



Chiang Mai J. Sci. 2008; 35(3) : 447-456

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Contributed Paper

Use of Natural Clinoptilolite for the Removal of Lead (II) from Wastewater in Batch Experiment

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Received: 25 February 2008

Accepted: 29 July 2008.

ABSTRACT

In this research, the ability of natural zeolite clinoptilolite to remove lead from aqueous solutions has been investigated in batch adsorption experiments. Adsorption tests of Pb(II) were carried out using a solid to liquid ratio of 20 g/L and agitation speed of 700 rpm. The effects of particle size of the minerals (75-250 μ m), solution concentration (100-1,200 ppm), initial pH (2-7), contact time (30-180 min) and temperature (30-75 °C) were examined. Experimental data obtained from batch equilibrium tests have been analyzed by Langmuir and Freundlich isotherm models. It was found that over 95% of the initial Pb(II) amount for solution containing 800 ppm was removed in the 120 min and the optimum pH value of solution to be treated for adsorption was found to be 7. In adsorption studies, residual heavy metal ion concentration reached equilibrium in short duration of 30 min for initial Pb(II) concentration of 100 and 300 ppm. Maximum adsorption capacity, 58.73 mg Pb(II)/g zeolite at 75 °C, showed that this adsorbent was suitable for lead removal from aqueous media. Adsorption phenomena appeared to follow Langmuir and Freundlich isotherms. The results show that there is a good fit between the experimental data and empirical isotherms.

Keywords : natural zeolite, clinoptilolite, lead, ion exchange, adsorption isotherms.

1. INTRODUCTION

Industrial wastewaters, which have heavy metals, are an important source of environmental pollution. Pb, Cd, Cu, Hg, Cr, Ni, and Zn are the main trace elements that are the most harmful for public health. These toxic metals are released into the environment in a number of different ways. Coal combustion, automobile emissions, mining activities, sewage wastewaters, and the utilization of fossil fuels are just a few examples [1]. Lead

has been found to be acute toxic to human beings when present in high amounts (e.g. >15 mg/L in drinking water). Lead is known to damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages [2].

The optimization of wastewater

purification processes requires a development of new operations based on low cost raw materials with high pollutant-removal efficiency. The complexity of effluents makes the process of heavy metals removal more difficult, as well as strict limitations that have been imposed to wastewater discharge everywhere in aquatic recipients. Among the methods such as precipitation, oxidation, ultrafiltration, reverse osmosis and electro-dialysis, ion exchange on natural zeolites seems to be more attractive method. Natural zeolites have been intensively studied recently because of their applicability in removing trace quantities of heavy metal ions from aqueous solutions by utilizing the ion exchange phenomenon [3,4]. Natural zeolites are low cost aluminosilicates, with a cage-like structure suitable for ion exchange due to isomorphous replacement of Al^{3+} with Si^{4+} in the structure, giving rise to a deficiency of positive charge in the framework. This is balanced by mono and divalent exchangeable cations such as Na^+ , Ca^{2+} , K^+ and Mg^{2+} . These cations are coordinated with the defined number of water molecules and located on specific sites in framework channels. Among natural zeolites, clinoptilolite is the most abundant and commonly used as ion exchanger or sorbent for inorganic or organic compounds. The specific structure of the clinoptilolite, consisting of a two-dimensional system of three types of channels (ten-member and eight-member rings) that are occupied by exchangeable alkali and alkaline earth metal ions, is responsible for its ion exchange and molecular sieve properties [5].

Although the large number of different studies on the removal of lead from aqueous solutions using zeolite, every special zeolite material requires individual research. The objectives of the present work describe the batch adsorption characteristics of Pb on clinoptilolite at various operational conditions

such as pH, temperature, contact time and initial metal concentration. Effect of particle size on adsorption is also investigated. Experimental data have been analyzed by adsorption isotherms.

