

Characteristics of Heavy Metals Adsorption Cu, Pb and Cd Using Synthetics Zeolite Zsm-5

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ABSTRACT

It is generally known that zeolite has potential for heavy metal adsorption. The objectives of this study were to synthesize and characterize zeolite ZSM-5 and to figure out the adsorption capacity of zeolite ZSM-5 for heavy metals of Cu²⁺, Pb²⁺ and Cd²⁺. Characterization of zeolite ZSM-5 included some variables i.e. crystal structure (XRD), morphology (SEM), specific surface area and total pore volume (*N*₂ physisorption). Adsorption capacity of zeolite ZSM-5 was analysed using a batch system with heavy metals of Cu²⁺, Pb²⁺ and Cd²⁺ in various concentrations (50, 100, 150, 200 and 250 ppm) with contact times 30, 60, 90, 120 and 250 minutes. Adsorption data was calculated by Langmuir and Freundlich isotherm. The results showed that the maximum adsorption capacity of zeolite ZSM-5 against heavy metals of Pb²⁺, Cu²⁺, and Cd²⁺, were 74.07, 69.93 and 60.24 mg g⁻¹, respectively. These indicated that synthetic zeolite ZSM-5 had potential to adsorb heavy metals. The results also suggested that the adsorption capacity was affected by the pore size of zeolite, negative charge of zeolite, diameter of hydrated and electronegative ion.

Keywords: Freundlich and Langmuir, isotherm equations, metal adsorption, zeolite

INTRODUCTION

Heavy metal pollution is a phenomenon that cannot be detached from daily life. The high level of metal pollution by heavy metal such as Cu, Pb, Cd, Hg, Zn, and Ni is a part of the most important global issue. These metals may become a problem if they get into ecological system and the human health. Therefore, we need to cope with heavy metal pollution into the environment system in order to prevent those heavy metals become pollutants.

There were several processes reported to reduce the heavy metals pollution, for instances, adsorption, precipitation, filtering, osmosis, and electrolysis (Buasri *et al.* 2008 and Minceva *et al.* 2007). Among the adsorption processes, adsorption using zeolite was an alternative method to be used. Zeolite is a silicate alumina crystal with three dimension framework structure formed by tetrahedral silicate [SiO₄]⁴⁻ and octahedral alumina [AlO₄]⁵⁻ that bundled by oxygen atom. Silicon atom is surrounded by 4 oxygen atoms to construct networks with regular pattern. In some spots in these networks, silicon atom is substituted by aluminum,

having a coordination number with only 3 oxygen atoms. The existence of aluminum atom causes zeolite to have a negative charge that can be used as an ion exchange site with heavy metals. In addition, zeolite is a porous material. Zeolite shows some important characteristics such as ion adsorption selectivity, molecule sieve, and active catalyst.

The researches about heavy metal adsorption using zeolite have been already done, but most researches show the use of natural zeolite like clinoptilolite (Buasri *et al.* 2008; Erdem *et al.* 2004; Inglezakis *et al.* 2004; Cincotti *et al.* 2006; Sprynskyy *et al.* 2006), phillip site natural zeolite (Al-Haj-Ali *et al.* 2004) and scolecite natural zeolite (Bosso *et al.* 2002). Natural zeolite has often been used as a heavy metal absorbent. However, the ability of this substance was relatively low. At present, there is a new technology to produce synthetic zeolites with higher quality (better characteristic and ability) than natural zeolites. The structure of synthetic zeolite can be modified with the necessity and uniformity of the structure.

Said and Widiastuti (2008) found that synthetic zeolites can adsorb 14.54 mg g⁻¹ of Cu²⁺ with concentration 50 mg L⁻¹ at pH 8 for 360 minutes. Gaurav *et al.* (2013) explained that synthetic zeolite made from fly ash can adsorb 13.35 mg g⁻¹ of Cd

using 2 g of zeolite in concentration 100 mg L⁻¹ at pH 6 and temperature 40 °C. Alvarez-Ayuso *et al.* (2003) found metal adsorption using synthetic zeolite NaP1 with 100 mg L⁻¹ metal concentration can adsorb 43.6 mg g⁻¹ of Cr, 20.1 mg g⁻¹ of Ni, 32.6 mg g⁻¹ of Zn and 50.5 mg g⁻¹ of Cu. The research of Silva *et al.* (2012) on synthetic ZSM-5 zeolite as heavy metal ion exchanger for Cr⁶⁺ showed that the efficiency of the heavy metal ion decreases to 78.50% with 11.90 mg g⁻¹ adsorption capacity. ZSM-5 zeolite modified with Na and H₃PO₄ can also adsorb Ni²⁺ as much as 28.09 mg g⁻¹ and 39.96 mg g⁻¹, respectively (Panneerselvam *et al.* 2009).

