounds contained in bentonit[11].

Optimization of Adsorption NAA with Bentonite

Timing Contacts Adsorption Bentonite With NAA

Adsorption is a process of withdrawal of the molecule by a solid surface. Another parameter that needs to be studied to assess the adsorption is determining of the optimum contact time between the adsorbate with an adsorbent. The determination of the optimum contact time during adsorption is intended to determine how long the maximum NAAwhich isadsorbed by bentonite to achieve equilibrium and saturated circumstances. The process of determining the optimum contact time between the NAA and bentonite performed at pH 4.5 at a concentration of 25 ppm NAA at the variation of contact time. In these conditions the H^+ ions generated under acidic conditions would potentially deprotonize bentonite functional groups, they are silanol (Si-OH) and also the degree of ionization of adsorbatespeciation. If the pH less than 4.5, it will competite with H^+ ions in the bentonite edges and it will has negatively charged on the surface of the silicate. This leads to the reduction of surface area of bentonite. This conditioninvolvesthe reduction ofadsorptionability[12]. Additionally if the pH is more than 4.5 surface bentonite became more negatively charged either on the surface or the surface of the silicate bentonite, it will involves the enhancement ofbentonite surface area. On the other hand there will be a greater repulsion interaction between negative charges on the surface of bentonite with NAA molecule that under alkaline conditions began to dissociate produce COO^- group, thus weakening the ability of adsorption.

The determination of optimum adsorption time have be done by calculate adsorption capacity value (Q). The adsorption capacity value (Q) expressed a certain amount of adsorbate that can diadsorps by an adsorbent. The adsorption capacity value will be increased to the optimum state (equilibrium) and then slightly decreased after passing the equilibrium time[13].
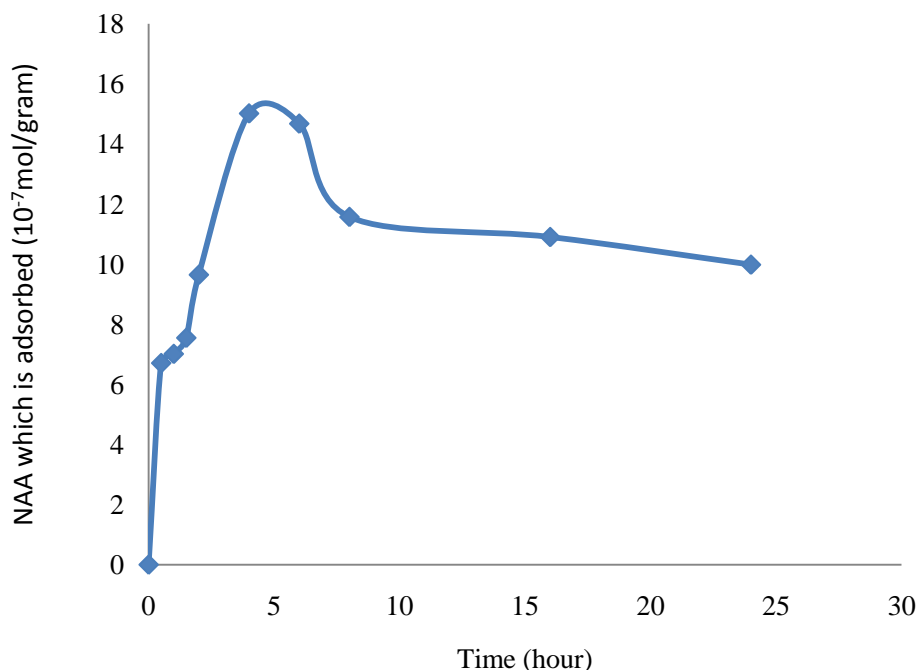
Figure 4. Correlation Between NAA adsorbed and Time

Figure 4 shows that the contact time is very influential on NAA adsorption by bentonite. It appears that 30-minute contact time for the adsorption capacity of bentonite to the NAA as much as 6.710×10^{-7} g / L. The number of NAA which is adsorbedcontinued tol increase up to 4 hours of contact time with the adsorption capacity of as many as $1,502 \times 10^{-6}$ g / L. Then after 4 hours of stirring, the adsorption capacity of bentonite to the NAA decreased, this is due to the interaction between the active site of bentonite with NAA supersaturated. Another assumption states that the stirring process will also result in collisions between particles of adsorbate with adsorbent particles accurately and continuously, so there is likely to be released back adsorbat by adsorben[14]. Based on the optimum contact time between the NAA with bentonite lasted for 4 hours.

