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ADSORPTION OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS USING ACID ACTIVATED OF NATURAL ZEOLITE COLLECTED FROM ENDE-FLORES, INDONESIA

Yantus A.B Neolaka[1,2], Eka B.S Kalla[3], Ganden Supriyanto[4,*], Suyanto[4] and Ni Nyoman Tri Puspaningsih[4]
[1]Mathematics and Natural Science Doctoral Program, Faculty of Science and Technology, Airlangga University, Mulyorejo, Surabaya, 60115, Indonesia.
[2]Chemical Education, Mathematics and Natural Science Education Department, Faculty of Education and Teachers Training, University of Nusa Cendana, Kupang, 85001, Nusa Tengara Timur, Indonesia.
[3]Magister of Chemical Science, Department of Chemistry, Faculty of Science and Technology, Airlangga University, Mulyorejo, Surabaya, 60115, Indonesia.
[4]Department of Chemistry, Faculty of Science and Technology, Airlangga University, Mulyorejo, Surabaya, 60115, Indonesia.
[*]E-mail: ganden-s@fst.unair.ac.id

ABSTRACT

Natural zeolite collected from Ende-Flores Indonesia was characterized and activated with acid solution for Cr(VI) adsorption from aqueous solution. This natural zeolite is mainly composed of quartz and 50% mordenite. The kinetic adsorption modeling was fitted best with the pseudo-second-order model, whereas isotherm adsorption followed the Langmuir model with the maximum adsorption (Qmax) of NZ and ANZ are 0.189 mg/g and 1.040 mg/g. Moreover the ANZ was favorable for adsorption of Cr(VI) respectively.

Keywords: Natural zeolite, acid activated, Cr(VI) adsorption, kinetic, isotherm.

INTRODUCTION

Hexavalent Chromium (Cr(VI) is one of the most dangerous heavy metal ion that receives high attention to be removed from wastewaters before getting discharged into the aquatic environment. Generally, the majority of chromium are found in forms of Cr(III) and Cr(VI) in aquatic environment[1]. Cr(III) is commonly less toxic and has been known to be essential in metabolism of glucose in mammals[2]. Cr(VI) is highly toxic and suspected as carcinogenic agent because it can modifies the process of DNA transcription causing chromosomal aberrations[3]. Furthermore, it can cause epidermal irritation and kidney and gastric damage[4]. Many processes have been used for the removal of Cr(VI) from industrial effluents namely membrane filtration, chemical precipitation, adsorption and ion exchange. Adsorption is one of most frequently methods used for Cr(VI) removal from aqueous solutions because of their economical and effective treatments. Many adsorbents have been developed for the Cr(VI) adsorption from aqueous samples such as non-conventional adsorbent (activated carbon)[5,6], granular activated charcoal (GAC)[7] and zeolites (natural and synthetic zeolite)[1].

Natural zeolite is one of the adsorbent used in adsorption of Cr(VI) because of its effective performance and low cost[1]. Generally, natural zeolite collected from different places has different characteristics. These unique characteristics of natural zeolite (NZ) are probably attributed to the differences in the geological formation of zeolite sources[8-11]. Therefore, each special zeolite material has its own special characteristics

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and still requires to be observed individually[8]. Recently, the modified Ende-Flores Natural zeolite use hydrothermal method for adsorption a cationic dye have been reported[12]. They used a base solution to activate the NZ. We report, in this paper, an investigation on adsorption of hexavalent chromium from aqueous solution using an acid activated of Indonesia (Ende-Flores) natural zeolite. Kinetic and isotherm adsorption of Cr(VI) in batch system were also studied and reported.

EXPERIMENTAL

Material and Methods

1,5-diphenylcarbazide, potassium dichromate, HF, NH_4Cl, H_2SO_4, $AgNO_3$ NaOH and HCL were purchased from Merck (Singapore). Aqua demineralization were prepared in our laboratory. Natural zeolite was collected from Ende Flores Nusa Tenggara Timur Indonesia.

