Malang natural zeolites

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Submission date: 02-Apr-2023 09:42AM (UTC+0700)
Submission ID: 2053159340
File name: Ammonium_adsorption_malang_natural_zeolites.pdf (868.39K)
Word count: 2490
Character count: 12688

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Cite as: AIP Conference Proceedings **2370**, 020017 (2021); https://doi.org/10.1063/5.0062206

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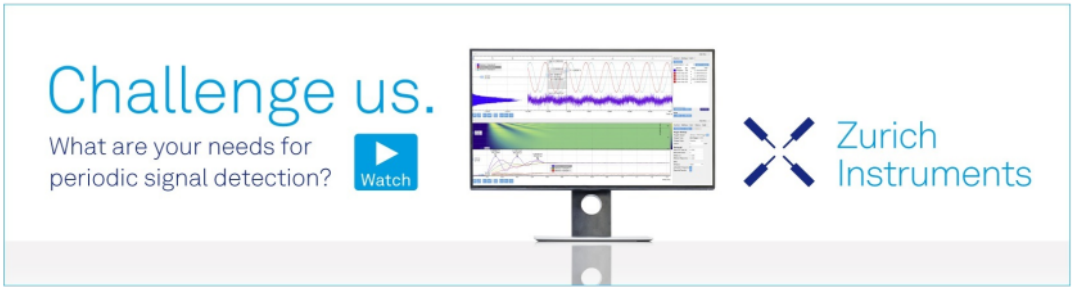

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Ammonium Adsorption from Wastewater using Malang Natural Zeolites

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Abstract. Zeolite is minerals contain alumina and silica that cross-linked forming a porous tetrahedron shape. This porous structure is enabling zeolites to have advantage as an adsorbent. One of the common technical application of zeolite is as an adsorbent and one of the ion that have high affinity on zeolites is ammonium. Ammonium is an ion form of ammonia and considered as a waste in environment. The objectives of the research were to characterize and study the ammonium adsorption kinetic and isotherm of the Malang natural zeolites. Characterization of the natural zeolites was conducted by X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscopy-Energy Dispersive of X-ray Spectroscopy (SEM-EDX) and nitrogen physisorption using Brunaurer, Emmet dan Teller (BET) model. According to the XRD patterns, the natural zeolites were dominated by mordenite and clinoptilolite type of zeolite with quartz as impurity phase. The mordenite phase finding was supported by SEM image that showed the needle shape. Analysis using FTIR showed the peaks correspond to functional groups zeolite framework formation. The SEM-EDX showed that the Si/Al ratio of Malang natural zeolite was 5.5. The surface area calculated by nitrogen physisorption was 52 m^2/g. Ammonium adsorption test was conducted by 100 ppm of ammonium solution in the batch reactor with variation on adsorption time and mass loading. Ammonium adsorbed onto the zeolites was increased with the adsorption time and mass loading. The kinetic model of Elovich and isotherm model of Langmuir were best fitted with the ammonium adsorption of Malang natural zeolite.

INTRODUCTION

Ammonium is an ionic form of ammonia with the chemical formula NH_4^+. There are various activities that can generate ammonium waste such as excessive fertilizer in agriculture activity, domestic waste and animal feed industry. Ammonium in nature could cause eutrophication, fish respiratory system interference, and disruptions to other aquatic life, hence efforts are needed to maintain its concentration in the environment [1]. Several methods have been studied to reduce ammonium content in nature. For instance, addition of NaCl or KCl for application in fish ponds, nitrification or denitrification as biological process, stripping, ion exchange and adsorption. From all of those methods, adsorption is one of the options that is generally considered simple to implement and relatively low cost to remove ammonium in waste [2].

The adsorption process requires an effective adsorbent so that it can separate ammonium from wastewater. The material for adsorbent is expected to have high adsorption capacity, having different charge with ammonium, insoluble in ammonium solution, large surface area, cheap and easy to obtain. One of material that fulfill the criteria is zeolite [3].

