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Ethanol Dehydration in Fixed Bed Column Using Pellet Adsorbent From Lampung Natural Zeolite

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Abstract

Zeolite is one of adsorbents easily found in nature, especially in Indonesia. One type of zeolite usually used for dehydration of ethanol-water mixtures is Lampung Natural Zeolite (LNZ). According to data from the Directorate of Regional Potential Development in 2012, the LNZ amount in Lampung Province is 31,173,505 tons. In this conducted research, the preparation was carried out in two stages, namely making the LNZ in the form of pellets, and activating the LNZ pellets. The manufacturing stage of the LNZ into pellets was carried out by pulverizing it into a size of 200 mesh, mixing it with distilled water and 35% wheat flour of the LNZ weight, and stirring the mixture until smooth. Then, it was formed into pellets with a diameter of 2 mm and a length of 1 cm, dried using an oven at a temperature of 100℃ until constant weight was obtained, and placed in a desiccator. Furthermore, in the LNZ activation stage, the zeolite was calcined using a furnace at 300℃ for 5 hours. Next, LNZ was ready to be characterized using FTIR, XRD, XRF, BET, and SEM. The activated LNZ pellets were used in the dehydration process of the ethanol-water mixture in an upflow fixed bed adsorption column with a flow rate of 10 ml/min and bed heights of 5, 10, and 15 cm. The Adam adsorption kinetics models of Boharts, Yoon Nelson, and Thomas were used to obtain a breakthrough curve and a suitable adsorption kinetics model. As a result, LNZ had been successfully formed into pellets as could be seen when it was immersed and the ethanol-water solution was flowed, it's shape did not change. The activated LNZ pellets had a surface area of 11,670 m^2/g, a pore size of 57,091, and a total pore volume of 0.035958 cc/g. The highest R^2 value obtained in the Adam Bohart equation model was 0.9742 with the highest concentration of 98.797% and a bed height of 15 cm. It was concluded that LNZ pellets could be used as an adsorbent in fixed bed adsorption column to purify ethanol.

Keywords: Adsorption, adsorption kinetics, and Lampung natural zeolite (LNZ)

1. Introduction

The efforts to protect the environment from continuous reduction of fossil fuels have led researchers to develop alternative fuels, such as biofuels, wind, hydropower, geothermal and solar energy (Frolkova and Raeva, 2010). The most promising biofuel fuels in the future are biodiesel, biogas and ethanol (Ranjbar, 2012). By using biofuels, there are several advantages that can be obtained ranging from environmental, energy reserves, and economic terms (Kumar et al., 2010). However, based on these advantages, reducing the amount of carbon dioxide emissions has the biggest benefit in reducing global warming caused by the excessive use of fossil fuels. Indeed, to be able to replace fossil fuels, biofuels must have a concentration of 99% (v/v).

Hence, currently many studies focuses their efforts on increasing the purity of ethanol. One technique that can be used to make 99% (v/v) ethanol concentration is the adsorption process based on the molecular sieve principle. Adsorption itself is usually used in industry sector during the separation process. It is mainly because it has high efficiency, low cost, and many types of sorbents that can be used as needed. Adsorption itself can be done in batches and continuously. In continuous adsorption the breakthrough curve, breakthrough time, adsorption capacity of a material, length of working zone, and mass transfer can be studied (Okewale et al., 2015).

Zeolite is one of the adsorbents that are easily found in the natural environment, especially in Indonesia. One type of Zeolite that is often used for the adsorption process of dehydration of ethanol-water mixture is Lampung Natural

Zeolite (LNZ), where the presence of Zeolite in Lampung Province is very large, according to data from the Directorate of Regional Potential Development at the time of 2012 the Zeolite natural resource reserves were abundant. There are 31,173,505 tons of zeolite found in Lampung. In addition, according to research conducted by (Ginting et al., 2017) stated that LNZ has a silica (SiO_2) content of 79.046% by weight and an alumina content of 15.815% by weight, so it can be used for the adsorption process because it is hydrophilic.

Research on the adsorption of water from an ethanol-water mixture has been carried out in several previous studies. According to research conducted by (Saputra, 2015), in order to obtain fuel grade bioethanol, bentonite is used as an adsorbent in the adsorption-distillation process. Bioethanol used as feed has an initial content of 70% (v/v). The various variables were the bentonite weight (30, 50, 70, 90, and 110 grams) and the adsorption-distillation time (30, 50, 70, 90, and 110 minutes) with a constant temperature of 80℃. The results obtained indicate that to obtain the highest ethanol content of 93.292% (v/v), bentonite weight of 50 grams and adsorption-distillation time of 110 minutes are required.

According to research conducted by (Handrian et al., 2018), to obtain fuel grade bioethanol, Zeolite 4A was used as an adsorbent and feed in the form of ethanol with an initial content of 95.61% (v/v). Variations carried out in this study were flow rates with a speed of 2 L/min, 4 L/min, and 6 L/min. The temperature inside the bed is also kept constant at 80℃, 85℃, 90℃, 95℃, and 100℃ by using an electric heater. The results obtained are 99.4% (v/v) bioethanol fuel grade using a flow rate of 2 L/min and a temperature in the bed of 80℃.

