ADSORPTION OF METHYLENE BLUE USING ACID ACTIVATED GREEN COLOR NATURAL ZEOLITE FROM ENDE-FLORES, INDONESIA

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ABSTRACT

The natural zeolite green color (GCNZ) from Ende-Flores, Indonesia has been activated with several acid solution series, characterized by XRF spectroscopy and used for methylene blue (MB) adsorption from aqueous solution. The characteristic of XRF showed that the natural zeolite has mainly composed of mordenite with Si/Al ratio of GCNZ before and after acid activated is 7.34 % and 16.28 % respectively. Surface area study was found out using the methylene blue adsorption method whereas adsorption process was done by the batch system. It was shown that average of surface area for GCNZ and activated green color natural zeolite (AGCNZ) is 49.069 m²/mol and 265.946 m²/mol respectively. The maximum adsorption capacity of MB onto the surface of GCNZ is 42.441 mg/g whereas AGCNZ is 87.592 mg/g. Kinetic modeling studies showed the adsorption process fits with pseudo-first-order rate mechanism. Isotherm studies show that adsorption process is best to describe by Freundlich isotherm model. Also, the thermodynamic process indicates that adsorption is an exothermic process and spontaneous.

Keywords: Natural zeolite, Green color acid, Activated, Methylene blue, Adsorption.

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INTRODUCTION

The rapid development of the textile industry in developing countries has triggered an increase in pollution of the aquatic environment. Methylene blue (MB) is a dye often used in the textile industry. This dye is an organic and non-degradable pollutant that is toxic and carcinogenic. MB is a dyestuff that is difficult to degrade by microorganisms. Therefore this dye must be removed out from the waste of the textile industry before being discharged into the aquatic environment¹. Adsorbents such as activated carbon²⁻⁵ and activated natural zeolite⁶ have been prepared and used to adsorb dyestuff from aqueous solution. Especially for natural zeolite, as a low cost and excellent material where can be modified and used in many applications. For example, natural zeolite used as a catalyst for fuel production⁷, an adsorbent for removal many pollutants in water or wastewater⁸, medic application⁹, agriculture¹⁰, purification and separation of gases¹¹ and environmental remediation¹².

So far, many different species of natural zeolites have been identified in Indonesia. Natural zeolite can be found in many places in Indonesia like South Lampung, Bayah, Cikembar, Cipatujah-West Java, Nangapada Ende-Flores NTT⁶, Malang, and Gunung Kidul¹³. Natural zeolite from Ende-Flores, NTT was found easily in mountain and marine area. Three natural zeolite samples from Ende-Flores, NTT such as mountain zeolite (ZG), marine zeolite (ZL), and brown-colored zeolite (ZC) were activated with a base solution and synthesized by a hydrothermal method for used in MB adsorption¹⁴. Recently, the green color

natural zeolite from Ende-Flores, Indonesia has been activated with several acids such as HF, HCl and NH_4Cl and used for adsorption Cr(VI) from aqueous solution⁶.

Research about removal or adsorption of MB using natural zeolite has been widely reported. As an example, preparation of the natural zeolite from Xinyang city in China and use for adsorption of MB; the maximum adsorption capacity of MB onto natural zeolite was about 19.94 mg/g¹⁵. The modified of commercial natural zeolite with acid and base and use for adsorption of MB from wastewater; the efficiency of adsorption of MB onto acid treatment and base treatment of natural zeolite is 41% to 98.8% and 52.2%, respectively¹⁶. Also, there has been reported about the treated of natural zeolite was purchased from the Chilean mining company with an acid, and use for the destroyed of MB. The result has shown that acid treatment of natural zeolite was potential for destroying MB using a heterogeneous ozonation process¹⁷.

In this work, adsorption of methylene blue using GCNZ and AGCNZ will be reported. It should be noted that natural zeolite from Ende-Flores has a three different color like white, brown and green color, so different color may have a different chemical composition before and after activation or synthesis. For that, the characterization was a performance using XRF spectroscopic to find out the chemical compound in GCNZ and AGCNZ. The surface area of GCNZ and AGCNZ using MB method was reported too. In addition, kinetics modeling, isotherms modeling and thermodynamic adsorption were leading to know a possible mechanism of MB adsorption onto the surface of GCNZ and AGCNZ was also reported.