3rd International Conference on Chemistry, Chemical Process and Engineering (IC3PE)
AIP Conf. Proc. 2370, 020017-1–020017-7; https://doi.org/10.1063/5.0062206
Published by AIP Publishing. 978-0-7354-4126-2/$30.00

Zeolites are rocky minerals those are composed of clusters of Al_2O_3 and SiO_2 which are tetrahedrally bound [4]. These tetrahedral structures form cavities that, in nature, generally contain water and alkali metal or alkaline metal ions [5,6]. The porous structure gives zeolite an advantage as ion or molecular adsorbent. Ions or molecules that are fit with the zeolite cavity and zeolite composition could be diffused and distributed throughout the zeolite cavity system [7]. Ammonium has a high affinity on zeolite. This is supported by study by Rahmani et. al. [8] that shows the order of zeolite affinity for cations from large to small are K^+, NH_4^+, Na^+, Ca^{2+}, and Mg^{2+}.

One zeolite mining area located in Malang, East Java, Indonesia. However, the literature of Malang natural zeolites for ammonium adsorption application is rarely found. Therefore, the aims of current research were to study the application of Malang natural zeolites for ammonium adsorption by characterizing and studying ammonium adsorption kinetic and isotherm of the Malang natural zeolites.

MATERIALS AND METHODS

Materials

Natural zeolites were obtained from Sumber Manjing, Malang, East Java, Indonesia.

Methods

Characterization of Malang Natural Zeolites

Malang natural zeolites were characterized using several methods. X-Ray Diffraction (XRD) analysis conducted to define the type of crystalline phase of natural zeolites. Fourier Transform Infra-Red (FTIR) conducted to determine the zeolite functional groups. Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) show Si/Al ratio of natural zeolite and Brunauer-Emmett-Teller (BET) method of nitrogen adsorption conducted to determine the surface area of zeolites.

Study of Ammonium Adsorption

Ammonium adsorption testing was carried out in two stages, which are kinetics and equilibrium. The kinetic study was performed by using zeolite with 80-100 mesh size. An amount of 10 g zeolite were mixed with 50 ml of 100 ppm of ammonium chloride. 1 mL of the mixture were taken at 0.5, 1, 2, 4, 8, 12, 24 and 32 hours. Then, each variation was analyze using colorimetric method (Hanna HI 733.25). The results were recorded and analyzed.

Ammonium adsorption kinetic data analyzed with the lagergren's first order, pseudo second order, elovich, and intraparticle diffusion model. Mathematic equations of each model were presented on Table 1.

TABLE 1. Adsorption kinetic mathematic equation

Adsorption kinetic model	Mathematic equation	
Lagergren's first order	$q_t = q_e - \dfrac{q_e}{\exp(k_L.t)}$	(1)
Pseudo-second order	$q_t = q_e - \dfrac{q_e}{1-(k_S.q_e.t)}$	(2)
Elovich	$q_t = \dfrac{1}{\beta}\ln(1+\alpha.\beta.t)$	(3)
Intraparticle diffusion	$q_t = k_i.t^{1/2} + C$	(4)

The equilibrium study conducted by using various mass loading with NH_4Cl 100 ppm. The mass loading of zeolite was varied 1, 1.5, 2, 2.5, 3, 3.5 and 10 g and mixed each variation with 50 ml NH_4Cl, then allowed to stand for 3 days. Then, 1 mL sample analyze using colorimetric method (Hanna HI 733.25). The results were recorded and analyzed.

Ammonium adsorption isotherm data analyzed with the Langmuir, Freundlich, and Temkin model. Mathematic equations of each model were presented on Table 2.

TABLE 2. Adsorption isotherm mathematic equation

Adsorption isotherm model	Mathematic equation
Langmuir	$q_e = \frac{q_{\max}.K_L.C_e}{1+K_L.C_e}$ (5)
Freundlich	$q_e = K_F.C_e^{1/n}$ (6)
Temkin	$q_e = B.\ln(K_T.C_e)$ (7)

The non-linear least squared method then applied to fit experimental data with the model. Difference analysis then performed based on the results of the sum of squared error (SSE).

$$SSE = \sum_{i=1}^{n}(q_e - q_{e,calc})^2 \tag{8}$$

RESULTS AND DISCUSSION

Characterization of Malang Natural Zeolite

XRD Analysis

XRD pattern on Fig. 1 shows Malang natural zeolite consist of quartz, mordenite and clinoptilolite. However, quartz dominate the mineral with the highest intensity peaks. The quartz peaks indicated on 2θ of 26.62^0 with intensity of 3156 cps as quartz. The two highest peaks of mordenite indicated on 2θ of 25.62^0 and 27.9^0 with intensity of 648 cps and 694 cps respectively, this result suggested that crystallinity of Malang natural zeolite was low. Natural zeolites from Bayah, Indonesia showed a lower quartz peaks intensities than Malang natural zeolites [9]. It was most likely that the crystalline phase content of silica was high in the Malang natural zeolites as compared with the Bayah natural zeolites.