According to research conducted by (Okewale et al., 2015) to obtain fuel grade bioethanol content, adsorbent in the form of pure corn starch and modified corn starch and ethanol with an initial content of 90% (w/w) was applied to the fixed bed adsorption column. Variations carried out in this study were the flow rate (6 L/min, 10 L/min, and 14 L/min) and the height of the adsorbent bed (40 mm, 80 mm, and 120 mm). From the results of this study, it can be concluded that the higher the adsorbent bed, the smaller the adsorption capacity.

A research on LNZ in the form of pellets has been carried out by (Wardono et al., 2018) to reduce fuel consumption and exhaust emissions on motorcycles. Meanwhile, in this study, LNZ pellets were used as an adsorbent in the fixed bed adsorption column for dehydration of the ethanol-water mixture and to obtain the kinetic model. The height of the adsorbent bed is a variable that is varied in this study. The height of the adsorbent bed affects the breakthrough time, length of the working zone, the mass transfer, and the percent of water removal. This study is conducted to evaluate LNZ pellets in dehydrating the ethanol-water mixture in a fixed bed column using the adsorption kinetics of Adam Boharts, Yoon Nelson, and Thomas.

The adsorption data are analyzed to study the kinetics and the breakthrough curve. FTIR analysis is carried out with Shimadzu IRAffinity-1S to identify the functional groups of the sample, XRD analysis with the XRD PANalitycal MPD PW3040/6 instrument to test the crystallinity of the sample, XRF analysis with the XRF PANalytical Epsilon 3 instrument to analyze chemical composition and concentrations of elements in the sample using the spectrometric method, SEM analysis with the SEM ZEISS EVO MA 10 instrument to test the structural model between independent and dependent constructs of the sample, and BET analysis with the BET NOVA touch 4LX instrument to analyze surface area, pore size, and total pore volume of the sample. Three models (Thomas model, Yoon and Nelson model, and Adams-Bohart model) were used to analyze the performance of the adsorption column.

2. Materials and Methods

The materials used in this study were ethanol from Harco ID Store with a concentration of 91.805% (v/v), Lampung Natural Zeolite, and wheat flour. Meanwhile, the tools used in this research are 200 mesh screening, peristaltic pump, fixed bed column, oven, furnace, porcelain mill, and glass beaker.

2.1. Making Zeolite Pellets

Zeolite pellets were made by grinding LNZ using a mortar, and sieving the LNZ powder with a screening tool (sieve tray) at 200 mesh size. At the same time, distilled water was mixed with a binder (wheat flour) 35% of the weight of the zeolite. The distilled water was then stirred and heated with a binder to form gelatin. After that, 100 grams of LNZ was mixed with the heated binder. These two ingredients were then mixed until homogeneous consistency was obtained. This

mixture was then being printed with a diameter of 2 mm and a length of 1 cm, and dried in an oven at 100℃ until the constant weight was obtained. Finally, the dried zeolite pellets were stored in a desiccator.

2.2. Zeolite Activation

To physically activate Zeolite pellets (calcination), a furnace with a temperature of 300℃ for 5 hours was used so that the water in the zeolite pellet was vaporized. Furthermore, the activated Zeolite pellets were analyzed with XRD, XRF, SEM, FTIR, and BET analysis.

2.3. Adsorption of Bioethanol on Zeolite Pellets by Using a Fixed Bed Column as an Adsorption Column

The activated zeolite pellet was then put into a fixed bed column as set by the tools on Figure 1, with variations in the height of the adsorbent bed of 5 cm, 10 cm, and 15 cm. Then, a bioethanol solution with a concentration of 90% (v/v) entered continuously into the fixed bed column with a flow rate of 10 ml/minute. Finally, ethanol content in the bioethanol solution leaving the fixed bed column was measured every 5 minutes.

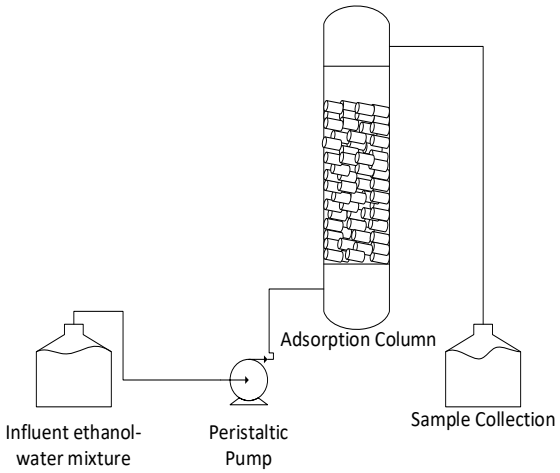


Figure 1. Block Diagram of the Experimental Set-up for Column Adsorption Study.

2.4. Preparation of Bioethanol Adsorption Breakthorugh Curve

To create a breakthrough curve, the initial concentration of bioethanol was firstly calculated. The bioethanol was flown into the fixed bed column and contacted to the adsorbent in the form of zeolite pellets. Then, bioethanol contacted to the adsorbent was taken every 5 minutes to calculate its concentration. The final stage is to draw the breakthrough curve by plotting the concentration of the output water in the bioethanol solution, and the time.