Preparation and Activation of Natural Zeolite

The natural zeolite (NZ) was grounded and sieved with a 150 mesh sieves. The material was then washed with aqua demineralization to remove any non-adhesive impurities and stirred at 70 °C. Then, the natural zeolite was filtered and dried in an oven at 105 °C for 24 hours in order to keep anhydrous. The NZ activation process was carried out by mixing NZ powder with 1% HF for 1 hour then washed with aqua demineralization, filtered and dried in an oven at 120 °C for 3 hours. Next, the activated NZ was washed again with 6 M HCl for 30 minutes, stirred at 50 °C, filtered and washed repeatedly with aqua demineralization. The activated NZ was then dried at 130°C for 3 hours in the oven. The activated NZ then washed again with NH_4Cl 1 M under stirring condition at 60 °C for 3 hours, filtered and washed repeatedly until no Cl^- ion are detected by $AgNO_3$ solution. Finally, the activated NZ was dried in an oven at 130 °C for 3 hours. The activated NZ was resulted from this processes and called as acid activated natural zeolite (ANZ).

Analysis and Characterization

The phases of NZ and ANZ was characterized through X-ray diffraction using Philips X'pert type. The morphological surface was examined using SEM (JEOL, Tokyo, Japan). The total pore volume, pore size distribution and surface area (SBET) were determined using Quantachrome Instruments NOVA 1200 (High Speed Gas Sorption Analyzer Versions 10.0 – 10.03). pH was measured using Pasco pH meter (spark PS-2008A) and the Cr(VI) concentration was determined by UV-Vis spectrophotometer type UV 1240 (Shimadzu, Japan).

Sorption studies

Batch system was used to investigate the adsorption of Cr(VI) on the NZ and ANZ particles from aqueous solution in order to obtain rate and equilibrium data. The kinetics study were carried out by adding the 0.4 g NZ or ANZ in 50 mL glass beaker contained with 25 mL solution of Cr(VI) with initial concentration of 14 mg/L and pH 2. The sample was kept stirring in a thermostat shaker and adjusted at temperature 303 K with different contact time from 5 to 45 minutes separately. The concentration of Cr(VI) in liquid phase after the process was measured by UV-Vis spectrophotometer. Isotherms adsorption were found out through Cr(VI) adsorption onto NZ and ANZ particles data at different initial concentrations ranging from 6 to 14 mg/L at constant temperature 303 K respectively. After this period, the Cr(VI) concentration was analyzed by UV-Vis spectrophotometer at 540 nm using 1,5-diphenylcarbazide as the complexion agent. The adsorption capacity of Cr(VI) was calculated using the following equation:

$$qe = \frac{(Co - Ce)V}{W} \tag{1}$$

Where Co and Ce are the initial and equilibrium concentrations of Cr(VI) in solution; V *is* the volume (L); and W is the mass (g) of the adsorbent respectively.

RESULTS AND DISCUSSION

Zeolites Characterization

XRD measurement indicates that the ANZ is mainly composed of 33.33 % mordenite before activation and increase to 50 % mordenite ($Ca_{3.4}Al_{7.4}Si_{40.6}O_{96}(H_2O)$) after acid activation of NZ (Fig.-1). The data were obtained by comparing XRD spectra of NZ and ANZ with quartz patterns from ICCD standard number 01-078-1253 and mordenite patterns from ICCD standard number 01-074-3677.