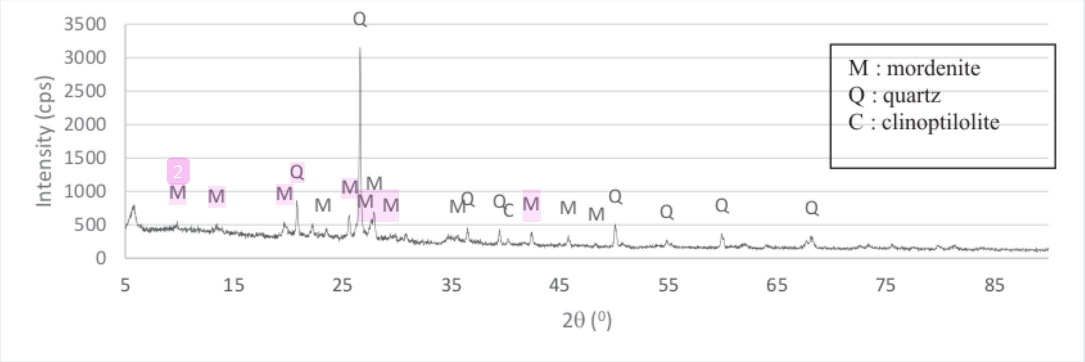


FIGURE 1. Malang natural zeolites XRD pattern.

FTIR Analysis

Based on Fig. 2, Al−O fragment vibrational pattern was in line with the vibrational bands at 780−820 cm^{-1}. The SiO_4 and AlO_4 asymmetric stretch mode vibrational pattern was in line with vibrational bands at 960−1250 cm^{-1}. While, the H-O-H vibrational pattern was in line with vibrational bands at 1560−1690 cm^{-1} [10].

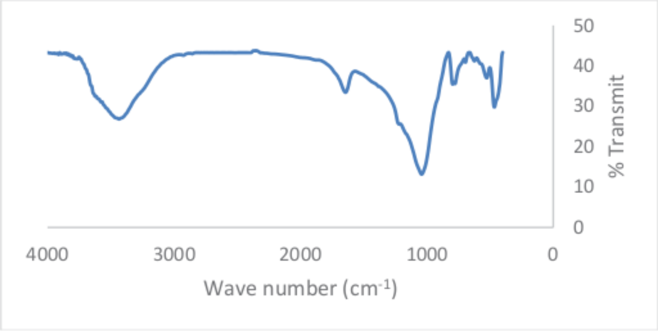


FIGURE 2. FTIR pattern of Malang natural zeolites.

SEM Analysis

SEM picture of Malang natural zeolite shown on Fig. 3. The pattern shows irregular crystal morphology. One might see the material mostly made of needle shape which suggest that the Malang natural zeolite is mordenite. This is in agreement with the XRD result that identified the mordenite as dominant phase. According to SEM image, the particle size of Malang natural zeolites was around 1 µm.

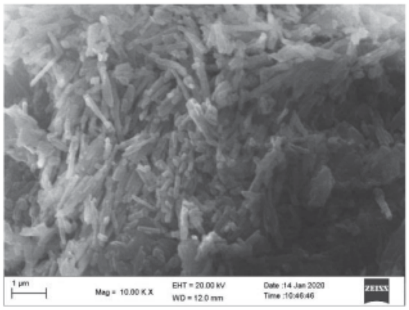


FIGURE 3. SEM pattern of Malang natural zeolites.

SEM-EDX Analysis

Table 1 shows SEM-EDX analysis result of Malang natural zeolite. Based on the result, Si/Al ratio of Malang natural zeolite was 5.5, which is in agreement with Lestari [11]. The previous research indicated that Malang natural zeolite Si/Al ratio was more than 5.