Determination of Capacity and Bentonite Adsorption isotherms with NAA

The process of adsorption of the NAA by bentonite adsorbent, can be seen from the of adsorption capacityvalue. It can be described adsorption isotherm models to determine the type of adsorption that occurs between the adsorbent andadsorbate, adsorption isotherm models which are used approach areLangmuir isotherm adsorption and Freundlich isothermadsorption. An adsorption isotherm adsorption occurs at a constant temperature.

Adsorption which is happen must to be in aequilibrium state, in which the adsorption and desorption take place in a equal raterelatively. Equilibrium adsorption usually described by the isotherms equation which the parameters show surface properties and affinity of the adsorbent at the constant conditions of temperature and pH[13]. Determination of adsorption capacity and adsorption isotherm conducted by reacting the 0.5 grams of bentonite with variation of NAA concentrations for 4 hours at pH 4.5 and at room temperature (± 29ºC). Langmuir adsorption isotherm model is a process of adsorption of a single layer (monolayer), it has means that the number of active sites in the adsorbent adsorb the adsorbate by the same amount, the interaction between the adsorbate andadsorbent can be kemisorpsiform or fisisorpsi form.The model of Freundlichisotemadsorption describes an multilayer adsorption process so more lacking to be fisisorpsiinteraction[14]. Langmuir isotherms adsorption curve and Freundlichisotherms adsorption curve between bentonite with NAA is presented in Figure 5 and Figure 6.
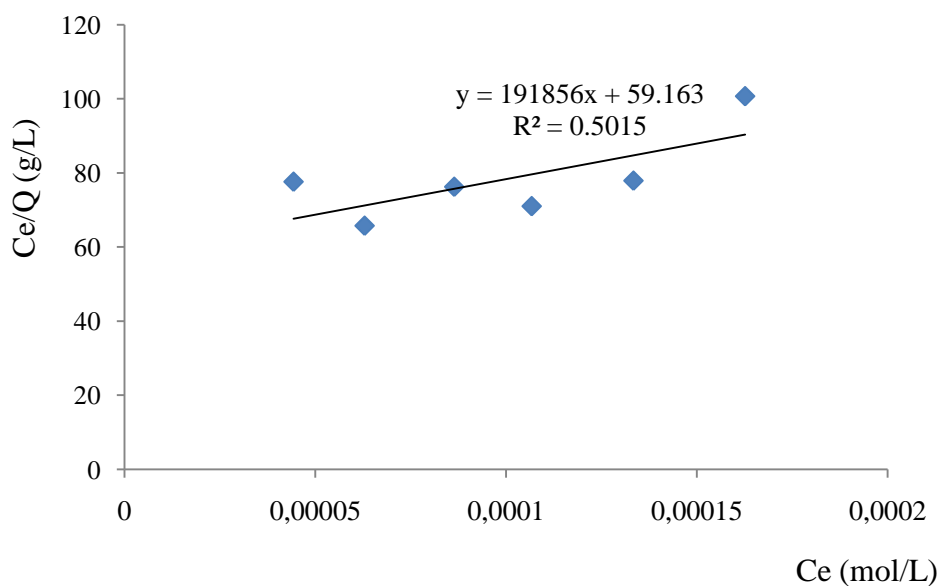