3. Results and Discussion

3.1. Durability of LNZ pellets

Durability shows how much LNZ pellet is still available after being immersed in an ethanol-water solution during the adsorption process. The durability of LNZ pellets is very important in this study, so a review is necessary in order to know the service life of LNZ pellets in the continuous adsorption process. A good pellet is a pellet that is sturdy, compact, and not easily brittle (Sholihah, 2011). The results of this study indicate that the formed LNZ pellets do not change physically. These ensures the fact that the product output in this adsorption process contains only ethanol and does not contain LNZ. One way to review the durability of LNZ pellets is by soaking them in an ethanol-water solution for a certain time; in this study LNZ pellets were immersed in an ethanol-water solution for 7 hours. From Figure 2. it can be seen that the binder from wheat flour has been able to bind LNZ very well so that LNZ pellets can maintain their shape.

Figure 2. LNZ Pellet Durability Test For 7 Hours.

In addition, when viewed in terms of color, the non-calcinated LNZ color is white, whereas the calcinated LNZ has a black color, this can happen because the binder in the form of wheat flour undergoes a combustion reaction at that temperature reffered by the picture on Figure 3.

a

b

Figure 3. (a) before calcining (b) after calcining.

3.2. FTIR Analysis

From Figure 4. it is known that unactivated natural zeolite has an absorption peak at the intensity of 1630 cm^{-1}, which indicates the presence of Si-OH bending vibrations. Then, it is also known that both unactivated natural zeolite and activated natural zeolite have asymmetric stretching vibrations of O-Si-O or O-Al-O, this can be seen from the absorption peak which is in the range of 1250-900 cm^{-1}. The unactivated natural zeolite has an absorption peak at 1020.13 cm^{-1}, this absorption peak also has a sharp, steep and intense shape while the activated natural zeolite has an absorption peak at 1015.5 cm^{-1}, the shape of the peak absorption has also reduced its sharpness and steepness and seen to be more tenuous. This indicates that the zeolite has an aluminosilicate framework (Ginting et al., 2017). The intensity shift of the absorption peak from 1020.13 cm^{-1} to 1015.5 cm^{-1}, and the shape change from sharp and steep absorption peak to tenuous and sloping one indicate an increase in the number of Al atoms in the framework of the tetrahedral site, and a reduction in other cations that bind to O-Si-O or O-Al-O bonds because of calcination on natural zeolite Lampung. Furthermore, it is also known that the inactivated Lampung natural zeolite has a stretching vibration in O-Si-O or O-Al-O symmetry, this is indicated by the presence of a sharp absorption peak which is at an intensity of 783.5 cm^{-1}. Apparently, the activated natural zeolite Lampung does not show an absorption peak so it does not have stretching vibrations in O-Si-O or O-Al-O symmetry. Based on this fact, it is known that the unactivated natural zeolite has an interaction between the alumina tetrahedra of the zeolite structure and Al^{3+} (Byrappa and Kumar, 2007). Then it can also be seen that the unactivated and activated natural zeolite in Lampung both have external vibrations of D4R or D6R or often known as double ring, this can be seen by the absorption peak of natural zeolite before being activated at an intensity of 562.35 cm^{-1}. Apart from that, the absorption peak has a sharp and steep shape, while the absorption peak for activated natural zeolite is at an intensity of 565.4 cm^{-1}, and the shape of the absorption peak is slightly more tenuous and sloping. Therefore, it can be concluded that both unactivated and activated natural zeolite have secondary building units in compiling this zeolite framework (Sriatun and Darmawan, 2005), which shows that LNZ has the same tendency as LTA zeolite where the LTA zeolite is considered as an adsorbent having a double ring vibration absorption band (double rings) of D4R or D6R. Furthermore, it is known that the Lampung natural zeolite which has not been activated does not show an absorption peak at an intensity of 420-300 cm^{-1} and for an activated Lampung natural zeolite it appears to have an absorption peak at an intensity of 338.8 cm^{-1}. This indicates that there is an external vibration gap or it can be said that the pores in the zeolite have been opened. These pores can be opened because of calcination on natural zeolite Lampung, which makes water and impurities in natural zeolite Lampung disappear. These results are in accordance with research conducted by (Sriatun and Darmawan, 2005).

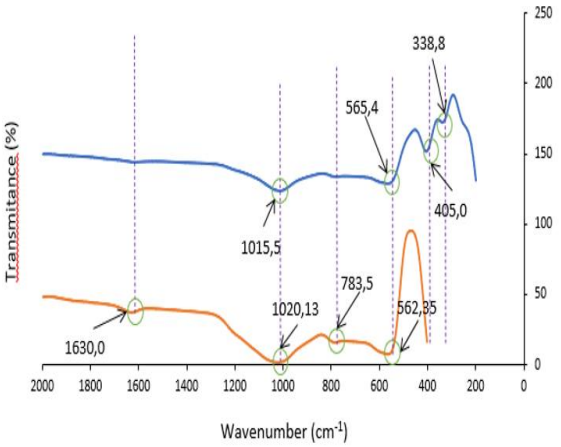


Figure 4. FTIR Analysis Results.