EXPERIMENTAL

Abbreviations

GCNZ: The natural zeolite green color, AGCNZ: activated green color natural zeolite, MB: Methylene blue, ZG: Mountain zeolite, ZL: Marine zeolite, ZC: Brown-colored zeolite

Material and Methods

Sodium hydroxide, hydrochloric acid, nitric acid, NH_4Cl , AgNO_3 , phenolphthalein indicator, methylene blue (MB), NH_3 were purchased from Sigma Aldrich. RO water. The Green color natural zeolite was taken from Ende Flores, East Nusa Tenggara, Indonesia.

XRF Characterization of GCNZ and AGCNZ

Ende-Flores, NTT natural zeolite green color before and after activating with combination acids such as HF, HCl, and NH_4Cl where the result of another part of our research⁶ than was characterized using X-Ray Fluorescence From PANalytical, Minipal 4 type to find out the chemical composition of GCNZ and AGCNZ.

Surface Area and Methylene Blue Adsorption Studies

Batch adsorption method was doing in a set of 100 mL Erlenmeyer flasks that contain 50 mL of MB solutions with various of initial concentrations from 25 mg/L to 200 mg/L. Then, the sample was added with 0.4 g of the GCNZ, or AGCNZ. After that, the solution was stirred for 30 minutes with a magnetic stirrer, filtered and measured with UV-Vis spectrometrically. Surface area determination was performed with the MB method where leading with 0.02 g of GCNZ or AGCNZ was placed in glasses beaker 25 mL and added the 10 mL of MB 100 mg/L. The solution for surface area determination was stirred with a magnetic stirrer for one hour to contact adsorbent and MB. After adsorption or surface area determination proses, the sample solution was a move to centrifuge vessel and centrifuged at 6000 rpm for 10 minutes. The cleared solution was taken and measure with UV-Vis spectrophotometer at 661 nm. The surface area of GCNZ and AGCNZ was determined by eq.-1:

$$\left[\text{SA}_t = \frac{W_m \cdot N \cdot A}{M} \right] \quad (1)$$

Where SA_t , W_m , N , A , and M are total of surface area (m^2/mol), amount of MB was adsorption on the adsorbent, Avogadro number ($6.23 \times 10^{23}/\text{mol}$), the surface area of 1 mol MB ($197.10^{20} \text{ m}^2/\text{mol}$) and molecular weight of MB (319.86 g/mol) respectively.

Adsorption capacity was fine out by using eq.-2:

$$q_e = \frac{(C_o - C_e)V}{m} \left(\frac{\text{mg}}{\text{g}} \right) \quad (2)$$

C_o (mg/L) is the initial concentration of MB in solution before adsorption while C_e (mg/L) is the concentration of MB after the process of adsorption. The q_e (mg/g) is the equilibrium adsorption capacity, m is the mass of adsorbent (g), and V is the volume of solution (L).

Kinetic, Isotherm and Thermodynamic Adsorption studies

In the kinetic studies, GCNZ or GCANZ with dosages 0.4 g was added to six erlenmeyer with containing 50 mL of MB 125 mg/L and stirred with a magnetic stirrer for 5 to 30 minutes for each erlenmeyer. Two kinetic models were used in observing the adsorption process that is pseudo-first-order and pseudo-second-order.

Pseudo-first order

The pseudo-first order can be calculated use Lagergren eq:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (3)$$

Integration at condition $t = 0 - t$ and $q_t = 0 - q_t$:

$$\ln \left(\frac{q_e}{q_e - q_t} \right) = k_1 t \quad (4)$$

And the linear equation can be can be expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

where q_e (mg/g) is the amount of solute adsorbed at equilibrium and q_t (mg/g) is the amount of solute adsorbed at any given time t per unit mass of adsorbent. k_1 is the rate constant. k_1 can be calculated from the slope of the linear plot between $\ln(q_e - q_t)$ vs t ¹⁸.