2. MATERIALS AND METHODS

2.1 Adsorbent and Solutions Preparation

The natural zeolite used was obtained by Pesticide Free Agriculture Association, in Thailand. Clinoptilolite 75-250 μm was used in this study. A sample of mineral was treated with 0.5 M NaCl solution for 24 h under slow stirring. The sodium treated zeolite was washed several times with deionized water to remove excess sodium ions from zeolite. It was dried for 24 h at 60 °C in an oven before starting the experiments. All chemicals used were analytical grade reagents (Merck, >99% purity). Stock solutions of metals were prepared in a concentration of 2,000 ppm using nitrate salts dissolved in deionized water with a resistant value of 17 M Ω . The chemicals used in the batch experiments were nitrate solutions of $Pb(NO_3)_2$.

Batch mode adsorption isotherm was carried out at 30 °C. An amount of 2.0 g clinoptilolite was introduced into conical flasks with 100 mL of lead solution. The flasks were placed in a thermostatic shaker and agitated for 30-180 min at a fixed agitation speed of 700 rpm. Samples were taken periodically for measurement of aqueous phase of lead concentrations. The pH of metal solutions was appropriate adjusted by using HNO_3 or NaOH. Adsorption isotherms were performed for initial Pb(II) concentrations of 100-1,200 ppm. The Pb(II) concentration of the samples was determined by using a Varian Liberty 220 inductive coupled plasma emission spectrometer (ICP-ES).

2.2 Characterization of Adsorbent

Identification of crystal structure

parameters of the zeolite was obtained by X-ray diffraction (XRD). The XRD pattern was acquired on a Philips Analytical PW 3710 Based generator X-ray diffractometer using CuK α radiation ($2\theta = 5-80^\circ$). The chemical compositions of the zeolite were determined through X-ray fluorescence spectroscopy (XRF: EDX Oxford Model ED2000).

2.3 Determining the Amount of Metal Ion Removal

The amount of adsorbed Pb(II) ions (mg metal ions/g zeolite) was calculated from the decrease in the concentration of metal ions in the medium by considering the adsorption volume and used amount of the zeolite:

...(1)

Here q_e is the amount of metal ions adsorbed into unit mass of the zeolite (mg/g) at equilibrium, C_i is the concentration of the metal ions in the initial solution (ppm), C_e is the concentration of the metal ions in the final solution (ppm), m is the amount of zeolite used (g), V is the volume of metal solution (L) and S is the slurry concentration (g/L).

The influence of a specific process parameter was determined by calculating Pb(II) uptake by zeolite and changing that parameter and keeping other parameters constant. Uptake efficiency was calculated using the equation:

...(2)

2.4 Adsorption Isotherms

Adsorption isotherms for lead ions removal by zeolite in terms of Langmuir and Freundlich models were expressed mathematically. The obtained experimental data here are expectedly well fitted with the linearized form of Langmuir and Freundlich models.

Basic assumption of Langmuir isotherm is that adsorption takes place at specific homogeneous sites within the adsorbent. Langmuir isotherm [16,17] can be represented as:

...(3)

The empirical constants K_L and a for Langmuir model are related to the adsorption maximum (L/g) and bonding strength (L/mg), respectively.

Freundlich isotherm assumes heterogeneous surface with a nonuniform distribution of heat of adsorption. Freundlich isotherm [17,18] is given as:

...(4)

The empirical constants K_F (mg/g) and n (g/L) are the constants for Freundlich model.

3. RESULTS AND DISCUSSION

3.1 Analysis of Adsorbent

The chemical compositions of the tested zeolite sample are presented in Table 1. The major mineralogical component is clinoptilolite with quartz, gypsum, amorphite and montmorillonite as main impurities. According to the XRD pattern shown in Figure 1, the zeolite is identified as clinoptilolite and its characteristic peaks were recognized [6]. The solid also contained small amounts of mica and clay minerals.

3.2 Effect of Initial Concentration

The kinetics of lead uptake by natural process is presented in Figure 2. Experiments conducted with different adsorption times show that the amounts of Pb(II) ions adsorbed increase with the adsorption time of metal ions. The slopes of the lines joining the data points in the figure reflect the

adsorption rates. As it is seen, high adsorption rates were observed at the beginning and then plateau values were reached. As seen from Figure the increase in metal uptake is fast till 30 minutes and after that slow increase is observed. Concentrations of Pb(II) found at the end of the treatment were 0, 0.21, 30 and 166.44 ppm for initial metal concentration of 100, 300, 800 and 1,200 ppm, respectively. Over 95% of the initial Pb(II) amount for solution containing 800 ppm was removed in the 120 min. Then up to the third hour the uptake increased only about 1%. And over

80% of the initial concentration 1,200 ppm was eliminated in the 120 min. Then up to 180 min the uptake increased only about 3%. In a previous study, several adsorbents were used for lead removal and several times are reported as equilibrium adsorption time [7]. The adsorption rate obtained with the zeolite seemed to be very satisfactory. Due to the preference of short adsorption times for the minimum energy consumption, clinoptilolite can be accepted as an efficient adsorbent for Pb(II) removal when its short adsorption time is considered.

