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Characterization of Zeolites from Tasikmalaya, Indonesia, and Its Application for Ammonium Removal

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ABSTRACTS

The objectives of the study were to characterize natural zeolites from Cikalong, Tasikmalaya, Indonesia, and test for ammonium removal. Characterization was performed by using X-ray fluorescence (XRF), X-ray diffraction (XRD), and Scanning Electron Microscope (SEM). According to XRF analysis, the ratio of Si/Al was 6.8. The XRD pattern revealed that the zeolites were mordenite dominant phase. The SEM images showed the needles shape of mordenite typical morphology. Ammonium removal test was performed in the batch reactor with a variation on natural zeolite mass loading and adsorption time. Various isotherm models, i.e., Langmuir, Langmuir-Vageler, Freundlich, and Tempkin were fitted with the kinetic data by using optimization of the sum of the least square method. The Langmuir-Vageler model was best fitted with the error sum of squares 0.01. Furthermore, the study on kinetic models such as Lagergren's 1st order, Pseudo 2nd order, Elovich, and Intraparticle diffusion was fitted with the ammonium adsorption isotherm data by using optimization of the sum of the least square method. The Pseudo 2nd order showed the smallest error sum of squares 0.007.

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1. INTRODUCTION

Despite the lower concentration of ammonium having a beneficial impact on human life, the presence of ammonium in higher concentrations could danger living creatures. Ammonium is commonly generated from industrial activities, human activities in the attempt of providing food such as farming and livestock, including household activities that generate domestic waste. The Indonesian threshold limit value of total ammonia on the surface of the water varies from 0.3 – 10 mg/L (Spanton & Saputra, 2017). As the Indonesia population growth is continuing to increase exponentially, this ammonium waste will likely be increased.

An excessive discharge of ammonium in the further mechanism of reaction with other species contained in the wastewater may result in eutrophication and acidification which then affects the environment. Research for reducing ammonium concentration in the aqueous environment has been widely conducted with various methods. The ion exchange mechanism has popularly chosen over biological mechanism because ion exchange is more efficient and non-destructive compared to biological mechanism (Kurniawan, 2020).

Zeolites are widely known as compounds of alumina hydrated silicate with exchangeable cations of alkali and alkaline earth, i.e., calcium (Ca^{2+}), potassium (K^{+}), magnesium (Mg^{2+}), sodium (Na^{+}) (Sukor *et al*., 2017). They can be utilized for various applications such as adsorption, catalyst, agriculture, soil remediation, as well as energy (Yulianis et al., 2018). Zeolites themselves are also reported as promising media for the removal of ammonium (NH^{4+}) cation from the water body. The main factor that makes zeolites suitable for this purpose, is their high ability of cations exchange properties due to the need for cations on the aluminum framework, besides other unique characteristics and porous structures which form three-dimensional spaces. The ion exchange mechanism of NH^{4+} with zeolites is as the following:

Ion exchange mechanism for monovalent ion like K^{+}, Na^{+}

$$M_x\boldsymbol{Z} + NH_4^+ \leftrightarrow (NH_4)_x\boldsymbol{Z} + xM^+$$

Ion exchange mechanism for divalent ion Ca^{2+}, Mg^{2+}

$$M_{x/2}\boldsymbol{Z} + NH_4^+ \leftrightarrow (NH_4)_x\boldsymbol{Z} + \frac{x}{2}M^{2+}$$

Intensive research of zeolites structures and characteristics is likely continuing conducted all over the world to find the zeolites with high potential capability in ammonium removal. Indonesia is zeolites-rich-country because it is located on the ring of fire and one of the places that produce an abundance amount of natural zeolites is Cikalong. It is located in Tasikmalaya, West Java, Indonesia. Other reports (Kurniawan, 2020; Soerardji *et al*., 2015; Dziedzicka *et al*., 2016; Ates and Akgül, 2016; Wibowo *et al*., 2017) were the previous studies of natural zeolites. Despite there being a lot of studies of Indonesia's natural zeolites; however, the comprehensive study for Cikalong zeolites is rarely found in the literature.

Hence, this comprehensive study of Cikalong natural zeolites was aimed to identify the characteristics of Cikalong zeolite, its capability in ammonium removal, as well as an understanding of kinetic and isotherm behaviors using various modeling of kinetic and isotherm equations.