Pseudo-Second Order

pseudo second order can be expressed by:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (6)$$

Integration at boundary conditions when $t = 0$ to $t > 0$ and $q_t = 0$ to $q_t > 0$, the eq.-6 can further simplifications as linear eq. And expressed in eq.-7⁶:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

The initial absorption rate, h (mg/g.min) at $t \rightarrow 0$ can be expressed using:

$$h = k_2 q_e^2 \quad (8)$$

h obtained from the value of intercept from pseudo-second order graphic.

Isotherm adsorption was found out only for adsorption of MB at the best temperature. The Langmuir model is isotherm adsorption model where base on the assumption that the surface of the adsorbent has the same energy to form an adsorbate monolayer layer on the surface of the adsorbent³.

Langmuir isotherm can determine use eq.-9:

$$q = \frac{q_{\max} K C_e}{1 + K C_e} \quad (9)$$

Where $q_{\max}$ (mg/g) and K (L/mg) are monolayer capacities was achieved at high concentration and equilibrium constant. C_e (mg/L) is a concentration in bulk solution at equilibrium, and q (mg/g) is solute adsorbed at equilibrium. The eq.-9 can be rewritten in non-linear to form a new equation as:

$$\frac{C_e}{q} = \frac{1}{K q_{\max}} + \frac{1}{q_{\max}} C_e \quad (10)$$

Where K is constant which accounts for the affinity of the binding sites (L/mg).

Freundlich isotherm was calculated to use eq.-11:

$$q = K_F C_e^{1/n} \quad (11)$$

K_F and $1/n$ are Freundlich capacity factor and Freundlich's intensity parameters, respectively. C_e (mg/L) is the equilibrium concentration in solution, and q (mg/g) is the amount compound where adsorb at the equilibrium. The logarithm of Freundlich isotherm can be express as:

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (12)$$

The graphic of Langmuir and Freundlich isotherm can be a plot from data C_e versus C_e/q_e and $\log C_e$ vs $\log q_e$ respectively. $Q_{\max}$ and K_L can be solved with intercept and slope from Langmuir graph while n and K_F can be determined from the slope and intercept from Freundlich graph.

The thermodynamic determination, that was led, which uses 0.4 g of GCNZ or AGCNZ and was added to four flask bottle with containing 50 mL of MB with different concentration from 25 mg/L to 100 mg/L. All of the flask bottle samples are then stirred at several different of constant temperatures from 303 K to 343 K. MB that was left in the sample solution for kinetic and thermodynamic studies was determined using UV-Vis Beckman DU-7500 at 661 nm. The data from temperatures studies is then counted by Van Hoff eq. To find out the thermodynamic adsorption of MB. The ΔH^0 (enthalpic) dan ΔS^0 (entropy) was calculated use eq:

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (13)$$

Where R is gas constant (8.3154 J/mol.K) and K is equilibrium thermodynamic constants (L/g). The Free energy (ΔG^0) for each temperature can be calculated use eq.:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (14)$$

T is absolute temperature (K).

RESULTS AND DISCUSSION

XRF Characterization of GCNZ and AGCNZ

XRF spectroscopic data from this research can be used as a guideline for developing a product base on natural zeolite Ende-Flores NTT. XRF characterization was used to find out the composition of the chemical of GCNZ and AGCNZ. XRF spectra of GCNZ and AGCNZ was showed in Fig.-1 and Fig.-2 and the chemical composition was collected in Table-1.