ZSM-5 zeolite is one of the synthetic zeolite. ZSM-5 zeolite has one of MFI framework shape. It has 3 dimension channel and 5.1-5.5 Å of micro pore size. Nowadays, ZSM-5 is commonly used as a catalyst and also used in dewaxing reaction, methanol conversion to gasoline, methanol to olefin, hydrocracking, benzene alkylation, NO_x reduction and methane partial oxidation (Cejka and van Bekkum 2005). ZSM-5 zeolite has much potential to be developed and used as the material in heavy metal adsorption. In addition, ZSM-5 zeolite has micro pore similar to the size of heavy metal ions Cu²⁺, Pb²⁺, and Cd²⁺. Only few information explained the use of ZSM-5 zeolite as heavy metal absorbent. The objectives of this study were to (1) synthesize and characterize ZSM-5 zeolite and (2) to study the adsorption and the selectivity of ZSM-5 synthetic zeolite to heavy metals of Cu²⁺, Pb²⁺, and Cd²⁺.

MATERIALS AND METHODS

Chemicals Materials

Chemicals used in this study were 1) materials for synthetic zeolite ZSM-5: colloidal silica (Ludox HS-40), sodium hydroxide (NaOH 50%), sodium alumina (NaAlO₂) as alumina source, tetrapropylammonium bromide (TPABr) for template of ZSM-5 and distilled water, and 2) heavy metals: CuSO₄·5H₂O (Merck), Pb(NO₃)₂ (Merck) and CdSO₄ (Merck).

Synthesize of Zeolite ZSM-5

To synthesize zeolite ZSM-5 low temperature method was used. The synthesis was started by dissolving 2.289 g of TPABr in 6.405 g of distilled water as first solution. Then, it was proceed with the second solution that consisted of 1.697 g of NaOH 50% and 0.082 g of NaAlO₂. Both solutions were mixed in a polypropylene bottle and shaken

for about 2 hours (homogenous), by adding 19.50 g of colloidal silica 40%. After a homogenous solutions were produced, it was allowed to stand overnight for aging process at room temperature. After that, the solution was put into an oven at 90 °C for 96 hours. The precipitate was filtered using Buchner and dried in an oven at 105 °C for about 24 hours.

Characteristics of Synthesized Zeolite ZSM-5

Characteristics of zeolite ZSM-5 were various i.e. crystal structure by XRD Philips PW1830, morphology using SEM Zeiss EVO50 and the zeolite ZSM-5 specific surface area and total pore volume, and it were measured using the multi-point-N₂-BET method on the Quantachrome Nova 2200e.

Adsorption of Heavy Metals Using Zeolite ZSM-5

Adsorption experiments were carried out with a batch system using 0.015 g of zeolite ZSM-5 in a 20 ml of solution containing heavy metals. Variation in the concentration of heavy metals were 50-250 ppm and 30-150 minutes of contact time. The concentration of heavy metals in the solution was determined before and after contacting with zeolite ZSM-5 and measured using AAS models GBC Avanta. In order to obtain the adsorption capacity, the amount of ions adsorbed per unit mass of adsorbent (in milligrams of metal ions per gram of adsorbent) was evaluated as follows:

$$\text{Adsorption Capacity (mg g}^{-1}\text{)} = \frac{[C_i] - [C_f]}{w} \times V$$

Where C_i (ppm) = initial metal concentration, C_f (ppm) = final metal concentration, V (L) = volume of reacting solution, W (g) = amount of zeolite in solution.

Two of the most commonly used isotherm theories have been adopted for interpreting adsorption data, namely the Freundlich and Langmuir equilibrium isotherm theories.

$$\begin{array}{ll} \text{Langmuir} & q = a.bC / 1 + b.c \\ \text{Linier form} & q/c = 1/a.b + c/a \end{array}$$

where c (ppm) was the amount of a metal adsorbed per mass unit of sorbent at equilibrium, q (mg g⁻¹) is the amount of adsorbate at complete monolayer and b (mg g⁻¹) is slope and a (mg g⁻¹) of adsorption capacity.

$$\begin{array}{ll} \text{Freundlich} & q = k.C^{1/n} \\ \text{Linier form} & \log q = \log k + 1/n . \log C \end{array}$$

where c and q were as defined for Langmuir with k and n were adsorption constant.