3.3. XRF Analysis

It is known that distilled water still has a lot of dissolved metal content in it (Heraldy et al., 2003) In addition, there is an increase in the Si/Al ratio in activated natural zeolite to 6.907, it is known from the Si/Al ratio that Lampung Natural Pellet Zeolite is a zeolite containing moderate silica with its hydrophilic properties.

Table 1. LNZ XRF Analysis Results Not Active and LNZ Active Pellet.

No	Compound	Concentration (%)	
		LNZ Before Activation	LNZ After Activation
1	Al_2O_3	15.815	8.42
2	SiO_2	79.046	58.158
3	K_2O	1.813	5.928
4	CaO	1.401	9.582
5	MnO	0.018	0.154
6	Fe_2O_3	1.157	6.577
7	Rb_2O	0.008	0.05
8	SrO	0.024	0.183
9	Y_2O_3	0.002	0.015
10	ZrO_2	0.013	0.096
11	Ag_2O	0.184	0.762
12	EU_2O_3	0.009	0
13	Cl	0.014	0.086

3.4. XRD Analysis Results

From Figure 5. It can be seen that the minerals arranged in LNZ before activation is clinoptilolite. Na and diopside crystals. Meanwhile, in the activated LNZ, the minerals composed are clinoptilolite minerals. In addition, it can be seen in Figure 5. that both calcined and uncalcined LNZ have minerals that are dominated by clinoptilolite, this can be seen from sharp peaks at an angle of 2 = 11.13°; 22.37o; 25.96°; 28,10°; 29.99°; and 35.63° for LNZ which has not been calcined and at an angle of 2 = 10.02°; 22.34°; 26.06°; 28.06°, 29.88°, 31.88° for LNZ which has been calcined. The highest peak in LNZ that has not been activated is at an angle of 2 = 22.37° that is equal to 580.24 cts while in LNZ which has been activated the highest peak is in the 2. region = 22.41o i.e. 219.26 cts. It is also known that in the angle range of 2 = 22 is identity angle of clinoptilolite, it is appropriate by standard ICSD using POWD-12++ (Johnson et al., 2003). Referring to LNZ which has been calcined, the structure does not experience significant changes because of the strong zeolite structure.

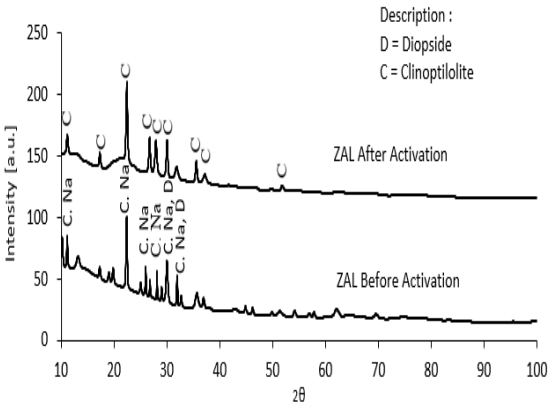


Figure 5. XRD Analysis Results.

3.5. BET Analysis Results

Figure 6. shows a graph of the results of the amount of nitrogen adsorption on the relative pressure P/P_0. The figure shows nitrogen adsorption isotherm of the activated natural Lampung zeolite with a rapid increase in low P/P_0 pressure, increases slowly in the middle, and increases again rapidly when P/P_0 approaches one. From Figure 5. it can be seen that when $P/P_0 = 0$, very little gas can be adsorbed, then the first increase occurs. This can occur due to the interaction of attractive forces between gas molecules and the solid surface (adsorbent). When this filling occurs, a single layer (monolayer) has been formed, but the monolayer area is formed incompletely.

Furthermore, when the pressure is increased to $P/P_0 = 0.42$, the monolayer region begins to saturate due to gas adsorption. Then when the pressure is increased again until $P/P_0 = 0.62$ multilayer adsorption begins to occur, this can occur due to the interaction of attractive forces between gas molecules and gas molecules, causing not all of the adsorbed molecules to come into direct contact with the solid surface (adsorbent). In this area, the amount of gas adsorbed is not too much, so the slope of the graph is small (the increase is not sharp). Then, when it rises to P/P_0 about 0.66 to 0.78, there is an interaction of gas molecules adsorbed on the opposite pore walls. After that, when the pressure is raised higher until it reaches $P/P_0 = 0.95$, the gas molecules have filled the mesoporous material. This causes the isothermal curve to increase sharply because the amount of gas adsorbed is very large. The gradual increase shows that the adsorbent pores are not uniform. The increase in the amount of

nitrogen gas adsorbed was due to the fact that the adsorbent had a fairly large pore (Perry, 2008). Furthermore, when the pressure is lowered for gas desorption, condensation of the adsorbed gas molecules occurs, this is shown in the isothermal curve. Capillary condensation will lead to the emergence of a hysteresis loop, i.e., when the amount of gas that is desorbed with the amount of gas that is initially adsorbed is not the same. Or, it can be said that the amount of gas that is adsorbed is smaller than that which is adsorbed.

