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Kinetic Study of Ammonium Desorption using Natural Zeolites from Cikalong

Thareqa Abdusattar[1], Abdul Hadi[1], Nuryoto[1,2], Teguh Kurniawan[1,2]*

[1]Jurusan Teknik Kimia, Fakultas Teknik, Universitas Sultan Ageng Tirtayasa
Jl. Jenderal Sudirman km.3, Cilegon, 42435, Indonesia
[2]Program Studi Magister Teknik Kimia, Pascasarjana, Universitas Sultan Ageng Tirtayasa
Jl. Raya Jakarta Km.4 Pakupatan, Serang, 42122, Indonesia

*Corresponding Author Email: *teguh@untirta.ac.id*

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ABSTRACT

Household liquid waste which contains ammonium is one of the major contributors to the wastewater effluent. The aim of investigation is to characterize and determine the adsorption capacity of natural zeolites from Cikalong for ammonium removal. The effect of cations type, K^+, Mg^{2+} and Ca^{2+}, on ammonium desorptions was studied. Kinetic desorption study was also performed and fitted with various kinetic models. According to X-ray diffraction (XRD) pattern, the Cikalong natural zeolites were mordenite and clinoptilolite dominant type. The morphology of the mordenite phase was appeared as needles shape. The ratio of Si to Al was 6.86 according to X-ray fluorescence (XRF). The surface area was 187 m^2/g which was determined by Brunauer–Emmett–Teller (BET) model. Desorption using K^+ solution showed the shortest time and the highest rate for ammonium desorption. The calculation using nonlinear method was carried out to optimize the desorption kinetic parameters. The pseudo 1st order desorption kinetics model showed the smallest error with sum of squared error (SSE) 0.00209.

Keywords: *Zeolites, Adsorption, Desorption, Kinetic, KCl*

1. INTRODUCTION

Human activities release waste into the environment in many different forms, including the wastewater called greywater. Greywater is wastewater that comes from the bathroom in households. Ammonium is one of the main contaminants in greywater found in bathrooms due to urine. Although ammonium is a very important nutrient for algae and agricultural plants, excessive ammonium in waterways and wastes causes eutrophication of rivers, lakes, and coastal seas.

Some adsorbent materials that have been commonly used in adsorption technology include synthetic materials such as activated carbon (Nejadshafiee & Islami, 2019), zeolitic synthetic materials (Darmayanti *et al*., 2019), metal–organic frameworks (MOFs) (Kobielska et al., 2018), mesoporous silica (Zhu *et al*., 2017), and natural materials such as clay, natural zeolite, and bottom ash and fly ash (João *et al*., 2019; Puspitasari, *et al*., 2019). However, Synthetic adsorbent materials require expensive preparation, a manufacturing process involving several chemicals, and long synthesis stages, which make this technology relatively impractical for heavy-waste removal. In contrast, natural adsorbent materials have several advantages, including their abundant availability in nature, ease of preparation, good adsorption properties, and relatively low prices (Hegazi, 2013)

Natural zeolites are naturally occurring microporous hydrated aluminosilicate minerals. Most common natural zeolites are formed by the alteration of glass-rich volcanic rocks (tuff) by freshwater in playa lakes or by seawater (Gandy *et al*., 2015). Natural Zeolites generally greenish-white to gray and greenish, mottled white and yellow, fine-grained to coarse, solid, but some are crushed when under pressure (Latief *et al*., 2003). Natural zeolites are formed due to complex chemical and physical processes of rocks that undergo various changes in nature. The study of ammonium adsorption and desorption using natural zeolites located in Cikalong, Tasikmalaya.

This study aims to determine the adsorption ability of Cikalong's natural zeolite against ammonium and to analyze the effect of the type of cation solution on ammonium desorption. Using theoretical aspects of adsorption such as adsorption isotherms and adsorption-desorption kinetics were also evaluated using non-linear regression methods. Kinetics parameters were optimized using MATLAB.