RESULTS AND DISCUSSION

Characteristics of ZSM-5 Zeolite

Synthetic zeolite was successfully made by non-hydrothermal method. Characterization to zeolite was conducted with XRD, SEM, and nitrogen physisorption method.

X-ray diffraction (XRD)

XRD is a qualitative analysis method that was functioned to analyze crystal structure of a solid substance. All of material having crystal will show peaks if it were analyzed by XRD. The result of

XRD diffractogram can show the crystallinity level of the materials. The result of ZSM-5 zeolite diffractogram is shown in the Figure 1. Diffraction pattern that was resulted by ZSM-5 showed the resemblance with the simulated ZSM-5 standard diffractogram, but there were difference at the intensity. The peak of synthetic zeolite appeared at $2\theta = 7.9364^\circ, 7.9569^\circ, 23.9541^\circ$ and 23.9746° , where approached the top a typical ZSM-5. Therefore, materials produced in this research fulfill the requirement to be classified as ZSM-5.

Scanning Electron Microscope (SEM)

SEM is a characteristic method to identify the morphology of zeolite, at surface, shape, and crystal size. The result of SEM analysis showed that ZSM-

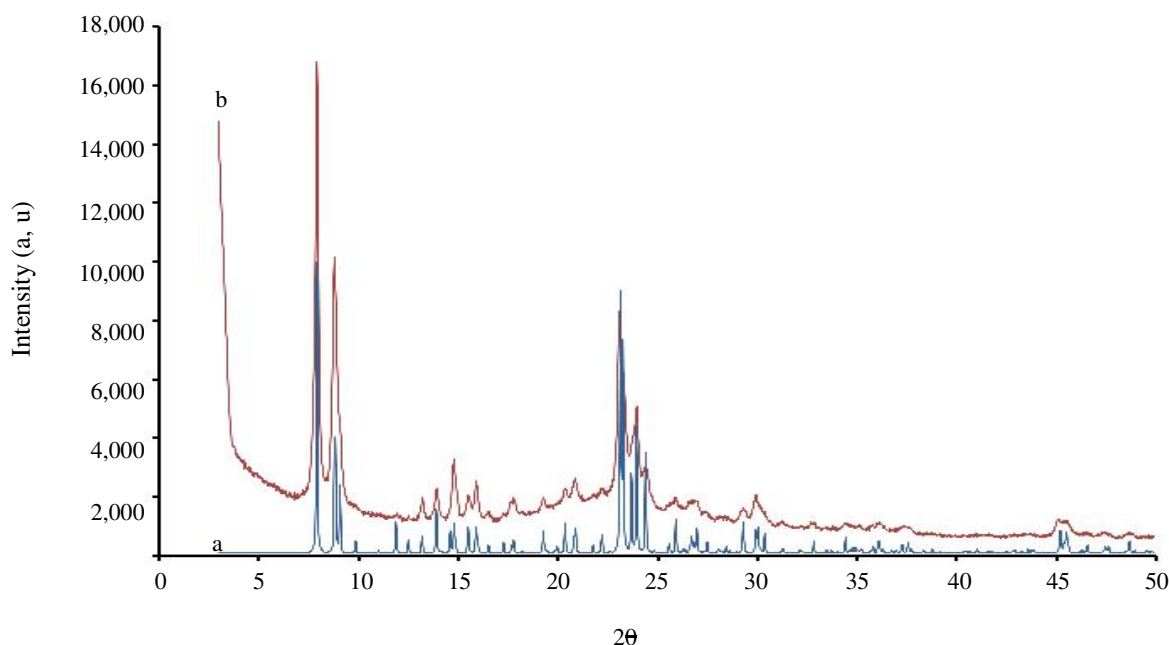


Figure 1. XRD pattern of ZSM-5 synthetic zeolite simulated standard difactogram (a) and Si : Ludox 40%.
 — : ZSM-5 (Si : Ludox 40%), — : ZSM-5 simulated standard difactogram.