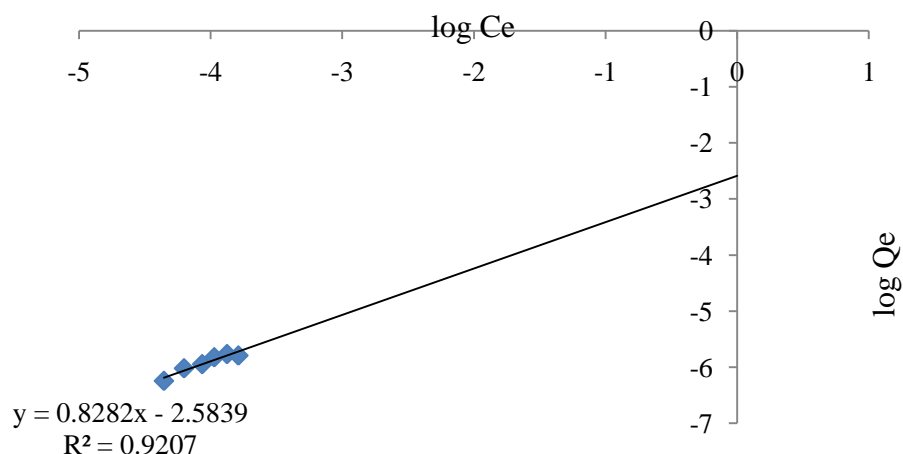**Figure 5. Graph of Langmuir isotherm of Bentonite with NAA**

Figure 6. Graph ofFreundlich isotherm of Bentonite with NAA

Based on the Langmuir isotherm curves obtained straight line y = 191856x + 59.163 with R^2 = 0.5015. From the equation can be calculated the maximum adsorption capacity 5.212×10^{-6}mol/g with Langmuir constant value (K_L) 3.2428×10^3 L/mol. Furthermore, based on Freundlich isotherm curve can be obtained straight line equation y = 0,8282x - 2.5839 with R^2 = 0.9207. From Freundlich isotherm equation above, the n value = 1.207 mol/g and Freundlich constants (K_F) 2.6068×10^{-3}mol/g. The determination of an appropriate model of adsorption isotherm can be determined by looking at thelinearity curves that hasdetermination coefficient price (R^2) $\geq$ 0.9 (close to 1) from the bothisotherms adsorpsicurves [15].

Based on the determination coefficient (R_2) of the both isotherm adsorption models, Wecan find out the NAA isotherm adsorption models to bentonite tend to follow the Freundlich isotherm adsorption model than the Langmuir isotherm adsorption model. Freundlich isotherm describe the interaction that between the adsorbateand the adsorbent which is dominated by physical interaction with weak bonding between the adsorbateand adsorbent and only involves theVan der Waals interaction[16].

Adsorption process that occured will be a heterogeneous multilayer form on the second layer and thereafter on bentonite with NAA. It shows that not all surfaces of natural bentonite layer occure adsorption process[17]. To reinforce that the NAA has been entered into the bentonite interlayer was analyzed by X-raydifraks.
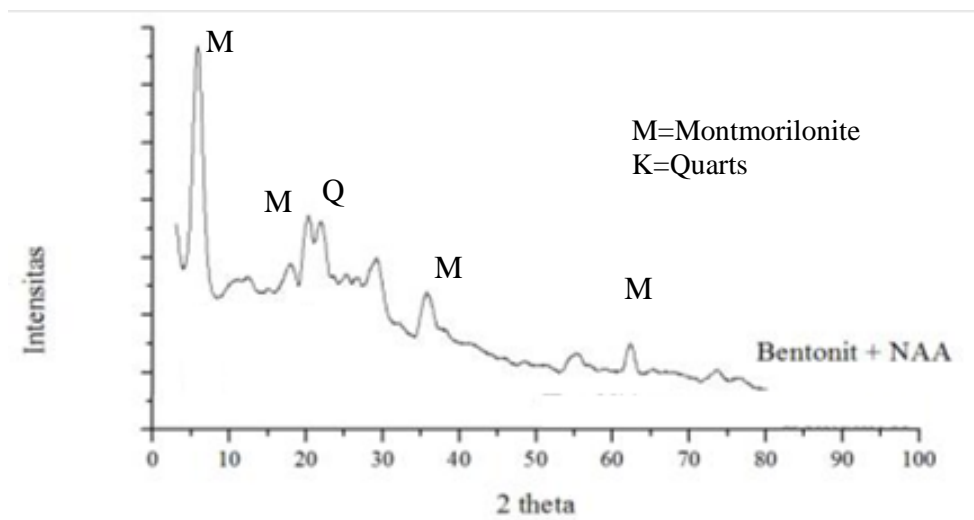
Figure 7. Diffractogramof X-Ray Diffraction (XRD) Natural Bentonite Bentonite After purification and Natural After Adsorption NAA

Based on Figure 7 can be seen a shift in the peak, the intensity difference and the rise of*basal spacing* between natural purified bentonite before adsorption proces and natural purified bentonite after adsorptionproces. 2Ө peak shift initially at 6,40o to be 5,82o, while the *basal spacing* value have increasing from 13.81 Å to be 15.18 Å. The enhanchmentof basal spacing afterNAA adsorption process showed that NAA molecules that are adsorped exist in the interlayer of natural bentonite after purification. The existence of NAA in the interlayer molecules cause the distance between layers becomes larger.