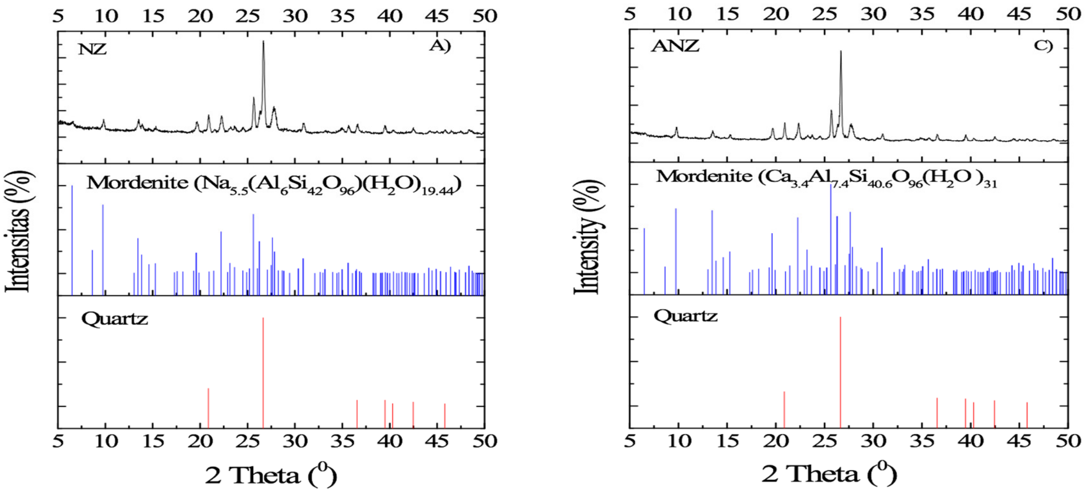

Fig.-1: XRD Spectra of NZ and ANZ

SEM characterization was conducted with the objective to know the surface morphological image of NZ and ANZ as shown in Fig.-2. Fig.-2a and Fig.-2b indicate that NZ has a smooth surface morphology may cause any non-adhesive impurities in NZ canal structures, whereas ANZ has more clearly opened structures. This result indicates that acid activation successfully removes impurities blocking the pore of zeolite and causes the increasing of pore diameter of zeolite where the SEM images showed that crystal of mordenite with crystal up to 20 μm (Fig.-2c) and 2 μm (Fig.-2d).

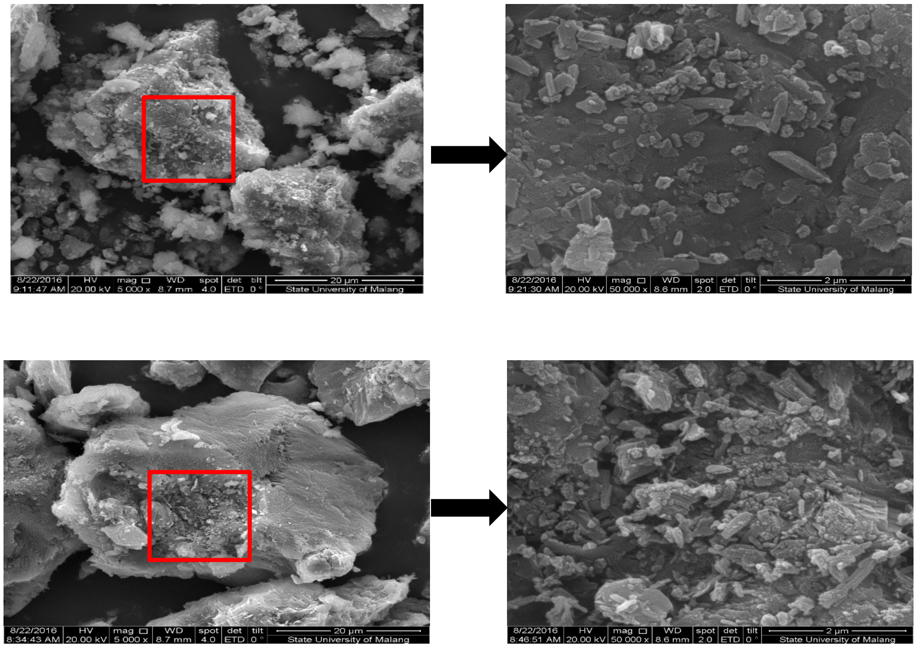

Fig.-2: SEM image of NZ and ANZ: (a) The NZ image was amplified in 5000x, (b) The NZ image was amplified in 50000x, (c) The ANZ image was amplified in 5000x and (d) The ANZ image was amplified in 50000x