Table 1. Chemical compositions of clinoptilolite (on weight basis).

Oxide	SiO ₂	Al ₂ O ₃	CaO	K ₂ O	Fe ₂ O ₃	MgO	Na ₂ O	TiO ₂	ZrO ₂	LOI
wt %	74.44	7.68	2.46	1.34	1.24	0.87	0.59	0.24	0.05	11.09

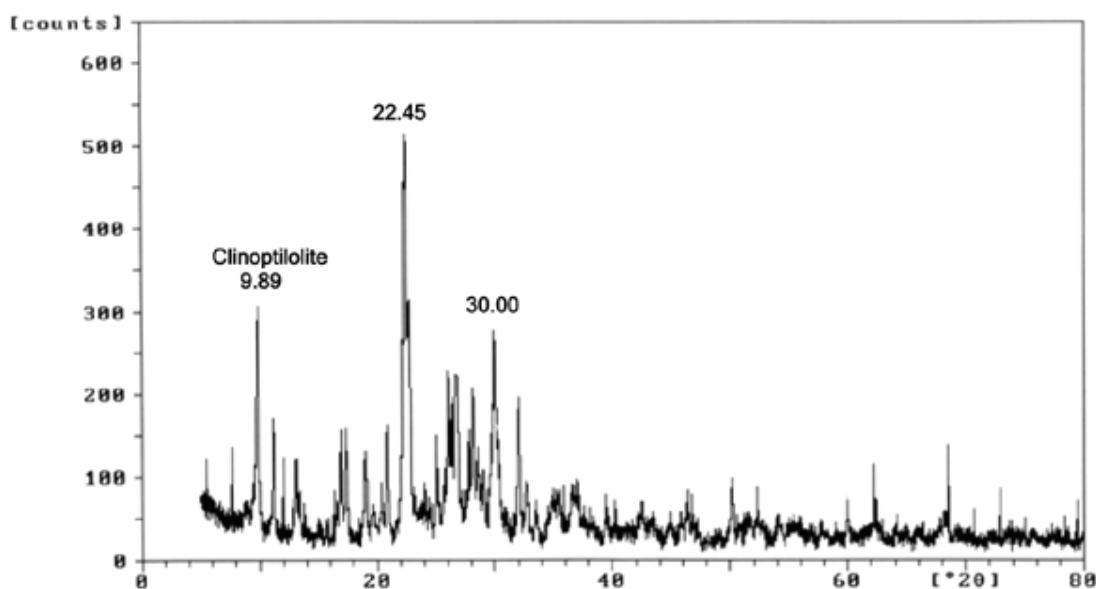


Figure 1. X-ray diffraction pattern of clinoptilolite showing the intensities in the region $2\theta = 5-80^\circ$.