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2. METHODS

2.1. Characterization of Cikalong natural zeolites

The object of study is zeolites that were obtained from Cikalong, Tasikmalaya, West Java, Indonesia. The zeolites samples were characterized using: (1) X-ray Fluorescence (XRF) to analyze the zeolite elements, (2) X-ray Diffraction (XRD) for analyzing the dominant crystalline phases of Cikalong zeolite, (3) Scanning Electron Microscope (SEM) to study the morphology of Cikalong zeolites crystalline, (4) N_2 physisorption using a Micromeritic Tristar II 3020 to determine surface area and pore volume.

2.2. Testing of ammonium cation removal

Testing of ammonium removal was conducted using Ammonium solution:

(i) 10 grams of zeolites were added to 100 ppm ammonium solution, and the effect of time variation on the ammonium cation removal was observed every hour.
(ii) Different zeolites masses, 0.5 – 10 grams were added to the 50 mL of 100 ppm ammonium solution ppm and sit for 3 days before analyzing the remained ammonium in the solution.
(iii) The amount of ammonium left in the solution was measured by the colorimetric method.

2.3. Kinetic study of Cikalong natural zeolite

For the kinetic study of Cikalong zeolites, data were analyzed using four kinetic equations of Lagergren's 1st order, pseudo 2nd order, Elovich, and Intraparticle diffusion. Those equations are described as the following:

The equation of Lagergren's 1st order is to be determined as in Equation [1]:

$$\frac{dq_t}{dt} = k_L(q_e - q_t) \tag{1}$$

where q_e represents the amount of milligram ammonium adsorbed per gram of zeolites at equilibrium (mg/g), q_t (mg/g) is the amount of milligram ammonium adsorbed per gram of zeolites at time t (min), while the rate constant of Lagergren's equation is indicated by K_L (L/mg). The equation 3 is rewritten into a non-linear equation which is obtained by separating variable method with initial condition at t = 0, q_t = 0 and at t=t, q_t =q_t (see Equation [2]).

$$q_t = q_e - \frac{q_e}{\exp(k_L t)} \tag{2}$$

The written equation of pseudo 2nd order is shown in the following Equation [3].

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{3}$$

where k_s is the constant rate of pseudo 2nd order equation. Separation of each variables using initial condition at t = 0, q_t = 0 and at t=t, q_t =q_t can solve the differential equation into non-linear equation (4):

$$q_t = q_e - \frac{q_e}{1-(k_s q_e t)} \tag{4}$$

Equation [5] shows the Elovich equation of kinetic adsorption.

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{5}$$

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where α and β are the Elovich's kinetic parameters. The non-linear equation of Elovich's model can be obtained by separating the variable method with the initial condition at t = 0, q_t = 0, and at t=t, q_t =q_t. The solved equation is presented in Equation [6].

$$q_t = \frac{1}{\beta}\ln(1+\alpha\beta t) \tag{6}$$

While the Intraparticle diffusion model is shown in Equation [7].

$$q_t = k_i t^{1/2} + C \tag{7}$$

where k_i is the constant rate of the Intraparticle model and C is the intercept of the linear equation.

2.4. Isotherm study of Cikalong natural zeolite

Isotherm study is conducted using four models of isotherm equation, i.e., Langmuir, Langmuir-Vageler, Freundlich, and Temkin.
The Langmuir isotherm model is stated as the following Equation [8]:

$$q_e = \frac{q_{max}K_L C_e}{1+K_L C_e} \tag{8}$$

where q_{max} is defined as the maximum capacity (mg/g) of Langmuir monolayer adsorption, while K_L is the constant for the Langmuir equilibrium model.
The Langmuir-Vagelar equation is described as the following Equation [9]:

$$q_e = \frac{r q_{max}}{r+K_{LV}} \tag{9}$$

where $r=VC_o/m$, V is ammonium solution volume (L), C_o is the initial concentration of ammonium in the solution (mg/L), with K_{LV} as the Langmuir-Vageler constant.
Isotherm equation of Freundlich is provided by the following model in the Equation [10]:

$$q_e = K_F C_e^{1/n} \tag{10}$$

where K_F is the Freundlich's capacity factor.
Temkin's isotherm equation is as follows (see Equation [11]):

$$q_e = B\ln(K_t C_e) \tag{11}$$

where B describes the heat of adsorption parameter and K_t is the constant of an equilibrium binding.
Non-linear least squared (NLLS) analysis was chosen over the linearization method, to fit the experimental data with models, which is believed to be more accurate. The sum of squared error (SSE) was used for the error analysis method (see Equation [12]).

$$SSE = \sum_{i=1}^{n}\left(q_e - q_{e,calc}\right)^2 \tag{12}$$

where $qe_{,calc}$ is the milligram amount of ammonium capture per gram of zeolites mass at equilibrium calculated by the model (mg/g).