Source: google maps

Fig. 1. The location of natural zeolites in Cikalong

2. METHODS

2.1 Materials

The study of ammonium adsorption and desorption using natural zeolites which was obtained from Cikalong, Tasikmalaya, West Java. The location of natural zeolites deposit is pointed in the map as presented in Fig. 1. Solution of 100 ppm NH_4Cl was used for the adsorption process. Solution of 100 ppm KCl, $MgCl_2$, and $CaCl_2$ was applied for the desorption process.

2.2 Characterization

X-ray diffraction analysis (XRD) aims to see and the crystallinity of the natural zeolite of Cikalong. The first is to prepare zeolite samples and wash with distilled water and stir for 1 hour. The samples were dried at 105°C using an oven. The dried zeolite samples were crushed and filtered to a size of 5-10 mesh, then analyzed using X-ray diffraction (XRD).

The morphology of natural zeolites was examined by using SEM (Scanning Electron Microscope). The SEM analysis were performed with a Zeiss.

Zeolites surface area was determined using adsorption-desorption nitrogen analysis. The samples were dried at temperature 300 °C under vacuum for 6 h. Nitrogen gas adsorption was carried out at a cryogenic temperature of -196 °C. The Brunauer-Emmett-Teller (BET) model was used to calculate the surface area of the sample. The t-plot method was used to determine micropore volume and surface area.

2.3 Adsorption-Desorption study

Methods and data analysis were tested using a colorimeter (Hanna HI 715-25) to measure the concentration of NH_4^+ solution over a predetermined time interval.

For the adsorption study purpose, the zeolites were sieved to obtain 5-10 mesh size. The zeolites weight was varied for the adsorption process, i.e., 0.5, 1, 1.5, 2, 2.5, 3, 3.5, and 10 g. The zeolites were introduced into 100 ppm NH_4^+ solution for 3 days using a batch reactor. The remaining NH_4^+ concentrations were recorded by colorimetric method using a colorimeter.

For desorption, take 30 g of adsorbed sample, then dry it in an oven at 105 °C for 6 hours. Amount of 10 g NH_4^+-zeolites was immersed using various solution i.e., KCl, $MgCl_2$, $CaCl_2$ with concentration of 100 ppm. The desorption process was performed in a batch reactor for 72 h. The NH_4^+ concentrations released from zeolites were analyzed by colorimetric method using colorimeter instruments.

2.4 Kinetics Model

The pseudo 1st order is an adsorption prosses in which the rate is determined only by one substance. The differential equation for the 1st order is stated in the following formula (Eq. 1).

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \qquad (1)$$

Where:

q_t = the amount of substance adsorbed at a certain time (mg/g)

t = time (min)

k_1 = First-order constant rate (g/mg min)

q_e = the amount of substance adsorbed at equilibrium (mg/g)

Pseudo 2nd order is an adsorptiom process in which extension is directly proportional to the product of the concentration of two reactants or directly proportional to the square of the concentration of one of the reactants. If the adsorption that occurs is a second-order reaction where the speed of adsorption that occurs is directly proportional to the two concentrations of adherents or one of the two adherents. The rate of second-order adsorption kinetics is expressed in the following differential equation

$$\frac{dq_t}{d_t} = (q_e - q_t)^2 \qquad (2)$$

Where:

q_t = the amount of substance adsorbed with a certain time (mg/g)

t = time (min)

k_1 = Second-order pseudo constant rate ($g.mg^{-1}min^{-1}$)

q_e = the amount of substance adsorbed at equilibrium (mg/g)

Elovich kinetic model is an adsorption rate based on the adsorption capacity on heterogeneous surfaces. This model is formulated by the equation below.

$$\frac{dq_t}{d_t} = \alpha\exp\left(-\beta q_t\right) \qquad (3)$$

Where:

q_t = the amount of substance adsorbed with a certain time (mg/g)

α = adsorption parameter (mg/g min)

β = desorption coefficient (g/mg)

The intraparticle diffusion adsorption equation is as follows by the equation below;

$$q_t = k_1 t^{\frac{1}{2}} + C \qquad (4)$$

Where:

q_t = the amount of substance adsorbed with a certain time (mg / g)

k_1 = the initial rate of adsorption (mg / g min)

C = Parameter of intraparticle model

t = time (min)

3. RESULTS AND DISCUSSION

3.1 Natural Zeolites Characterization

XRF analysis is carried out to see the elemental component of the natural zeolites. Based on the results of the XRF, it can be seen that the silica and calcium are the main components of zeolites. The complete list of zeolite component is presented in Table 1.