TABLE 3. SEM-EDX analysis result of Malang natural zeolites

Element	% atom
Carbon	6.01
Oxygen	65.41
Sodium	1.38
Magnesium	0.26
Alumunium	4.08
Silicon	21.68
Potassium	0.16
Calcium	1.00

BET Nitrogen Physisorption Analysis

Table 2 shows BET analysis results of Malang natural zeolite which indicate surface area of 52 m^2/g. As comparison, Kurniawan, et. al. [10] showed surface area of Klaten natural zeolite was 133 m^2/g. The lower surface area of Malang natural zeolites is most likely because of the low zeolite phase and high crystalline silica content.

TABLE 4. BET conclusion of Malang zeolites

Type	BET Surface Area (m^2/g)	Pore Volume Total (cc/g)	Average pore radius (Å)
Zeolite	52	0.23	88.10

Ammonium Adsorption Study

Ammonium Adsorption Mechanism

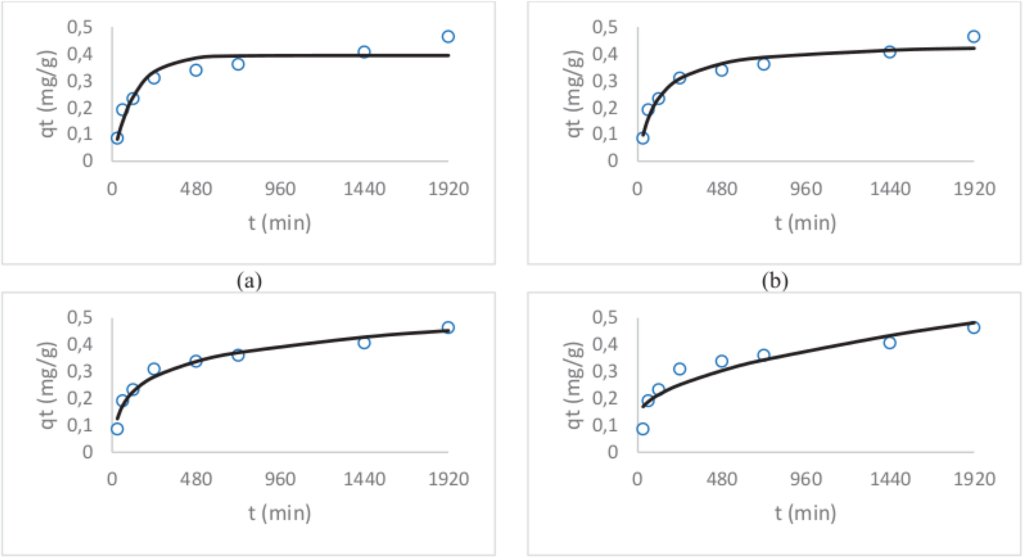
Equation 9 shows mechanism of ammonium adsorption onto zeolite. As ammonium has higher affinity to zeolite than some alkali and alkaline metal [8], reaction of natural zeolite with ammonium replaced the innate alkali and alkaline metal ion on the zeolite surface.

$$Zeolite.M + NH_4^+ \leftrightarrow Zeolite.NH_4 + M^+ \tag{9}$$

M = innate alkali or alkaline metal ion

Ammonium Adsorption Kinetic Model

Kinetic models of ammonium adsorption were fitted with experimental data on Fig. 4. Kinetic models used in this research were lagergren's first order, pseudo second order, elovich and intraparticle diffusion. The elovich models gives the smallest SSE with 0.003. The result suggests that the ammonium adsorption into zeolite was chemisorption.



(a) (b)

(c) (d)

FIGURE 4. Curve fitting of (a) Lagergren's first order, (b) Pseudo-second order, (c) Elovich and (d) Intraparticle diffusion of ammonium adsorption of Malang natural zeolites.