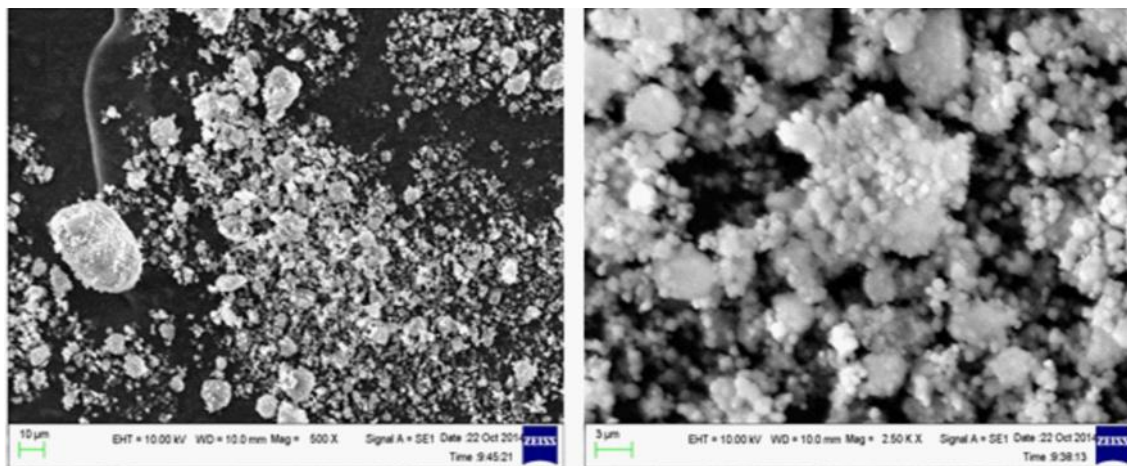


Figure 2. SEM of ZSM-5 zeolite by 500x (A), and 2500x (B).

5 crystal had rather spherical crystal morphology (Figure 2). The morphology in Figure 2 was the original shape of ZSM-5 because of low temperature. Low temperature influenced the stability of crystal structure, surface and composition composed of pore in zeolite. Mimura *et al.* (2001) proposed that synthetic zeolite made from hydrothermal method at 160 °C gave products with the best crystallinity.

Specific Surface Area and Total Pore Volume

Characterization of synthetic zeolite pore was done with nitrogen physisorption. This method was used to determine the distribution of pore, specific surface area and pore size. Bruenne Emmett Teller (BET) method was used to determine specific surface area at synthetic zeolite and Barret Joyner Halenda (BJH) to determine distribution of pore size. The result showed that ZSM-5 zeolite has 213.82 m² g⁻¹ of specific surface area and 0.22 cc g⁻¹ of total pore volume.

Heavy Metals Adsorption using ZSM-5 Zeolite

Experiments of heavy metal adsorption was conducted using Cu²⁺, Pb²⁺ and Cd²⁺. Adsorption

was done at various concentration between 50-250 ppm and contact time for 30-150 minutes. The result of heavy metal ion adsorption by ZSM-5 zeolite is shown in Figure 3.

The adsorption capacity of each heavy metals by ZSM-5 did not show significantly increase at 30 minutes through 150 minutes of contact time. It was due to ZSM-5 zeolite had reached a saturation level since first 30 minutes of contact time. Thereby nevertheless time passed, will not influence the capacity of heavy metal ion adsorption. It also showed that ZSM-5 zeolite had adsorption ability relatively fast to heavy metal ions.

The influence of concentration to the adsorption capacity showed that the higher concentration of heavy metal ion the higher adsorption capacity. The same idea with Tofighy and Mohammadi (2011), higher concentration, the strength of mass transfer that pushed will also be greater, so can increase the ability of adsorption. The research of Said and Widiastuti (2008) also obtained that the increase in metal ion will give greater puss capacity, so metal ion will move from outer surface into zeolite micropores. It explained that the ability of zeolite was not only related to the adsorption of ion, but was also influenced by zeolite pores. Besides, those