The BET characterization study was performed on the powder of NZ and ANZ to identify the effect of acid activation on the zeolite surface area and average of pore size diameter. Graphic describing isotherm adsorption/desorption of nitrogen on NZ and ANZ is presented in Fig.-3 and concluded at Table-1.
Figure- 3 shows that the adsorption process is categorized as adsorption type IV. In general, adsorption type IV indicates that both NZ and ANZ have the mesopore structures which generally have hysteresis loop at P/P0 between 0.75 – 0.95. As shown that the average of pore diameter distribution indicated by peak at 39.43 Å (3.943 nm) and 48.32 Å (4.832 nm) for NZ and 38.31 Å (3.831 nm) for ANZ respectively. This data means that NZ or ANZ has a very small pore. The similar range of pore size diameter average distribution was reported for Australian natural zeolite where average of pore size diameter is 40 Å[13]. Table-1 shows the physical parameters of NZ and ANZ measured by N_2 adsorption–desorption isotherms. The findings show that the BET surface area was increased after acid activation as indicated by active sites formed not only on the first layer of NZ but on the second layers too. Pore total volume, mesopore volume and pore diameter size average were getting smaller indicating that the formation of active sites occurs on most channels of mesopores and micro pores existed in NZ.

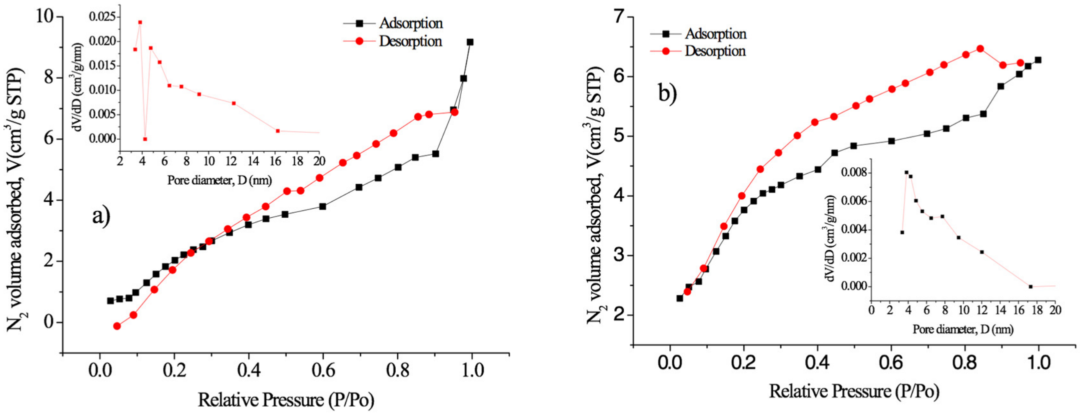

Fig.-3: N_2 Adsorption–Desorption Isotherms and Pore Size Distribution of (a) NZ and (b) ANZ

Table-1: Physical parameters of NZ and ANZ measured by N_2 adsorption–desorption isotherms

Samples	BET surface area^a (m^2/g)	Total pore volume^b (cm^3/g)	Micropore volume^c (cm^3/g)	Mesopore volume (cm^3/g)	Average of pore size diameter (Å)
NZ	12.928	0.0142	0.0000	0.0142	39.43; 48.32
ANZ	13.713	0.0097	0.0050	0.0047	38.33

a: Multi point BET, b: total volume pore total at P/P0 = 0.9945 (NZ) and 0.9984 (ANZ),
c: Mesopore volume = Total pore volume – Micropore volume