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3. RESULTS AND DISCUSSION

The results and discussion of the characterization, NH_4^+ removal efficiency, kinetic and isotherm studies were as the following:

3.1. Temperature

Elemental analysis of Cikalong zeolites sample using XRF shows the result as presented in **Table 1**. The characteristics of Cikalong zeolite were determined successfully using XRF, XRD, SEM, and N_2 physisorption. XRF elements analysis result shows that dominant metal cations of Cikalong zeolites were calcium (Ca^{2+}) and potassium (K^+) as indicated by the metals amount of Ca=12.3% and K=5.67%. The ratio mol of silicon to aluminum according to XRF analysis was 6.8. Theoretically, the numbers of monovalent cations attached in the zeolites framework would be the same as the numbers of aluminum in the framework.

Table 1. Element analysis of Cikalong zeolite.

Element	% Atomic Weight
Si	59.5
Ca	12.3
Al	8.36
Fe	6.89
K	5.67
P	5.35
Ti	1.11
Mg	0.42
Sr	0.255
Cu	0.12

The XRD result of the Cikalong zeolites sample is seen in **Figure 1**. XRD pattern shows that Cikalong zeolite crystalline was mainly mordenite and with less amount of clinoptilolite and quartz. **Figure 2** presents the SEM images and EDX of Cikalong zeolites.

The presence of mordenite and clinoptilolite was further strengthened by the SEM image of 5.000x and 10.000x magnification. At 10.000x magnification, it clearly shows the presence of mordenite by the appearance of needle-shaped crystalline phase which is typical of mordenite. Clinoptilolite was also observed on the SEM image which was indicated by the platy-shape crystalline phase.

Nitrogen (N_2) physisorption of Cikalong natural zeolites which conducted using a Micromeritic Tristar II 3020, under temperature -196°C shows the result as the following **Figure 3**.

The N_2 physisorption result indicated the BET surface area calculation of Cikalong zeolite was 186 m^2/gram. Compared to the previous research on various sources of natural zeolites, this research has remarkable results because the BET surface area of Cikalong zeolite was reported as the highest. **Table 2** shows the comparison of various zeolites characteristics that have ever been studied.

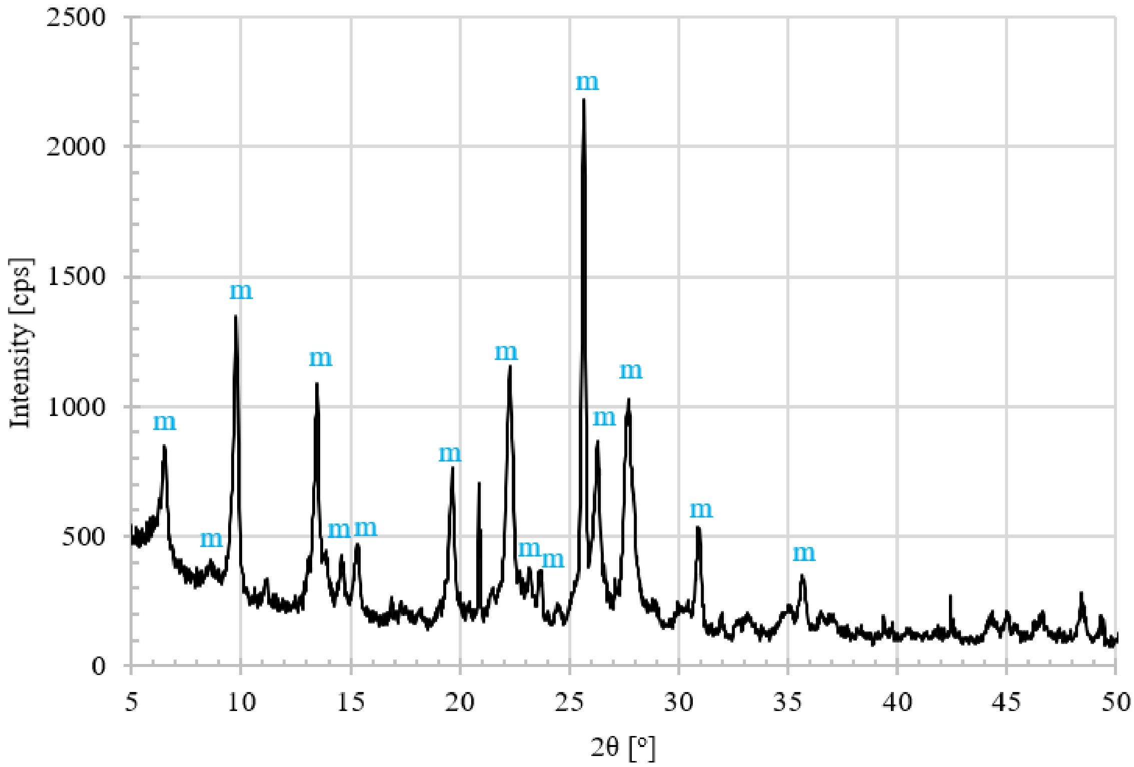

Figure 1. XRD pattern of Cikalong natural zeolites.