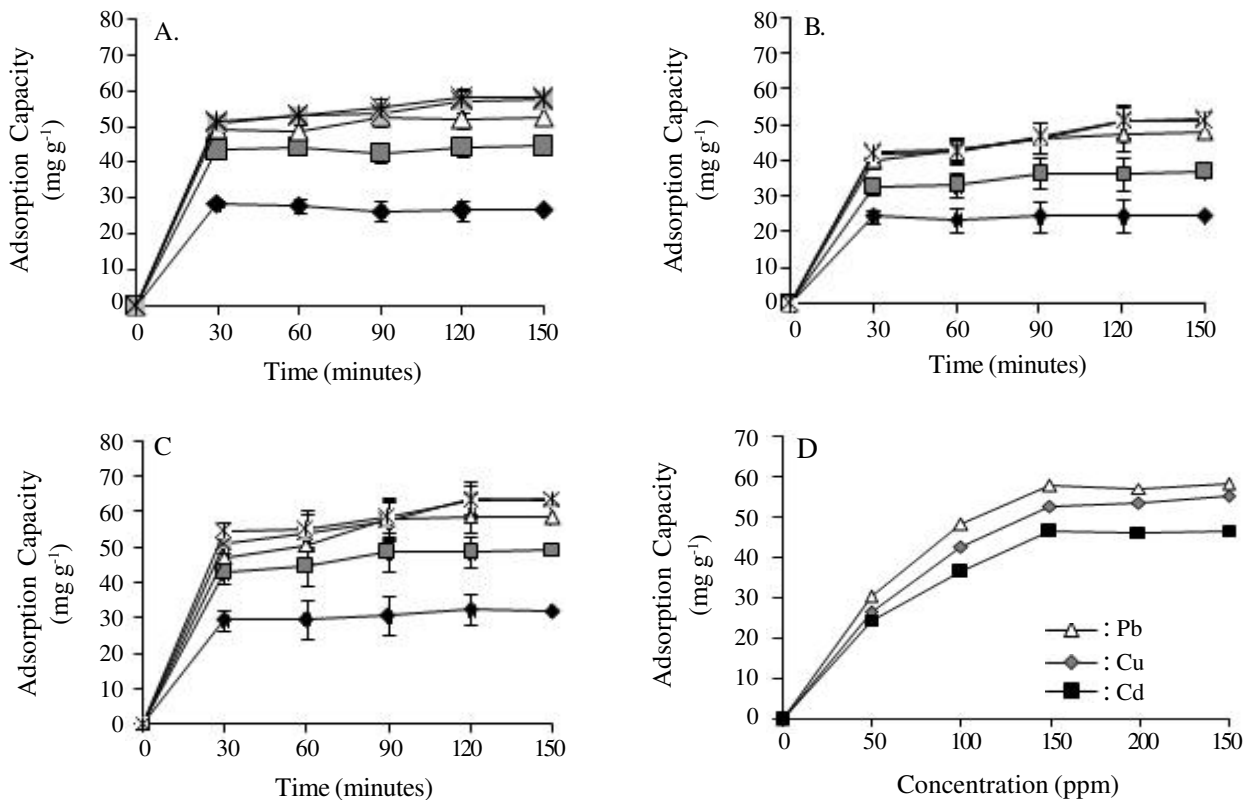


Figure 3. Metal adsorption by ZSM-5 at various concentration and contact time (A) Cu²⁺; (B) Cd²⁺; (C) Pb²⁺ and (D) fitting adsorption capacity by ZSM-5 to metals Pb²⁺, Cu²⁺ and Cd²⁺. ◆: 50 ppm, ■: 100 ppm, ▲: 150 ppm, ✕: 200 ppm, ✖: 250 ppm.