Based on the IUPAC (*International Union of Pure and Applied Chemistry*) classification, activated Lampung natural zeolite has a type 4 isotherm pattern to categorize it into the mesoporous group, besides that, Lampung activated natural zeolite has branching commonly called the H4 type hysteresis loop (Fauzi et al., 2019). The branching can occur due to a phenomenon of capillary condensation, which occurs in the pores of the material. So that when the pressure is lowered the amount of gas that is desorbed is not the same as the amount of gas that was initially adsorbed. The shape of the curve in Figure 6. also has the same shape as the research conducted by (Neolaka et al., 2018).

Figure 6. shows a graph of the results of the amount of nitrogen adsorption on the relative pressure P/P_0. The figure shows the nitrogen adsorption isotherm of the activated Lampung Natural Zeolite sample showing a rapid increase when the P/P_0 pressure is low, then increases slowly in the middle and increases again rapidly when P/P_0 approaches one.

From Figure 5. it can be seen that when P/P_0 = 0, very little gas can be adsorbed, then the first increase occurs. This can occur due to the interaction of attractive forces between gas molecules and the solid surface (adsorbent). When this filling occurs, a single layer (monolayer) has been formed, but the monolayer area is stated to be incomplete. Furthermore, when the pressure is increased to P/P_0 = 0.42, the monolayer region begins to saturate due to gas adsorption. Then when the pressure is increased again until P/P_0 = 0.62 multilayer adsorption begins to occur, this can occur due to the interaction of attractive forces between gas molecules and gas molecules, causing not all of the adsorbed molecules to come into direct contact with the solid surface (adsorbent). In this area, the amount of gas adsorbed is not too much, so the slope of the graph is small (the increase is not sharp). Then, when it rises to P/P_0 about 0.66 to 0.78, there is an interaction of gas molecules adsorbed on the opposite pore walls. After that, when the pressure is raised higher until it reaches P/P_0 = 0.95, the gas molecules have filled the mesoporous material. This causes the isothermal curve to increase sharply because the amount of gas adsorbed is very large. The increase that occurs gradually concludes that the adsorbent has pores that are not aligned in size.

The increase in the amount of nitrogen gas adsorbed was due to the fact that the adsorbent had a fairly large pore (Perry, 2008). Furthermore, when the pressure is lowered for gas desorption, condensation of the adsorbed gas molecules occurs, this is shown in the isothermal curve. Capillary condensation will lead to the emergence of a hysteresis loop, i.e., when the amount of gas that is desorbed with the amount of gas that is initially adsorbed is not the same. Or, it can be said that the amount of gas that is adsorbed is smaller than that which is adsorbed.

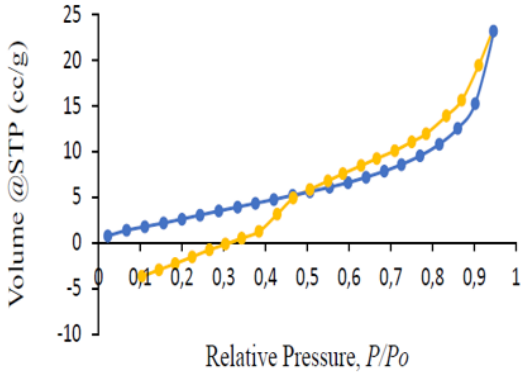


Figure 6. Adsorption–desorption isotherm curve

Based on the IUPAC (International Union of Pure and Applied Chemistry) classification, activated Lampung natural zeolite has a type 4 isotherm pattern which make them belongs to the mesoporous group, besides that, Lampung activated natural zeolite has branching commonly called the H4 type hysteresis loop (Fauzi et al., 2019). The branching can occur due to a phenomenon of capillary condensation, which occurs in the pores of the material. So that when the pressure is lowered the amount of gas that is desorbed is not the same as the amount of gas that was initially adsorbed. The shape of the curve in Figure 6. also has the same shape as the research conducted by (Neolaka et al., 2018).

Based on Figure 7 and Table 2, the activated Lampung natural zeolite has a non-uniform pore size, and shows microporous and

mesoporous size pores. The distribution graph of adsorption pore size shows an increase in pore diameter in the range 1.7–5.7 nm. IUPAC classification states that the pore size of the material less than 2 nm and in the range of 2–50 nm are microporous and mesoporous, respectively.

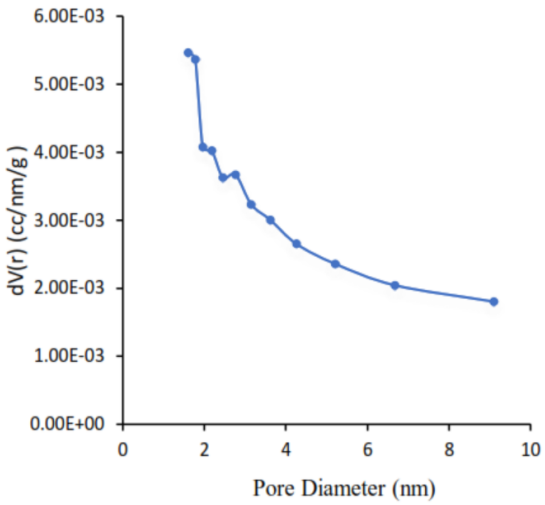


Figure 7. Zeolite Pellets Pore Size Distribution Chart.