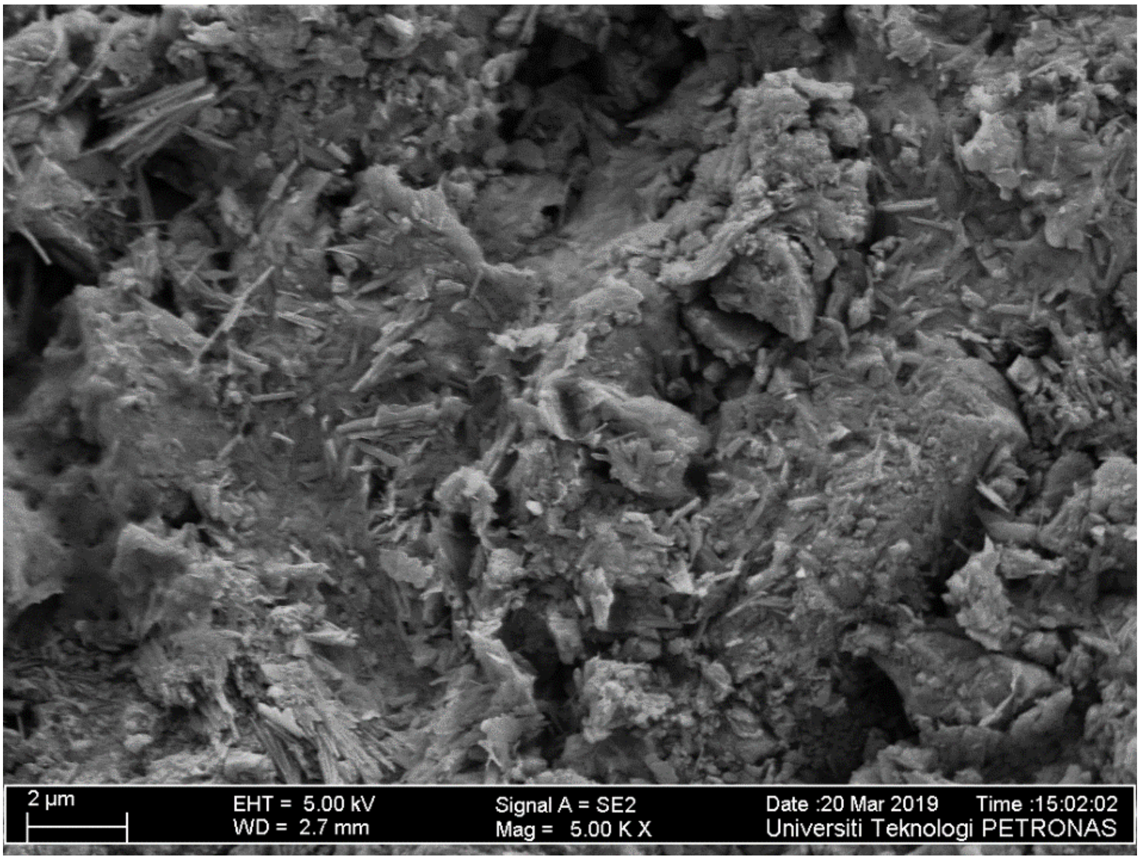

Figure 2. SEM image of Cikalong zeolite.