Kinetics Study

Kinetics adsorption modeling was conducted in order to determine the controlling mechanism of sorption processes such as mass transfer and chemisorption. Here, pseudo-first and the pseudo-second order kinetic models were used to test the experimental data and was calculated using eq. 2 and 3 from Table-2. The kinetics model of adsorption Cr(VI) onto NZ and ANZ particles were shown in Fig.-4 and the results was presented in Table-3. Table-3 explains that the correlation coefficient (R^2) for Cr(VI) adsorption onto NZ and ANZ particle showed that the Pseudo-second order > Pseudo-first order, which indicates that the pseudo-second-order model is more suitable in describing the kinetics adsorption of Cr(VI) onto ANZ and NZ particles.

Table-2: Kinetics Model Equation

Kinetic models	Equation	References
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$ (2)	14
Pseudo-second-order	$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{1}{qe} t$ (3)	15

Table-3: The kinetic parameters of Cr(VI) adsorption onto NZ and ANZ

Kinetic models	Parameters	Adsorbent	
		NZ	ANZ
Pseudo-first order	$(k_1/10^{-3})$/min	0.006	0.057
	q_e/(mg/g)	0.069	0.130
	R^2	0.003	0.113
Pseudo-second order	$(k_2/10^{-3}g)$/(mg.min)	0.017	0.037
	q_e /(mg/g)	1.553	1.413
	$(h/10^{-2}mg)$/(g.min)	0.042	0.074
	R^2	0.843	0.989

Isotherms Adsorption

In general, an isotherm adsorption is defined as the phenomenon of retention or a substance mobility from liquid phase (the aqueous porous media or aquatic environments) to a solid-phase at a constant temperature and pH[16-18]. Langmuir isotherm is an empirical model which assumes that adsorption take place monolayer (the adsorbed layer is one molecule in thickness) where adsorption can only occur in a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites[19]. Meanwhile, the Freundlich isotherm assumes that the adsorption process takes place on heterogeneous surfaces and adsorption capacity is related to the Cr (VI) concentration at equilibrium.. Heterogeneity in Freundlich isotherms is indicated by the value of n. The n value is larger than or equals to 1 ($n \geq 1$) shows that the system is homogeneous and if the n value lower than 1 ($n \leq 1$), the system is heterogeneous. Langmuir and Freundlich isotherm models were implemented to investigate this phenomenon and were calculated based on eq. 4 and eq. 5 from Table-4. As an illustration, plots for two isotherm model for NZ and ANZ are shown in Fig.-5 while the result are presented in Table-5. The result proves that isotherm data are better fitted by the Langmuir isotherm model than Freundlich model, which is indicated by higher R^2 values for Cr(VI) adsorption on NZ and ANZ. The Qmax in Langmuir model for NZ and ANZ are 0.819 and 1.040 mg/g respectively. Based on the value of n, NZ has n = 9832 and ANZ n = 28,169, this means the adsorption occurs in the homogeneous system.

The adsorption process favorability of Cr(VI) adsorption on to ANZ was determined from Eq.(6):

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

An adsorption process is favorable if $0 < R_L < 1$ and considered unfavorable if $R_L > 1$. The result showed that the R_L for ANZ at 303 K is 0.248, this means that the ANZ was favorable for adsorption of Cr(VI).