As seen in Fig.-1, Fig.-2, and Table-1 that ratio of Si/Al was 7.34 % and 16.28 % for GCNZ and AGCNZ respectively. The changes in the ratio Si/Al will be changing the charge, and finally, the charge of the cation balancing will be changed too. If Al atom was less on zeolite structure, means that zeolite has a few negative atoms, so it has a little the cation balancing too. Zeolite with high Si concentration has hydrophobic properties. Therefore, acid treatment will reduce the cation-exchange capacity due to dealumination, and it also can improve the capacity and Si/Al ratio offering advantages for the adsorption/separation of non-polar molecules of water or gas flows¹⁹. Base from XRF data known that GCNZ has Si/Al molar ratio is 7.34 %, it can be said that this mineral can be classified in zeolite mordenite type. Mordenite is

orthorhombic structural zeolite type with the dimensional unit cell such as a) $\frac{1}{4}$ (18:13) b) $\frac{1}{4}$ (29:49) and c) $\frac{1}{4}$ (7:52). Zeolite mordenite usually has Si/Al ratio is $2 < \text{Si}/\text{Al} < 5$. Because GCNZ has a Si/Al molar ratio ≥ 5 , make this natural zeolite very resistant to chemical and thermal treatment²⁰.

Fig.-1: XRF Spectra of GCNZ.

Fig.-2: XRF Spectra of AGCNZ.

Table-1: Chemical compounds of GCNZ and AGCNZ.

Chemical Compounds	Conc. unit (%)	
	GCNZ	AGCNZ
Al	7.6 ± 0.1	4.3 ± 0.1
Si	55.8 ± 0.3	70.04 ± 0.3
K	7.74 ± 0.04	6.86 ± 0.05
Ca	13.0 ± 0.04	7.68 ± 0.098
Ti	1.46 ± 0.01	1.93 ± 0.03
V	0.03 ± 0.01	0.04 ± 0.02
Cr	0.061 ± 0.003	-
Mn	0.23 ± 0.004	0.14 ± 0.005
Fe	11.1 ± 0.03	9.44 ± 0.11
Ni	1.36 ± 0.01	1.69 ± 0.03
Cu	0.20 ± 0.005	0.25 ± 0.005
Zn	0.04 ± 0.005	0.02 ± 0.004
Sr	1.2 ± 0.03	1.2 ± 0.02
Re	0.2 ± 0.02	0.3 ± 0.002

The surface area of GCNZ and AGCNZ

The general method for determining the surface area of adsorbent is used by adsorption approach. Commonly MB was used as adsorbed for finding out the surface area of adsorbent, and it is known as methylene blue method. From equation-1, it was found the surface area of GCNZ is $49.069 \text{ m}^2/\text{mol}$ and $265.946 \text{ m}^2/\text{mol}$ for AGCNZ. There was known that washing natural zeolite with acid can remove impurities that block the pore of zeolite, change cation into H-form and dealuminate the structure of zeolite¹⁹. Therefore, acid activation will cause an increase in surface area of natural zeolite.

Adsorption of Methylene Blue onto GCNZ and AGCNZ

MB is a heterocyclic aromatic compound, part of dyes compound and widely used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics, and food industries²¹. MB is one of large pollutant in water and it will cause several problems on human health like shock, cyanosis, jaundice, and tissue necrosis²²⁻²³.

The results of adsorption capacity of MB adsorption onto the surface of GCNZ and AGCNZ was shown in Fig.-3.

Fig.-3: Variation of adsorption capacity MB onto GCNZ and AGCNZ in correlation with the initial concentration of methylene blue.

As seen from Fig.-3 where adsorption capacity of MB on GCNZ was increased from initial concentration 25 mg/L to 125 mg/L, and after initial concentration 125 mg/L the adsorption capacity is relatively constant although the initial concentrations of MB were raised. From Fig.-3 can be concluded that the maximum adsorption of MB onto GCNZ and AGCNZ was found out at an initial concentration of MB is 125 mg/L.

with an average of q_e are ± 87 mg/g and ± 42 mg/g for AGCNZ and GCNZ respectively. q_e for each initial concentration of MB was showed in Table-2, and adsorption capacity of acid activation of green color (AGCNZ) comparison with base activation of ZG, ZL and ZC Ende-Flores natural zeolite was showed in Table-3.

Table-2: Adsorption capacity of acid activation of green color (AGCNZ) comparison with base activation of ZG, ZL and ZC Ende Flores natural zeolite.