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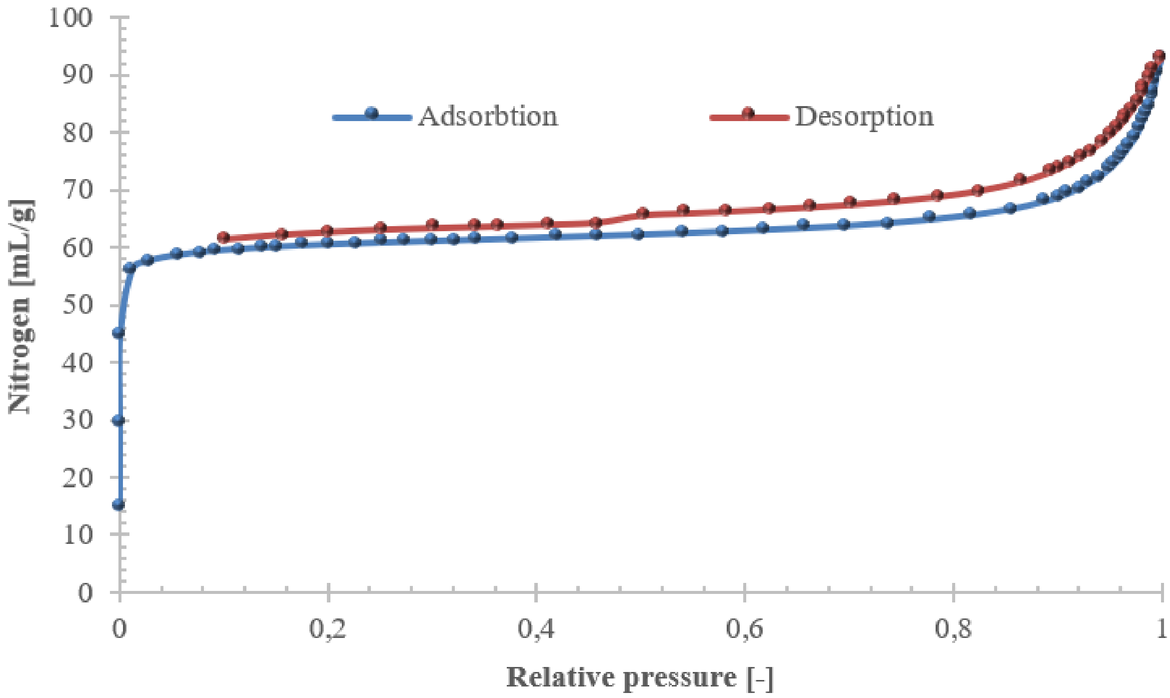

Figure 3. Nitrogen adsorption-desorption of Cikalong natural zeolites.

Table 2. Element analysis of Cikalong zeolite.

Origin of natural zeolites	Zeolites type	BET surface area	Pore volume	Micropore volume	Si/Al	Ref
Tasikmalaya, Indonesia	Mordenite, clinoptilolite	186	0.138	0.084	6.8	this work
Sukabumi, Indonesia	Clinoptilolite, mordenite	31	0.089	ND	4.6	(Wibowo *et al.*, 2017)
Ponorogo, Indonesia	Mordenite	30	0.116	0.002	4.5	(Soetardji *et al.*, 2015)
Klaten, Indonesia	Mordenite, clinoptilolite	107	0.074	0.040	5.5	(Nasser *et al.*, 2016)
Kucin, Slovakia	Clinoptilolite	33	0.135	0.003	4.1	(Dziedzicka *et al.*, 2016)
Demirci, Turkey	Clinoptilolite	112	0.330	0.045	4.7	(Ates & Akgül, 2016)

3.2. Testing of Ammonium removal using Cikalong zeolite

A 24-hours observation of Ammonium removal amount on the constant amount of zeolite mass added, shows the efficiency of cation removal as seen in **Figure 4. Figure 4** shows the efficiency of ammonium removal using Cikalong zeolite. The first 3 hours of 100 ppm Ammonium cation removal by the 10 grams of zeolite were observed as the highest removal rate, after that the removal efficiency was relatively stable. The effect of the different masses of zeolite was added and presented in **Figure 5**, indicating that the ammonium removal

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efficiency was increased as the zeolite mass increased. The removal efficiency data showed that Cikalong zeolite has a high capability in capturing ammonium cation from the solution.