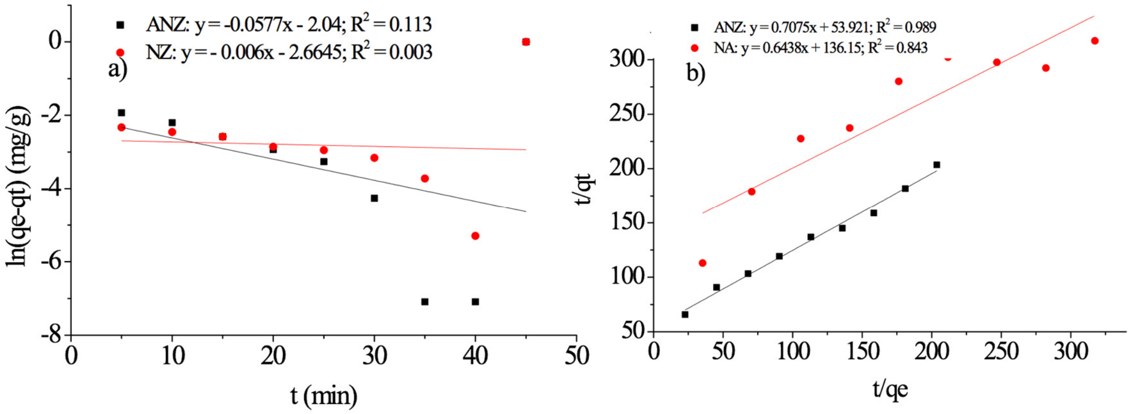

Fig.-4: Kinetic models of NZ and ANZ: (a) Pseudo-First Order and (b) Pseudo-Second Order

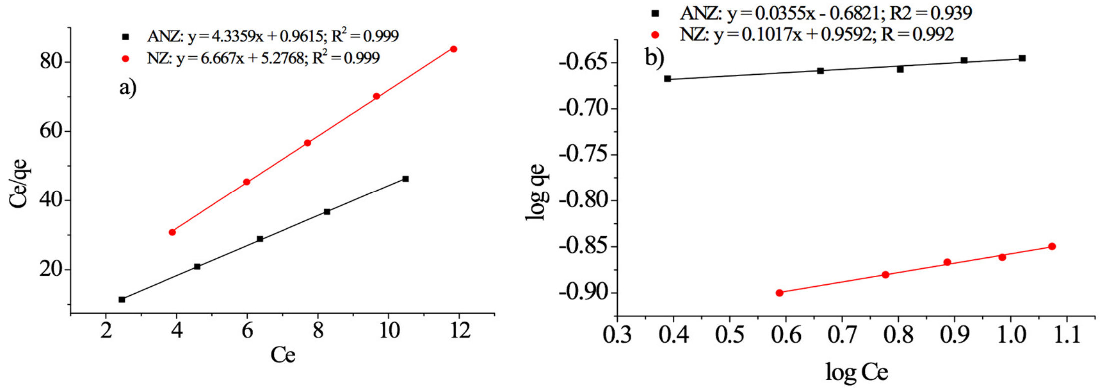

Fig.-5: Isotherm adsorption models: (a) Langmuir and (b) Freundlich

Table-4: Langmuir and Freundlich Isotherm Models Equations

Isotherm models	Equation	References
Langmuir	$$\frac{Ce}{q} = \frac{1}{Kq\max} + \frac{1}{q\max}Ce \quad (4)$$	20
Freundlich	$$\log q = \log K_F + \frac{1}{n}\log Ce \quad (5)$$	20

Table-5: Isotherm parameters of Cr(VI) adsorption onto NZ and ANZ

Isotherm adsorption models	Parameters	Adsorbent	
		NZ	ANZ
Langmuir	Qmax (mg/g)	0.189	1.040
	K_L (L/mg)	0.154	0.303
	R^2	0.999	0.999
Freundlich	n	9.832	28.169

	KF (mg/kg)	0.109	0.207
	R^2	0.992	0.939

CONCLUSION

Indonesian (Ende Flores) natural zeolite was collected, activated and used for adsorption of Cr(VI). The adsorption kinetic model follows pseudo-second order while isotherm adsorption follows Langmuir isotherm. It is found that adsorption for Cr(VI) onto ANZ slightly higher than onto NZ with Qmax are 0.189 mg/g and 1.040 mg/g for NZ and ANZ. Finally, the ANZ shows the favorability for Cr(VI) adsorption from aqueous solution.

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