Tabel 1. Elemental composition of Cikalong natural zeolites

Component	Mol (%)
Si	53.84
Ca	25.97
Al	7.84
Fe	3.11
K	3.67
P	4.37
Ti	0.58
Mg	0.43
Sr	0.0737
Cu	0.0470
Zn	0.0192
Rb	0.0062
Total	100

The Si and Al ratio of zeolites determined capacity of cation exchange function. XRF analysis data shows that the ratio of Si to Al is 6.86. The theoretical Si to Al ratio shows that the cationic capacity is large. The natural zeolites ion-exchange capacity normally decreases when using acid treatment. The acid reacts with zeolite causing Al extracted from the zeolite. This results in a decrease in the Al content in the zeolite so that the Si/Al mole ratio increases.

Zeolites phase type was determined by using XRD. The data is obtained by looking directly at each diffraction peak resulting from the x-ray diffraction measurement. In this study, the characterization of natural zeolites from Cikalong was carried out by comparing with zeolite standard XRD pattern to determine the type of crystal phase in Cikalong's natural zeolite. After being analyzed, Cikalong's natural zeolite contained mordenite, clinoptilolite, and quartz phases. This can be seen from the X-ray Diffraction (XRD) analysis graph (Fig. 2).

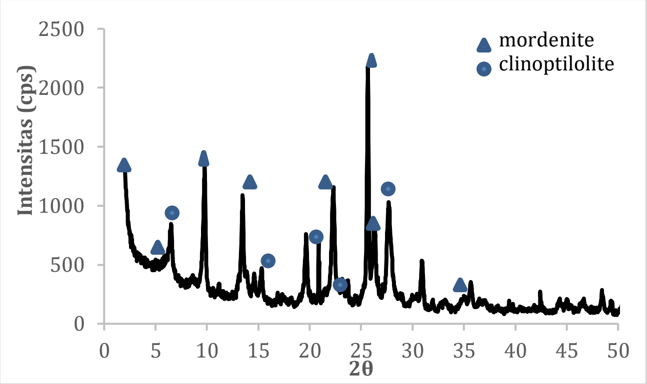
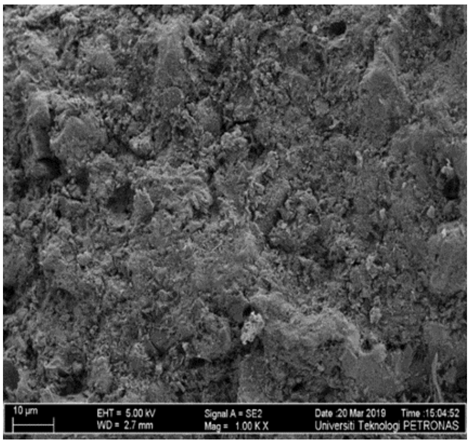


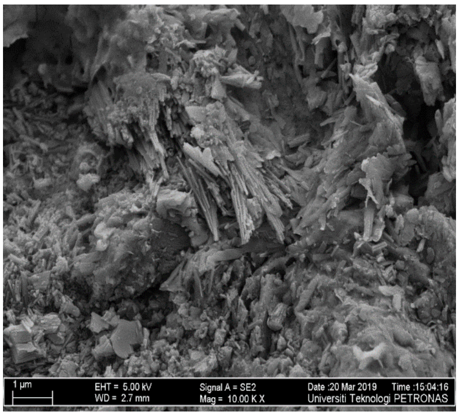
Fig. 2. XRD pattern of Cikalong natural zeolites.