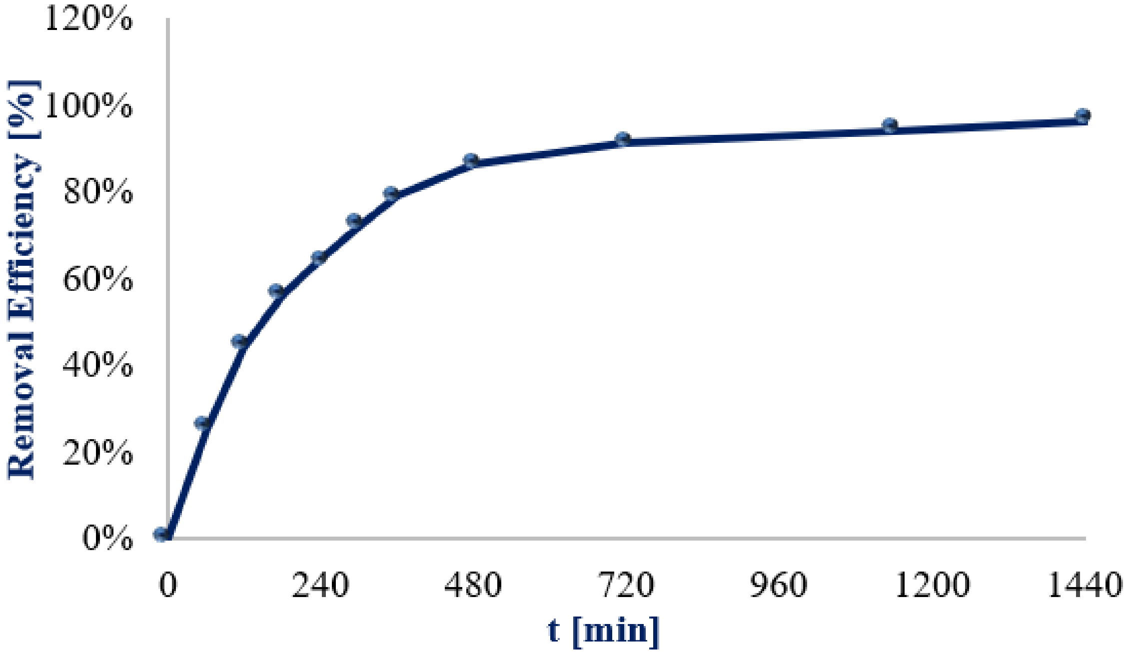

Figure 4. Time effect of Cikalong natural zeolites on the Ammonium removal efficiency.

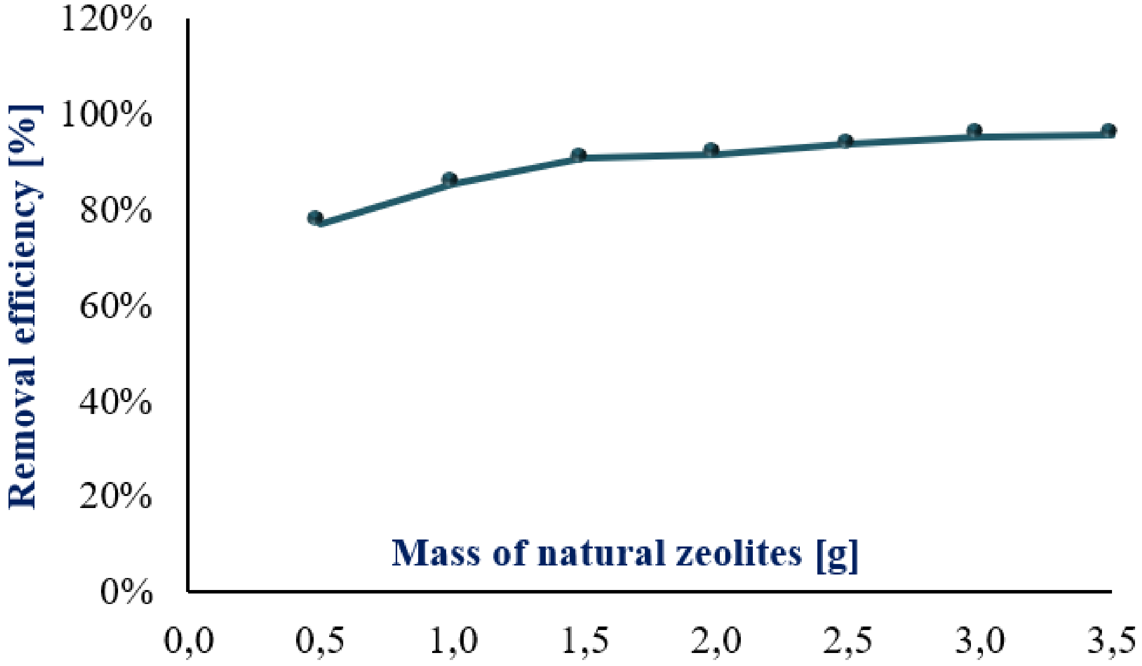

Figure 5. Zeolite mass effect of Cikalong zeolites on the Ammonium removal efficiency.

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3.3. Kinetic study result of Cikalong natural zeolite

The kinetic study with 4 different models of equations: Lagergren's 1st order, pseudo 2nd order, Elovich & Intraparticle diffusion; shows the results like the following **Figure 6**. The kinetic study was conducted to understand the speed of mass transfer from ammonium solution which the information of it would be useful and important for the unit operation design aspect. Four models of kinetic study of ammonium cation adsorption using Cikalong zeolites are presented in **Figure 6**. Well-fitted model following SSE value was found for Elovich and Pseudo 2nd order equations with the level of error 0.007 and 0.009 respectively. The equilibrium condition was reached at 0.4855 mg/g. The calculation of kinetic parameters was solved with Matlab, and detailed parameters of each kinetic model are shown in **Table 3**.