Table 2. BET analysis results

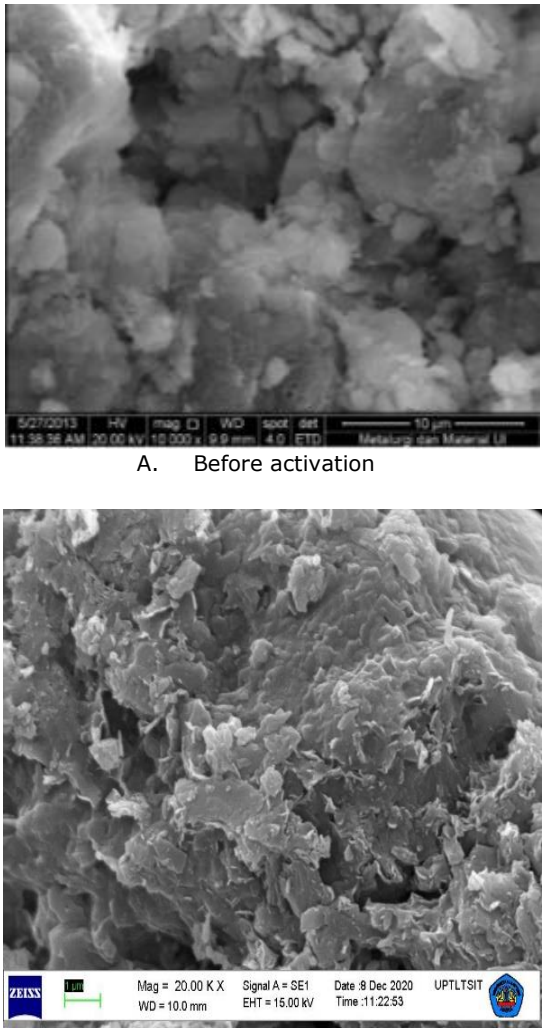
Sample	Surface area (m^2/g)	Total Pore Volume (cc/gram)	Pore Size (Å)
LNZ activation	17.670	0.035958	57.091

3.6. The morphology of zeolite

Figure 8 showed that, unactivated LNZ by the calcination process, the crystal form resembling flat plates is not clearly visible and the existing pores look less open and less clean. The activated LNZ by calcination process, the morphological structure is clearly more visible, the crystal shape resembles flat plates with more opened and clean pores (Panek et al., 2014). This shows that activation using high temperatures (calcination) can cause the crystal form in the zeolite to be clearer and more visible, besides that the activation process can also make the pores in the zeolite more open and look cleaner.

3.7. Effect of bed height

The effect of bed height of 5 cm, 10 cm, and 15 cm on water adsorption with a flow rate of 10 ml/min of an ethanol-water mixture, and a feed concentration of 91.805% (v/v) ethanol-water mixture is shown in Figure 9.



A. Before activation

B. After activation

Figure 8. SEM image of Lampung natural zeolite.

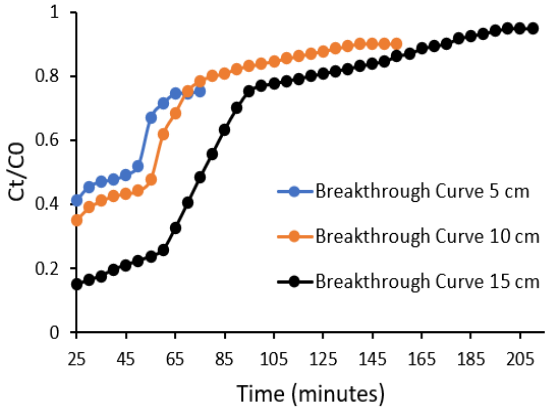


Figure 9. Breakthrough curve.

The results of this study shows that the higher the zeolite adsorbent bed, the greater the

contact zone of the ethanol-water solution with the zeolite adsorbent, thus the longer the saturation time. This is because of the large active surface area of the zeolite adsorbent, which creates a water mass transfer zone from the ethanol-water solution. To the zeolite adsorbent is getting bigger. This is also in accordance with research conducted by Okawale and Attia groups (Okewale et al., 2015; Attia et al., 2018).

3.8. Kinetic Studies

Three adsorption kinetics models (Thomas model, Yoon and Nelson model, and Adam-Boharts model) were selected to analyze the capability of the column.

Thomas Models: This model following Langmuir and adsorption kinetics. The driving force follows the kinetics of a second order reversible reaction, in this case the chemical reaction is not a rate limiting step but a process regulated by mass transfer at the adsorbent interface. The Thomas model of adsorption kinetics equation can be seen in Equation (1).

$$ln\left(\frac{C_0}{C_t}-1\right)=\frac{k_{Th}q_{Th}m}{v}-K_{Th}C_0 \qquad (1)$$

Where k_{Th} (ml/mg/min) is the Thomas kinetic constant, q_{Th} (mg/g) is the adsorption capacity of the Thomas model, m (g) is the mass of the adsorbent, Q (ml/min) is the volumetric flow rate, and t (min) is sampling time.