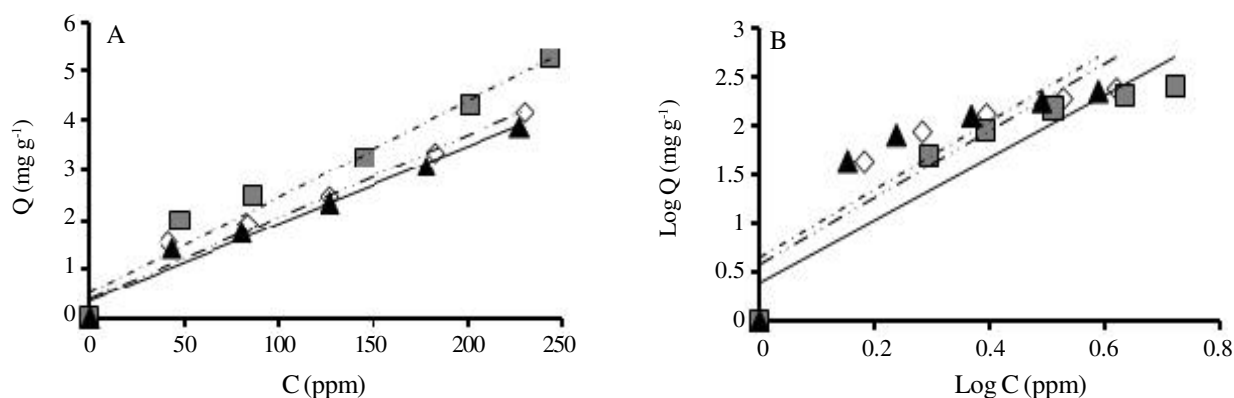


Figure 4. The equation of Langmuir isotherm (A) and Freundlich (B) heavy metals Pb²⁺, Cu²⁺ and Cd²⁺ by ZSM-5 zeolite. \diamond : Cu, \blacksquare : Cd, \blacktriangle : Pb.

metal ions fastened to the capacity at zeolite structure shaped from silica [SiO₄]⁴⁻ and alumina [AlO₄]⁵⁻, heavy metals could also enter into zeolite pores. In this case, zeolite also acts like ion filter. Ion is caught on zeolite pores and stuck to zeolite, so the concentration of metal ions in solution decreased.

To compare the ability of ZSM-5 adsorption to each metals ion and to understand the characteristic that affects it, we did the fitting the adsorption capacity of each metal ion. Figure 4 shows that the capacity of ZSM-5 zeolite to adsorb Pb²⁺ was higher than adsorb Cu²⁺ or Cd²⁺. The amount of ions adsorbed by ZSM-5 zeolite were 30.56-58.70 mg g⁻¹ of Pb²⁺, 27.24-55.06 mg g⁻¹ of Cu²⁺ and 24.40-46.47 mg g⁻¹ of Cd²⁺. It is organized based on the ability of adsorption level which are Pb²⁺ > Cu²⁺ > Cd²⁺.

The difference of this adsorption ability is affected by some characteristics, not only from zeolite but also from the characteristic of those metal ions. Pores of a certain size allows metal ion to enter that pore. Metal ion with bigger size than the pore size would decrease the adsorption ability. Chang and Shih (2000) described that the adsorption ability of zeolite X synthetic to heavy metals was bigger than zeolite A synthetic, because zeolite X synthetic had bigger pore size than zeolite A synthetic. Danny *et al.* (2004) explained that adsorption of Cu²⁺ and Cd²⁺ using apatite hydroxy nano-sized with ion hydrate diameter Cu²⁺ (4.19 Å) were smaller than Cd²⁺ (4.26 Å). It was seen from the amount of Cu adsorbed that was higher than Cd ion.

Minceva *et al.* (2007); Zamzow and Murphy (1992) and Kesraoui-Ouki *et al.* (1993) revealed that bigger metal ions have lower capacity of solidity and electrostatic adsorptive power. These will limit metal interaction with certain size to the adsorption ability. However, smaller ion radius and bigger ion

valence will be more densely and strongly adsorbed. In research of Lide (1998), diameter of ion hydrate were 4.01 Å for Pb, 4.19 Å for Cu²⁺ and 4.26 Å for Cd²⁺. Other characteristic that was related to the ion metal adsorption is electronegativity value. Metals with high electronegativity value will be easier to be adsorbed than low negativity value (Minceva *et al.* 2007). The electronegativity values of each metal ion used were 2.33, 1.90 and 1.69 for Pb²⁺, Cu²⁺, and Cd²⁺, respectively. Zeolite also showed characteristic bond structure of SiO₂ and AlO₃. Because of this bound, zeolite has excess negative ion capacity that is used to bind the metal ions with cation exchange mechanism.

Langmuir and Freundlich were used to interpret adsorption models of heavy metals by ZSM-5 through the linearity coefficient determination with R² approaching unit value (Figure 4). Because the Langmuir and Freundlich constant calculation only involve one q value (adsorption ability) from one level concentration, the adsorption ability of zeolite at each concentration was obtained by counting the average adsorption at each concentration level. To find adsorption model from this test, the maximum capacity to each heavy metals adsorption can also be obtained. Both equations are also widely used to evaluate the equilibrium characteristics in adsorption process. Langmuir equation explains adsorption process at the homogeneous surface, while Freundlich explained adsorption at heterogeneous surface. Parameter values from the three kinds of metals are summarized in Table 1.