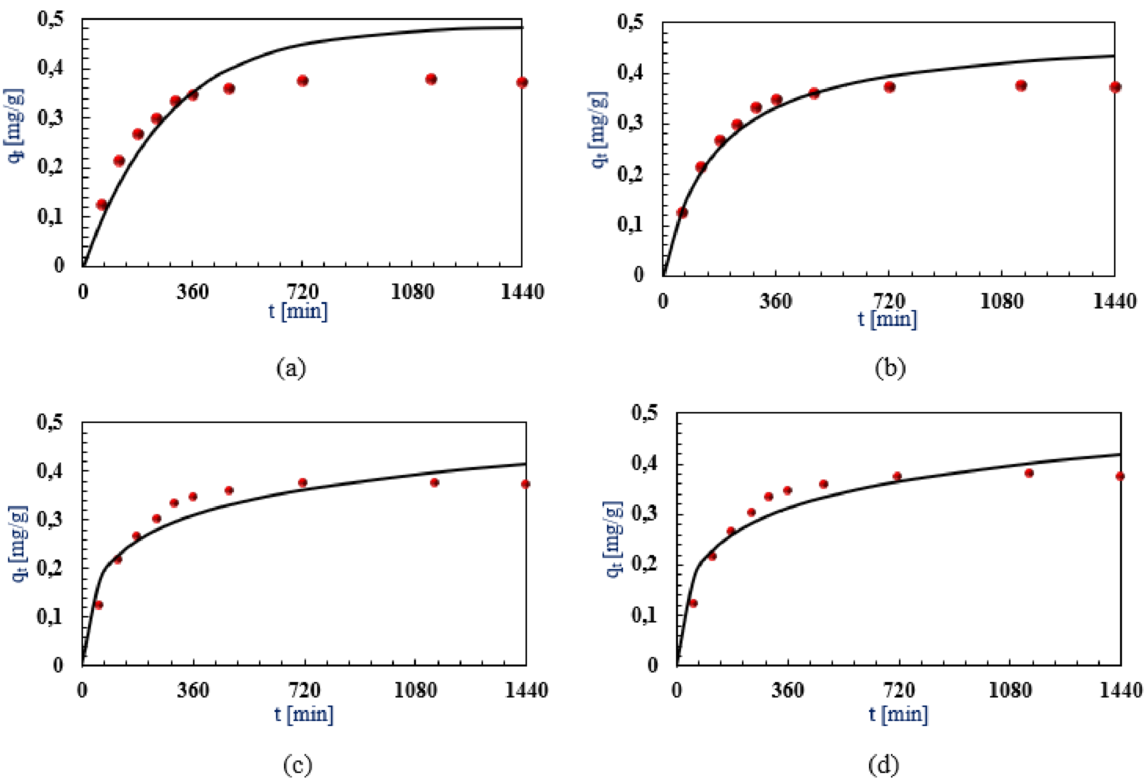

Figure 6. Non-linear least-square fitted kinetic model of (a) Lagergren's 1st order (b) pseudo 2nd order (c) Elovich (d) Intraparticle diffusion.

Table 3. Parameter of various models for NH^{4+} capture.

Kinetic Model	Parameter		SSE
Legergren's 1st order	k_L	q_e (mg/g)	0.034
	0.0036	0.4855	
Pseudo 2nd order	k_s	q_e	0.007
	-0.0125	0.4855	
Elovich	α	β	0.009
	0.0117	12.896	
Intraparticle diffsion	k_i	C	0.021
	0.0069	0.1656	

3.4. Isotherm study result of Cikalong natural zeolite

The isotherm study with 4 different models of equations: Langmuir, Langmuir-Vageler, Freundlich, and Tempkin; shows the results in **Figure 7**. **Figure 7** describes the fitted experiment data with various isotherm models, i.e. Langmuir, Langmuir-Vageler, Freundlich, and Temkin. Langmuir-Vageler equation shows the best-fitted model for ammonium adsorption of Cikalong zeolites, with a sum square of error 0.01. The maximum ammonium cation adsorbed based on this equation was 19 mg/g. This value is significantly higher compared to previous research of natural zeolite characterization, i.e. capacity of Bayah zeolite was reported to be 5.84 mg/g [6]. The calculation of isotherm parameters was solved with Matlab, and detailed parameters of each isotherm model are shown in **Table 4**.