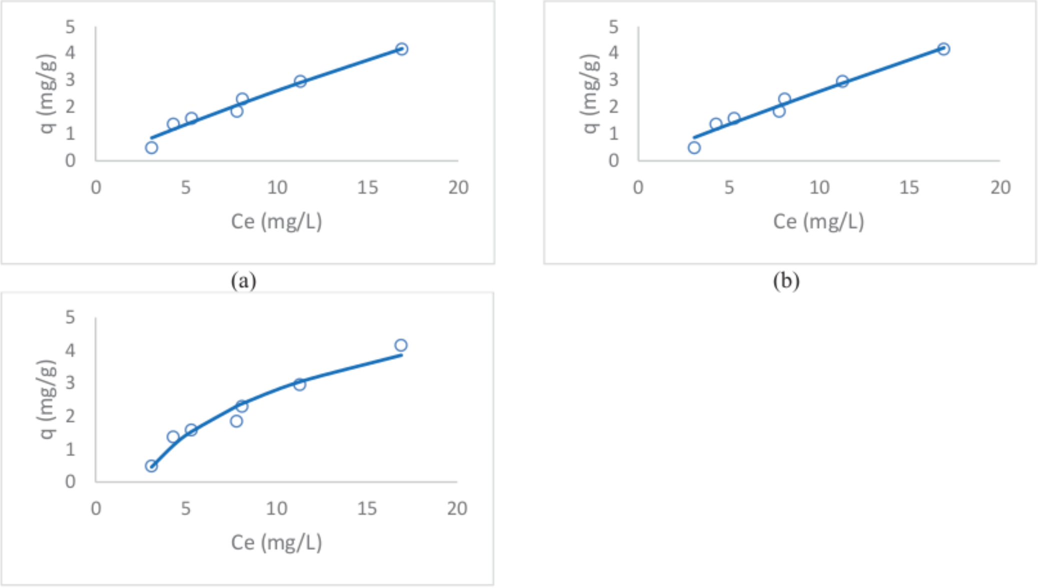
TABLE 5. Ammonium adsorption kinetic parameters

Kinetic models	**Parameters**		**Error**
Lagergren's first	k_L	q_e [mg/g]	SSE*
order	0.0078	0.39	0.011
Pseudo second	k_S	q_e [mg/g]	SSE
order	-0.02	0.44	0.004
Elovich	α	ß	SSE
	0.0096	11.93	0.003
Intraparticle	k_i	C	SSE
diffusion	0.0081	0.125	0.013

*SSE = Sum of Squared Error

Ammonium Adsorption Isotherm Model

Isotherm models of ammonium adsorption were fitted with experimental data on Fig. 5. Isotherm models used in this research were Langmuir, Freundlich and Temkin. The best fitted model was presented by the Langmuir model with SSE 0.27. This suggested that adsorption mechanism was chemisorption and the adsorption occurred on one layer. Table 4 showed that the maximum amount of ammonium adsorbed per gram of natural zeolite predicted by the Langmuir model of Malang natural zeolites was 32.4 mg/g.



(a)

(b)

(c)

FIGURE 5. Curve fitting of (a) Langmuir, (b) Freundlich and (c) Temkin of ammonium adsorption onto the Malang natural zeolites.

TABLE 6. Ammonium adsorption isotherm parameters

Isotherm models	**Parameters**		**Error**
Langmuir	q_{max} [mg/g]	K_L [L/mg]	SSE
	32.38	0.01	0.27
Freundlich	K_F [$L^{0.93}.mg^{0.07}/g$]	n [-]	SSE
	0.30	1.07	0.28
Temkin	B [mg/g]	A [L/mg]	SSE
	2.00	0.41	0.39

CONCLUSION

The Malang natural zeolites were successfully characterized by XRD, FTIR, SEM-EDX and nitrogen physisorption. Malang natural zeolites were identified by XRD generally as modernite and clinoptilolite with quartz as major impurities phase. The morphology of natural zeolites mostly made of needle shape which suggest mordenite type of zeolite. SEM-EDX analysis result of Malang natural zeolite showed Si/Al ratio as 5.5. The nitrogen physisorption indicated that surface area was 52 m^2/g. The kinetic best fitted with Elovich model with SSE 0.003 and the isotherm best fitted with Langmuir model with SSE 0.27.

ACKNOWLEDGEMENT

Author would like to thanks DIKTI for funding the research through project number B/03/UN43.9/PT.00.03/2020 scheme of Penelitian Dasar Unggulan Perguruan Tinggi.

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