The result showed that the adsorption isotherm of metal Pb²⁺, Cu²⁺ and Cd²⁺ using ZSM-5 zeolite are more suitable with Langmuir isotherm that was shown with regression value near to 1 (Figure 4). Based on Table 1, the ability of maximum adsorption of zeolite were Pb²⁺, Cu²⁺ and Cd²⁺ adsorption

Table 1. Langmuir and Freundlich parameters calculated from Cu, Pb and Cd isotherms using ZSM-5 synthetic zeolite.

Metal	Langmuir			Freundlich		
	a	b	R ²	k	n	R ²
Pb ²⁺	74.1	0.02	0.99	29.7	0.63	0.96
Cu ²⁺	69.9	0.02	0.99	25.3	0.62	0.95
Cd ²⁺	60.2	0.02	0.99	18.5	0.62	0.96

Table 2. Adsorption ability of ZSM-5 synthetic zeolite and natural zeolite.

Zeolite	Ratio Si/Al	Metal	Adsorption capacity (mg g ⁻¹)	Reference
ZSM-5 synthetics	100	Pb ²⁺	74.1	Present study
		Cu ²⁺	69.9	
		Cd ²⁺	60.2	
Natural clinoptilolite	-	Pb ²⁺	10.1	Inglezakis <i>et al.</i> (2004)
		Cu ²⁺	11.7	
		Cr ³⁺	6.80	
Natural clinoptilolite	-	Pb ²⁺	58.7	Buasri <i>et al.</i> (2008)
Naturaclinoptilolite	-	Cu ²⁺	9.23	Erdem <i>et al.</i> (2004)
		Co ²⁺	14.4	
		Zn ²⁺	8.75	
		Mn ²⁺	4.22	
Natural clinoptilolite	-	Cu ²⁺	11.1	Cincotti <i>et al.</i> (2006)
		Cd ²⁺	2.81-10.68	
Sardinian natural zeolite	-	Pb ²⁺	27.97-124.31	
		Zn ²⁺	3.27	
Naturalphillipsite	-	Pb ²⁺	24.24-35.74	Al-Haj-Ali and Al-Hunaidi (2004)
Natural clinoptilolite	-	Pb ²⁺	27.70	Sprynskyy <i>et al.</i> (2006)
		Cu ²⁺	25.76	
Ukrain natural zeolite	-	Ni ²⁺	13.03	Bosso and Enzweiler (2002)
		Cd ²⁺	4.22	
Natural scolecite	-	Pb ²⁺	5.80	
		Cu ²⁺	4.25	
		Zn ²⁺	2.09	
		Ni ²⁺	0.91	
		Cd ²⁺	0.18	

* activated

process which was calculated by Langmuir equation. Adsorbed substances from metal ion at every zeolite surface are calculated in mg ion per gram unit of zeolite weight. The results of maximum adsorption capacity ZSM-5 to each heavy metals were 74.07 mg g⁻¹ for Pb²⁺, 69.93 mg g⁻¹ for Cu²⁺, and 60.24 mg g⁻¹ for Cd²⁺.

The result showed that adsorption ability of ZSM-5 zeolite to the heavy metals were higher than adsorption by natural zeolite. It was because synthetic zeolite has better characteristic than natural zeolite. Adsorption ability of natural zeolite to the

heavy metals is shown in Table 2. The adsorption of Pb studied by Buasri *et al.* (2008) showed that the maximum adsorption ability of synthetic zeolite used was higher than that of natural zeolite but not as high as ZSM-5. Adsorption to heavy metals increased because zeolite used had been activated through saturation using 0.5 M of NaCl for 24 hours.

CONCLUSIONS

As concise as possible ZSM-5 synthetic zeolite has been created with low temperature method and

characteristic diffractogram pattern with typical peaks $2\theta = 7.9364^\circ, 7.9569^\circ, 23.9541^\circ$ and 23.9746° , crystalline form spherical morphology with porous crystalline surfaces, $213.82 \text{ m}^2 \text{ g}^{-1}$ of specific surface area and 0.22 cc g^{-1} of total pore volume.

The ability of synthetic zeolite adsorption ZSM-5 against the metal ion Pb^{2+} , Cu^{2+} and Cd^{2+} was influenced by the differences in zeolites pore size, the negative charge of zeolite, hydrate and electronegativity diameter of each metal ion. The results showed that the adsorption of heavy metal ions adsorption occurred at a relatively rapid contact with the maximum adsorption capacity of each of the metals Pb^{2+} 74.07 mg g^{-1} , Cu^{2+} 69.93 mg g^{-1} , and Cd^{2+} 60.24 mg g^{-1} .

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