The Thomas kinetic constant (k_{Th}) and the adsorption capacity of the column (q_{Th}) can be determined from the plot of ln $((C_0/C_t)-1)$ against t at a certain flow rate, as slope and intercept respectively (Figure 10). As the height of the adsorbent bed increases, the adsorption capacity decreases. The results showed that the LNZ pellet adsorbent was able to absorb a maximum of 0.108 (g/g) water at a height of 5 cm adsorbent bed, where these results can be seen in Table 1.

Yoon and Nelson models: This model has the assumption that the rate of decrease in the probability of adsorption of adsorbate molecules is proportional to the probability of adsorption of the adsorbate and the probability of breakthrough adsorbent on the adsorbent bed. Yoon and Nelson model adsorption kinetics equation can be seen in Equation (2),

$$ln\left(\frac{C_t}{C_{0-}C_t}\right)=k_{Yn}t-\tau k_{Yn} \qquad (2)$$

Where is k_{Yn} (ml/min) is the Yoon-Nelson kinetic constant, (minutes) is the time required to reach 50% adsorbate breakthrough, and t (minutes) is the sampling time.

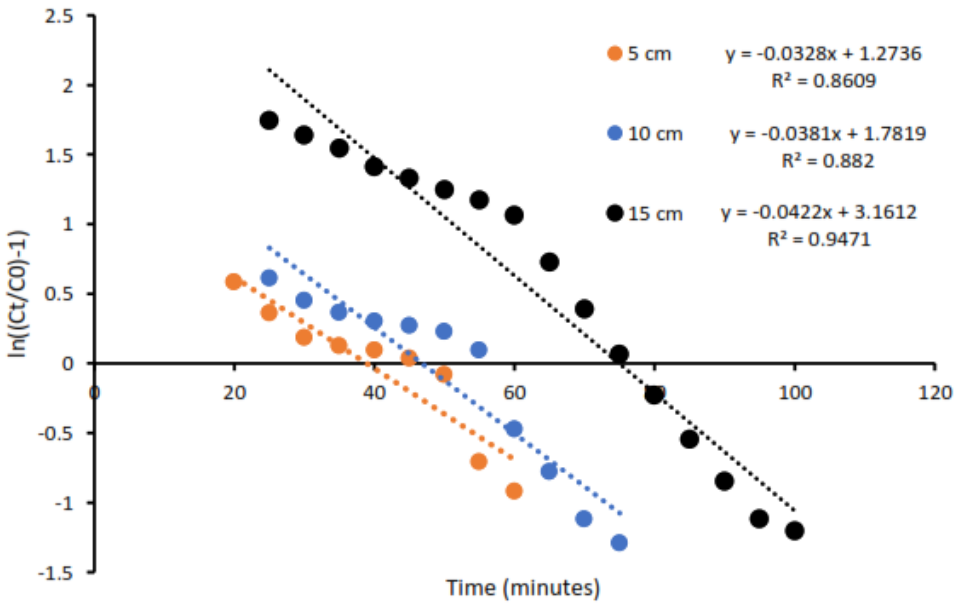


Figure 10. Effect of bed height on Thomas adsorption kinetic curve for water adsorption with lampung natural pellet zeolite adsorbent.

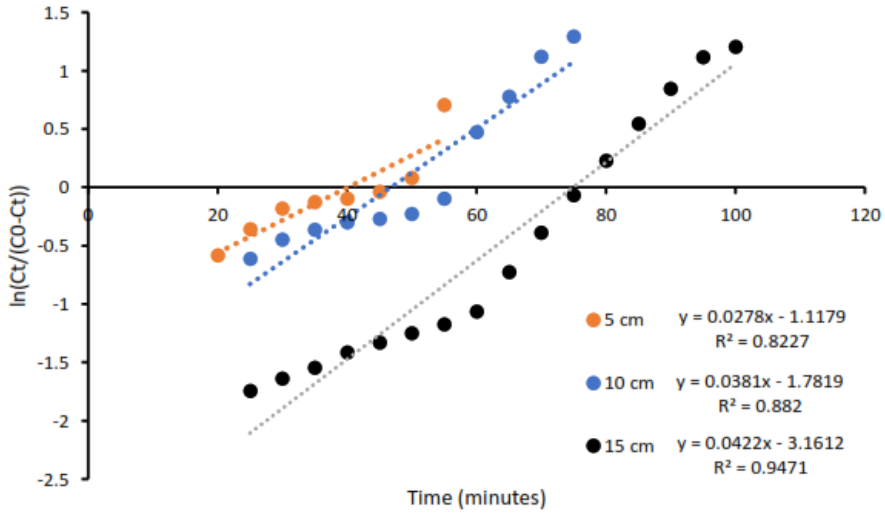


Figure 11. Effect of bed height on Yoon-Nelson adsorption kinetic curve for water adsorption with natural pellet zeolite adsorbent Lampung.