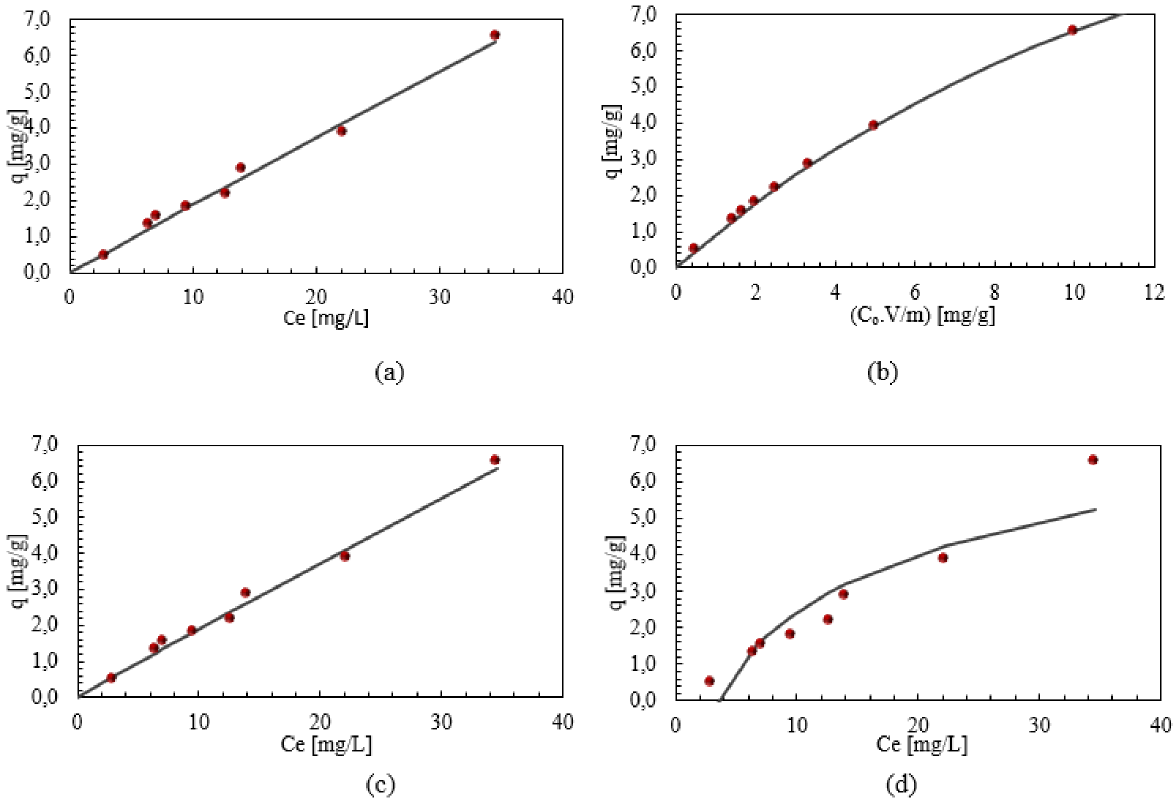

Figure 7. Non-linear least-square fitted isotherm model of (a) Langmuir (b) Langmuir-Vageler (c) Freundlich (d) Tempkin.

Table 4. Isotherm parameter of various models for NH^{4+} capture.

Isotherm Model	**Parameter**		**Error**
Langmuir	**q_{max} [mg/g]**	**K_L [L/mg]**	Sum Square of Error. **SSE[a]**
	353	0.0005	0.25
Langmuir-Vageler	**q_{max} [mg/g]**	**K_{LV} [L/mg]**	**SSE**
	19	19.083	0.01
Freundlich	**K_F [$L^{1.1}$/(g.$mg^{0.1}$)]**	**n [-]**	**SSE**
	0.20	1.0	0.25
Tempkin	**B [mg/g]**	**A [L/mg]**	**SSE**
	2.2811	0.289	5.56

4. CONCLUSION

Cikalong zeolites are promising to be utilized for ammonium removal of water surfaces. This study shows that Cikalong zeolites are one of the best zeolites that have ever been reported in the world in terms of BET surface area 186 m^2/g and the high efficiency of ammonium removal 19 mg/g, with mordenite and clinoptilolite as the main zeolitic phase. Cikalong zeolites are typical of high silica content zeolites with Si/Al ratio 6.8 along with calcium (Ca^{2+}) and potassium (K^+) as the dominant cations.

5. ACKNOWLEDGMENT

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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