Adsorbent		The initial concentration of MB (mg/L)							
		25	50	75	100	125	150	175	200
GCNZ	Average of	13.2	31.6	40.9	42.5	42.7	42.4	42.7	42.9
	q_e (mg/g)	15	04	11	39	96	41	32	37
AGCNZ	Average of	23.5	44.5	65.1	83.7	87.5	87.2	87.5	87.1
	q_e (mg/g)	36	06	96	86	92	36	27	77

Experimental conditions: T: 303 K.

Kinetic Modeling of Methylene Adsorption

Kinetic modeling was performed to determine the time effect on the process of adsorption and to identify any mechanisms that control the adsorption reactions such as mass transfer, and chemical reactions. The plot of t vs $\ln(q_e - qt)$ for pseudo-first-order and $1/q_e$ vs $1/qt$ for pseudo-second order showed in Fig.-4. The rate constants and the correlation coefficients were calculate used the eq (5) and eq (7) and it was summarized in Table-4.

Fig.-4: Kinetic modeling of adsorption MB onto GCNZ and AGCNZ: (a) pseudo-first-order and (b) pseudo-second order.

Table-3: Adsorption capacity of acid activation of green color (AGCNZ) comparison with base activation of ZG, ZL and ZC Ende Flores natural zeolite.

Adsorbent	Contact time (h)	Dose (g)	Activation type	Range of initial concentration (mg/L)	MB (Ads) (mg/g)	Literature
ZG	24	0.2	Base	250 to 1250	19.938	14
ZL	24	0.2	Base	250 to 1250	19.103	14
ZC	24	0.2	Base	250 to 1250	18.676	14

AGCNZ	0.5	0.4	Acid	25 to 200	87.592	This study
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ZG: Ende Flores mountain zeolite, ZL: Ende Flores marine zeolite, ZC: Ende Flores brown-colored zeolite.

Table-4: Kinetics modeling of methylene blue adsorption use GCNZ and AGCNZ.

Kinetic models	Parameters	Adsorbent	
		GCNZ	AGCNZ
Pseudo-first order	$k_1/10^{-3} \text{ min}^{-1}$	0.105	0.1683
	$q_e, \text{ mg.g}^{-1}$	2.8982	18.0005
	R^2	0.9976	0.9994
Pseudo-second order	$k_2/10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$	0.0170	0.0369
	$q_e, \text{ mg g}^{-1}$	0.2563	0.2720
	$h/10^{-2} \text{ mg g}^{-1} \text{ min}^{-1}$	0.0044	0.0100
	R^2	0.4471	0.364

As shown from Fig.-4 and Table-4 that adsorption of MB onto the surface of GCNZ and AGCNZ followed pseudo-first order reaction. The result showed that adsorption system followed pseudo-first order reaction for a whole period of adsorption, with R^2 is 0.9976 and 0.9994 for GCNZ and AGCNZ respectively. q_e for AGCNZ also showed the good value of this experiment. This result indicating that MB adsorption is directly proportional to the difference between the concentration of saturation and the amount of MB uptake with time²⁴. This result indicates that the adsorption of MB to the surface of GCNZ and AGCNZ is controlled by non-dissociated molecules adsorption and adsorption controlled by the diffusion process.

Isotherms Modeling of Methylene Blue Adsorption

The adsorption performance of MB onto GCNZ and AGCNZ was modeling with two isotherm models (Langmuir and Freundlich) to provide evaluate a better the equilibrium condition and understanding of adsorption process of MB onto natural zeolite. Generally, Langmuir isotherm assumes that all of the sites adsorptions were occurs in monolayer with equal energies and making the surface homogenous. The value of Langmuir constant (KL) was used to predict the affinity of MB molecules onto the GCNZ and AGCNZ. A lower of KL value causing a low affinity and vice versa. Meanwhile, Freundlich isotherm model usually used to describe the heterogonous process of adsorption. If the value $n \geq 1$, it was indicating adsorption process occurs in a homogeneous system and heterogeneous system if vice versa. The result of Langmuir and Freundlich isotherm models are shown in Fig.-5 and Table-5.

Fig.-5: Isotherm modeling of adsorption MB onto GCNZ and AGCNZ: (a) Langmuir isotherm and (b) Freundlich isotherm.