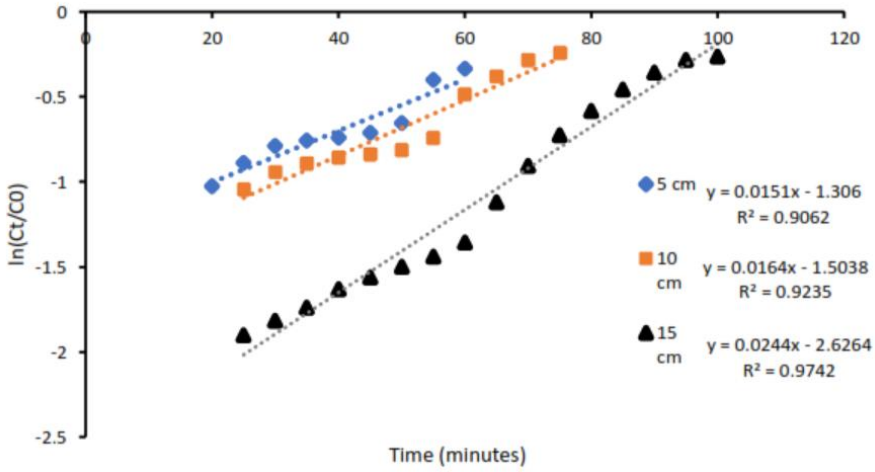


Figure 12. Effect of bed height on Adam Boharts adsorption kinetic curve for water adsorption with natural pellet zeolite adsorbent Lampung.

The plot of the value of ln ($C_t/(C_0-C_t)$) against t forms a straight line with the slope showing the value of k_{Yn} and the intercept showing the value $-k_{Yn}$, this can be reviewed on Figure 11. Based on value Thus, the adsorption capacity of the column in the Yoon-Nelson model (q_{Yn}, mg/g) can be determined by the following Equation (Patel and Vashi, 2012):

$$q_{Yn} = \frac{q_{total}}{m} = \frac{C_0 v\tau}{1000m} \quad (3)$$

The results show that adsorption capacity decreases with increasing bed height, this is because it has been determined that k_{Yn} and inversely proportional

Adam-Boharts model: This model have assumptions that the adsorption equilibrium is not fast and the adsorption rate is directly related to the remaining adsorbent capacity and the concentration of the adsorbate species. The equation of adsorption kinetics of Adam Boharts model can be seen in Equation (4),

$$ln\left(\frac{C_0}{C_t} - 1\right) = k_{AB}N_0\frac{Z}{F} - k_{AB}C_0 t \quad (4)$$

Where is k_{AB} (ml/mg/min) is the Adam-Bohart kinetic constant, N_0 (mg/ml) is the saturation concentration, Z (cm) is the thickness of the adsorbent, and F (ml/min) is the flow rate. The kinetic constant (k_{AB}) and the adsorption capacity of the column (N_0) can be determined from the plot of ln C_t/C_0 against t, respectively as slope and intercept (Sekhula et al., 2012), this can be reviewed on Figure 12. Based on the resulting N_0 value, the adsorption capacity of the column in the Adam and Bohart model

(q_{AB}, mg/g) can be determined by the following Equation (Trgo et al., 2011).

$$q_{AB} = \frac{N_0 V_{bed}}{m} = \frac{N_0}{\rho} \quad (7)$$

Where is V_{bed} (ml) is the volume of the adsorbent, and ρ (g/ml) is the density of the adsorbent. The results show that the adsorption capacity of the column decreases with increasing bed height.

Table 3 shows the results of constant adsorption kinetic, adsorption capacity, and coefficient determination which were obtained from the intercept and slope plots of the Thomas model, Yoon-Nelson model and Adam-Boharts model; the intercept and slope plots for each model are shown in Figure 10, 11, and 12.

Table 3. Adsorption kinetics of Lampung natural zeolite.

	Bed Height		
	5 cm	**10 cm**	**15 cm**
	Yoon and Nelson Kinetic		
k_{Yn} (min^{-1})	0.0328	0.0381	0.0422
τ (min)	38.829	46.769	74.9
q_{Yn} (g/g)	0.000108	0.000063	0.000066
R^2	0.08609	0.882	0.9471
	Thomas Kinetic		
k_{TH} (ml/g.min)	8.356	9.707	10.751
q_{TH} (g/g)	0.108	0.063	0.0666
R^2	0.8609	0.882	0.9471
	Adam Boharts Kinetic		
K_{AB} (ml/g.min)	3.847	4.178	6.216
N_0 (g/ml)	0.678	0.359	0.198
R^2	0.9062	0.9235	0.9742

4. Conclusion

From the results of the study, it can be seen that LNZ pellets are adsorbents with a moderate Si/Al ratio. In addition, they have asymmetric stretching vibrations of O-Si-O or O-Al-O, external vibrations of D4R and D6R or often referred to as double ring, and external vibration ring gap 12. LNZ pellets also have an average pore size of 57.091, a surface area of 17.670 m^2/g and a pore volume of 0.036 cc/g. When viewed from the morphological structure of LNZ pellets, the crystalline form resembles flat plates. Then LNZ pellets also have good durability and are able to increase the purity of ethanol up to 98.797% v/v at a height of 15 cm adsorbent bed. The most suitable adsorption kinetics model equation for this research is the Adam-Bohart equation with a bed height of 15 cm Zeolite Pellet adsorbent, where the R^2 value obtained is 0.974.

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