The evidenceof NAA which is adsorped by bentonite is also shown from the FTIR characterization results, in Figure 8 spectra bentonite which has adsorpthe NAA is showen by the appeare the absorption peak at wave number around 2368.59 cm⁻¹; 2337.72 cm⁻¹ and 354.90 cm⁻¹. It shows a group of organic compounds which is contained within the NAA molecule (based on the number FTIR NAA wave).
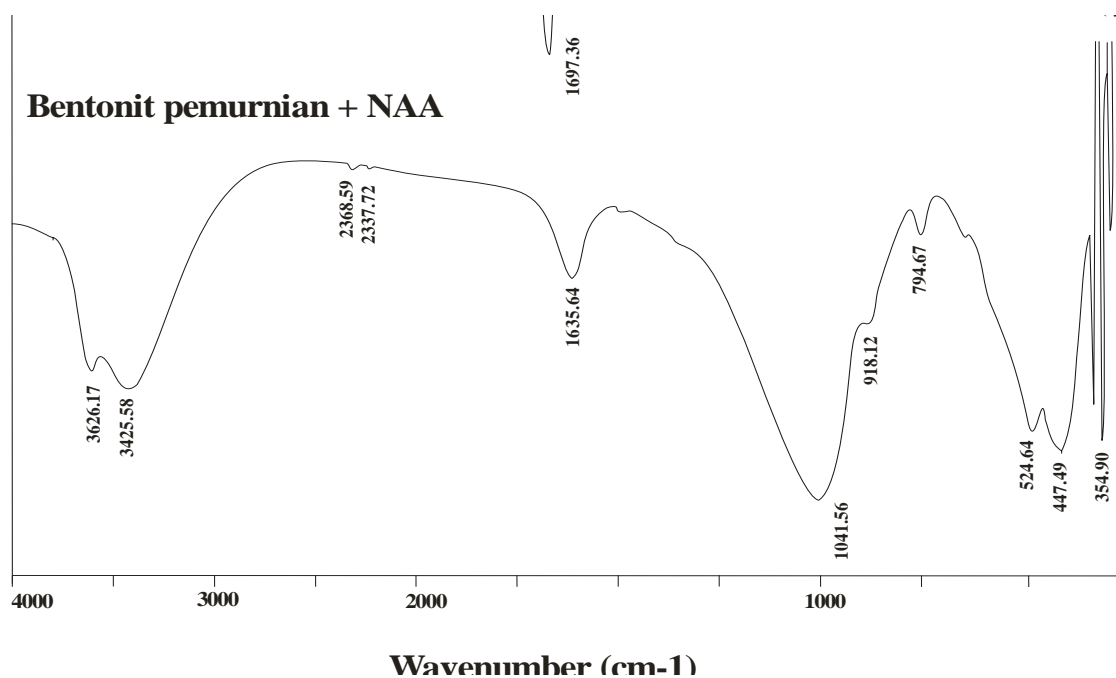
Figure 8. FTIR spectra of Bentonite which has been contacted with NAA

More over, it can also be seethe results of bentonite adsorption with NAA does not make a new cluster from the FTIR spectra. It reinforces the assumption that the bentonite adsorption interaction and NAA only involve dipoles force which collectively are called Van der Waals interaction and it has nature of physical adsorption.

Conclusion

Purification process to obtain high-purity natural bentonite as a carrier material for hormone auxin NAA (Naphthalene Acetic Acid) can be done by adding H_2O_2 30% on bentonite to oxidize organic compounds in the pores of the bentonite. Bentonite adsorption interactions of the hormone auxin NAA included in Freundlich adsorption isotherm models that assume the Van der Waals bonding on heterogeneous multilayer surface, so that the interaction of bentonite with NAA happens is physical adsorption.

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