Table-5. Isotherm modeling of methylene blue adsorption use GCNZ and AGCNZ.

Isotherm models	Parameters	Adsorbent	
		GCNZ	AGCNZ
Langmuir	Q _{max} (mg/g)	0.249	0.668
	K _L (L/mg)	-6.784	0.461
	R ²	0.937	0.922
Freundlich	N	1.793	1.513
	KF (mg/kg)	0.602	0.979
	R ²	0.993	0.999

As seen in Table-5, that adsorption process followed Freundlich isotherm model for GCNZ and AGCNZ respectively. The value of $n \geq 1$ which indicates that adsorption occurs in a homogeneous system. The value of Freundlich constant (KF) is 0.979 indicates that MB is not so easy to adsorb from aqueous solution by AGCNZ. Freundlich isotherm modeling does not predict any saturation of the AGCNZ of the MB; therefore mathematically indicating the adsorption of MB on the AGCNC surfaces is multilayer adsorption²⁵.

Thermodynamic adsorption of Methylene Blue

The temperature is an important factor for the adsorption of MB on the AGCNZ surfaces. The ΔG^0 , ΔH^0 , and ΔS^0 were studied for estimating the effect of temperature for MB adsorption on the AGCNZ or GCNZ surfaces.

ΔH^0 and ΔS^0 were calculated from the slope and intercept from graphic $1/T$ vs $\ln K$ at Fig.-6 respectively. Values of the ΔG^0 for the adsorption process of MB obtained from eq.-14 were listed in Table-6.

Fig.-6: Thermodynamic adsorption of MB used GCNZ and AGCNZ.

Table-6: Results of a thermodynamic experiment for adsorption MB onto GCNZ and AGCNZ.

T (K)	ΔG^0 (kJ/mol)		ΔH^0 (kJ/mol)	
	GCNZ	AGCNZ	GCNZ	AGCNZ
303	-12.600	-14.589	-24.122	-47.421
313	-12.219	-13.506	ΔS^0 (kJ/mol)	
323	-11.839	-12.422		
333	-11.459	-11.339	GCNZ	AGCNZ
343	-11.079	-10.255	-0.038	-0.108

As seen from Table-6 that the negative ΔG^0 values indicating, the adsorption processes were spontaneous is a high preference of MB onto AGCNZ or GCNZ surfaces. The ΔG^0 increases with an increasing temperature, also indicating that adsorption of MB is higher favorable at a lower temperature condition. The negative value of ΔH^0 indicating that adsorption of MB is an exothermic process, meanwhile, ΔS^0 value also negative shows a decrease in randomness in the solid/liquid interface during the adsorption process²⁶. This results showed AGCNZ was potential to use as an adsorbent for removal dye compound from a water sample because do not need the high energy to running the adsorption process (spontaneous reacting properties at normal temperature condition). The price of this sorbent is low because as the raw material that was a considerable abundance in the world nature causes the cost production of this material is low (\$30 -\$120/ton²⁷) comparing with the price of another sorbent²⁸.

CONCLUSION

Acid activates of natural zeolite will make this material applicable for the adsorption organic dye compound. Washing GCNZ with several acid solutions was successful to eliminate the impurities were block the pore of natural zeolite and also a rearrangement of the zeolite structure. XRF data showed the ratio of Si/Al increased from 7.34 to 16.28% before and after acid activation respectively. The surface area of GCNZ and AGCNZ are 166.267 and rise to 383.110 m²/mol with the maximum adsorption capacity of methylene blue onto AGCNZ, and GCNZ is 87.592 mg/g and 42.441 mg/g respectively. Kinetic studies show that the adsorption process fits with pseudo-first-order rate mechanism. Isotherm studies indicate that adsorption process is best described by Freundlich isotherm model. The thermodynamic process indicates that adsorption process is exothermic and spontaneous. This result revealed that AGCNZ was potential low-cost adsorbent that can be used for adsorption of a dyes pollutant in water or waste-water treatment.

ACKNOWLEDGMENT

The First authors are grateful for research grants of the Ministry of Research, Technology and Higher Education, Republic of Indonesia.

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