Mordenite is a type of zeolite that has MOR (Mordenite) structure and Clinoptilolite is a type of zeolite that has HEU (Heulandite) structure. The HEU structure has two zeolite types which are clinoptilolite and heulandite types. The difference in diffraction patterns occurs because of the atoms present in the phase in the database but not in the sample or vice versa. It could also be due to a change in the angle of the zeolite sample frame (Anita *et al.*, 2019). Based on the analysis, Cikalong's natural zeolite is dominated by mordenite and clinoptilolite phases. Natural zeolites that have been mined intensively in Indonesia, including in the West Java region, namely Bayah, Cikalong, and Tasikmalaya, are mostly known as clinoptilolite and mordenite zeolites (Hardjatmo, 1996).

To see the surface morphology of natural zeolites, tests were carried out using SEM (Scanning Electron Microscopy). The analysis was carried out on samples of natural zeolites to see the morphology of natural zeolites which had previously been tested with XRD. SEM analysis on natural zeolites obtained the following figure.



a



B

Fig. 3. Comparison of SEM zeolite (a) 1.000x magnification (b) 10.000x magnification

At 1000x magnification indicates that the particles have different shapes, which are composed of smaller particles. At 10,000x magnification, it can be seen that the surface texture has pointed fibres like needles and lots of non-fibres. The needle-shaped fibres indicated that the zeolites was mordenite type.

Textural properties analysis was used to determined pore size using the BET method. The analysis of porous material (mesoporous) can be determined through the isotherm chart method based on the assessment of the ratio of P/P° (mmHg) to the volume of N_2 per gram of sample (ml/g). The Cikalong natural zeolite isotherm is presented in Fig.4 .

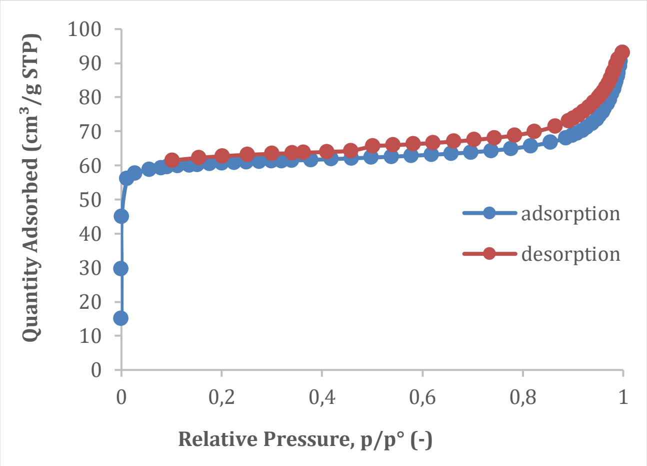


Fig. 4. Graph of Analysis of Textural Properties of Cikalong Natural Zeolites

Brunner-Emmet-Teller (BET) analysis was performed to see the specific surface area. The micropore area was determined by using t-plot method. The mesoporous area was determined by subtraction of BET total area with the micopore area. In this study, the surface area of Cikalong natural zeolite was 187 m^2/g which is considered as one of the zeolites with a large surface area because of the large amount of mordenite content in the zeolite.

Tabel 2. Textural properties of natural zeolites

Property	Quantity
Surface Area	187 m^2/g
Micropore Area	167 m^2/g
Mesopore Area	20 m^2/g
Micropore Volume	0.085 cm^3/g
Mesopore Volume	0.053 cm^3/g
Total Volume	0.138 cm^3/g

3.2 Ammonium Adsorption-Desorption

The ammonium adsorption process was carried out by the batch system for 72 h at room temperature. The amount of adsorbent used is 0.5 to 10 g added to the Erlenmeyer flask containing 50 ml of ammonium chloride solution with a concentration of 100 ppm. The different weight of natural zeolites showed different absorption from each mass variation of 0.5 g; 1 g; 1.5 g; 2.5 g; 3 g; 3.5 g; and 10 grams as presented in Fig.5.

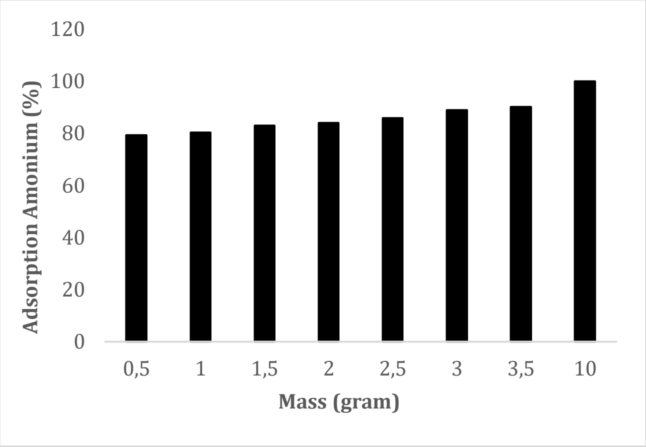


Fig. 5. diagram of the adsorption of ammonium by Cikalong's natural zeolite.

The nature of zeolite as an adsorbent and molecular filter is possible because the zeolite structure is able to adsorb a large number of molecules that are smaller in size or according to the size of their cavity.

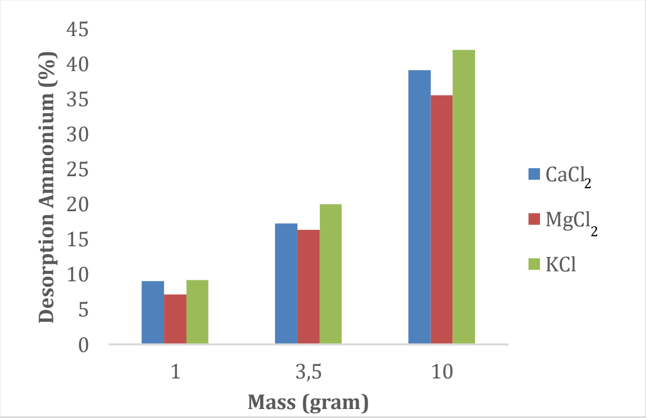


Fig. 6. Ammonium desorption diagram by Cikalong natural zeolite

The natural zeolite has been desorbed using 3 different solutions. the three of them have different desorption releases from each mass variation. The solution where each mass variation is 1 g; 3.5 g and 10 g can release ammonium levels using a solution of $CaCl_2$, $MgCl_2$ and KCl. in 1 g variation of 9%; 7.1%; 9.1%, on the variation of 3.5 gram of 17.2%; 16.3%; 20%, and the variation of 10 grams is 40%; 35%; 45%. In this case, the largest ammonium release is at 10-gram mass variations of 40%, 35%, and 45% by using $CaCl_2$, $MgCl_2$ and KCl, respectively (Fig. 6).

The kinetics models used were pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion. This kinetic model is used to describe both adsorption and desorption phenomena. The SSE value is a value that shows the error of the kinetics model with the experimental results, the smaller the value, the better results.

In our study, we used MATLAB to obtain the minimum error squares (SSE) for non-linear SSE values. As well as approaching SSE, making graphical comparisons is also decisive. This is done by comparing experimental data with model.

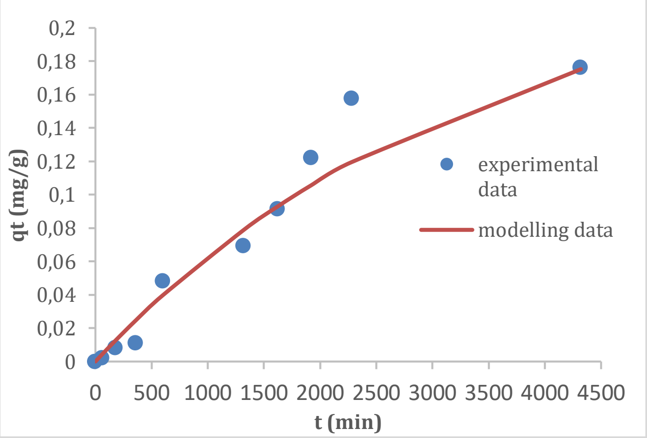


Fig. 7. Simulation of KCl variation desorption kinetics modeling

Fig. 7 shows the results of the desorption kinetic model and the ammonium desorption experiment using Cikalong's natural zeolite with KCl solution. From these results indicate that the first-order quasi kinetics model was fitted with experimental data with an SSE value of 0.000214.

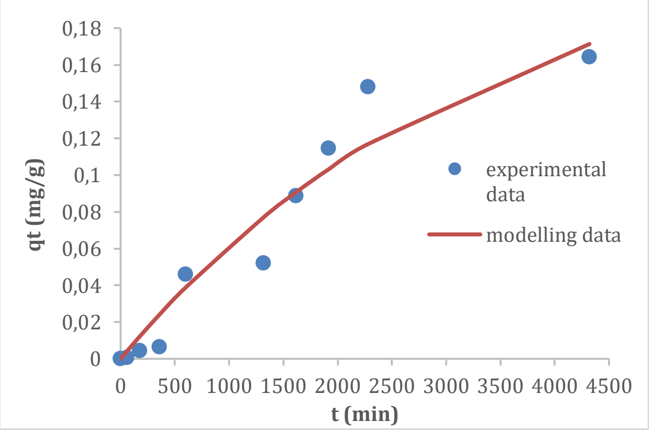


Fig. 8. simulation of $CaCl_2$ variation desorption kinetics modeling

Fig. 8 shows the results of the desorption isotherm modeling and the ammonium desorption experiment using Cikalong's natural zeolite, $CaCl_2$ solubility variation. From these results indicate that the first-order quasi kinetics model was fitted with experimental data with SSE value of 0.000209.

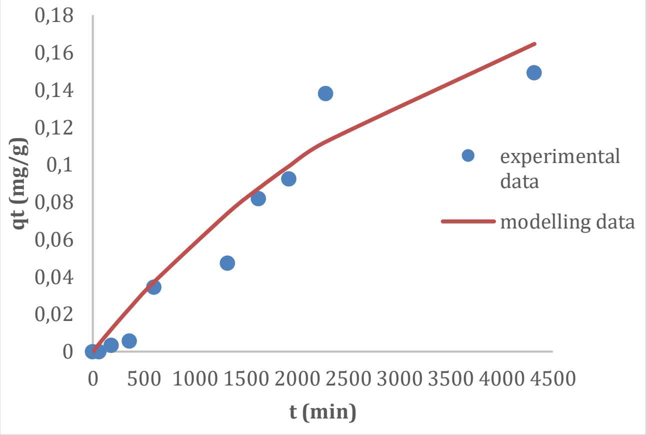


Fig. 9. simulation of $MgCl_2$ variation desorption kinetics modeling

Fig. 9 shows the results of the desorption isotherm modeling and the ammonium desorption experiment using Cikalong's natural zeolites, $MgCl_2$ solubility variation. From these results indicate that the first-order quasi kinetics model fitted with experimental data with an SSE of 0.000226.

Desorption using K^+ solution showed the shortest time and the highest rate for ammonium desorption. The calculation using nonlinear method was carried out to optimize the desorption kinetic parameters. The pseudo 1st order desorption kinetics model showed the smallest error with sum of squared error (SSE) 0.00209.

Potassium ion has lost one of its electrons similar with the NH_4^+. This is most likely the reason of why the desorption using potassium ion show the shortest time instead of the magnesium and calcium ion.

4. CONCLUSION

Cikalong natural zeolites was identified as mordenite rich zeolites accompanied with clinoptilolite and quartz. The adsorption of Cikalong's natural zeolite showed high adsorption capcity, with a mass of 0.5 g zeolite was 79.05% and 10 g zeolite was 99.85%. Desorption ammonium from 10 g zeolite using KCl, $CaCl_2$, and $MgCl_2$, solution was 45%, 40% and 35%, respectively. The types of cations affect the desorption of ammonium from zeolite. Based on the SSE value from comparisons and calculations with 4 models that have been carried out to get desorption kinetics parameters. The pseudo 1st order desorption kinetics model showed the smallest error with sum of squared error (SSE) 0.00209.

5. ACKNOWLEDGMENTS

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