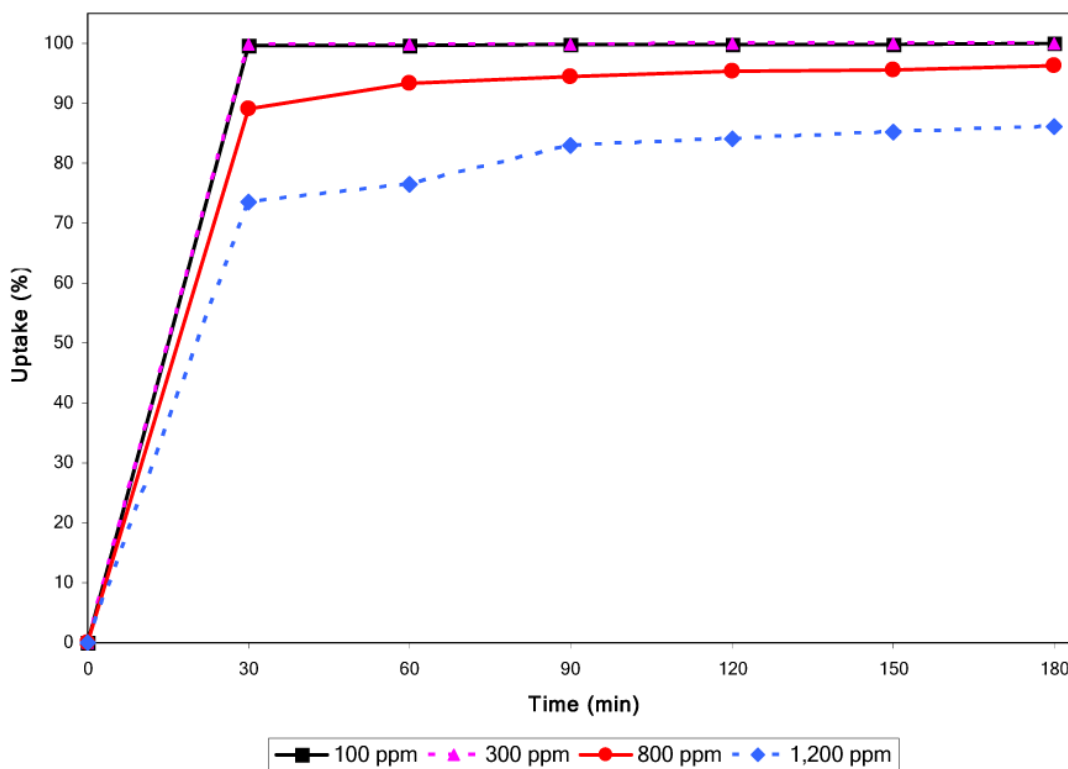


Figure 2. Effect of initial concentration on the kinetics of Pb(II) uptake by clinoptilolite.

3.3 Effect of Particle Size

To investigate the influence of zeolite particle size on Pb(II) removal, tests were made under the initial solution concentration of 800 and 1,200 ppm. The adsorption characteristics of zeolite with respect to grain sizes are shown that the using of clinoptilolite zeolite with finer particles (75-150 μm) leads to an increase in Pb(II) uptake or adsorption capacity. Application of zeolite with more coarse particles (150-250 μm) considerably decreases Pb(II) removal for solutions with higher Pb(II) concentration. Removal efficiency of zeolite with finer particles was 90.18 and 49.6%, but the uptake of clinoptilolite with more coarse particles was 88.34 and 41.04% for initial Pb(II) concentration 800 and 1,200 ppm, respectively. This probably is due to the smaller number of sites available for ion exchange and adsorption [8,9].

3.4 Effect of Initial pH

The pH level of the aqueous solution is an important variable for the adsorption of metals on the adsorbents. The effect of the pH on the metal adsorption by clinoptilolite was studied for pH 2, 3, 5 and 7, where the material exhibits chemical stability. Efficiency of metal sorption depends on the pH level of aqueous solution. The pH dependence of Pb(II) adsorption onto zeolite is shown in Figure 3. As it is seen in figure, q_c is low at low pH values. The value of q_c is increased by increasing the pH value and reaches a plateau at a pH value of 5 for initial concentration of 800 ppm. It is apparent that using solutions at pH values over 7 gives the highest q_c values due to the precipitation (precipitate of metal hydroxide) occurs during ion exchange experiments by NaOH. It revealed that the adsorption capacity is low at

pH values below 5 because of the dissolution of crystal structure and the competition between the protons (H^+) and metal ions (Pb(II)) for the exchange sites on the zeolite particle [8-10].

Metal adsorption decreases with the pH decrease from 7 up to 2 due to competition of hydrogen ions. As the pH level increases the concentration of the hydrogen ions as

competitors decreases and this leads to an increase of the amounts of sorbed metals. The amount of complex hydrated forms of the metals increases with pH value increase that also intensifies adsorption. Thus it is possible to manage metal uptake from aqueous solutions by changing the pH value [11, 12].

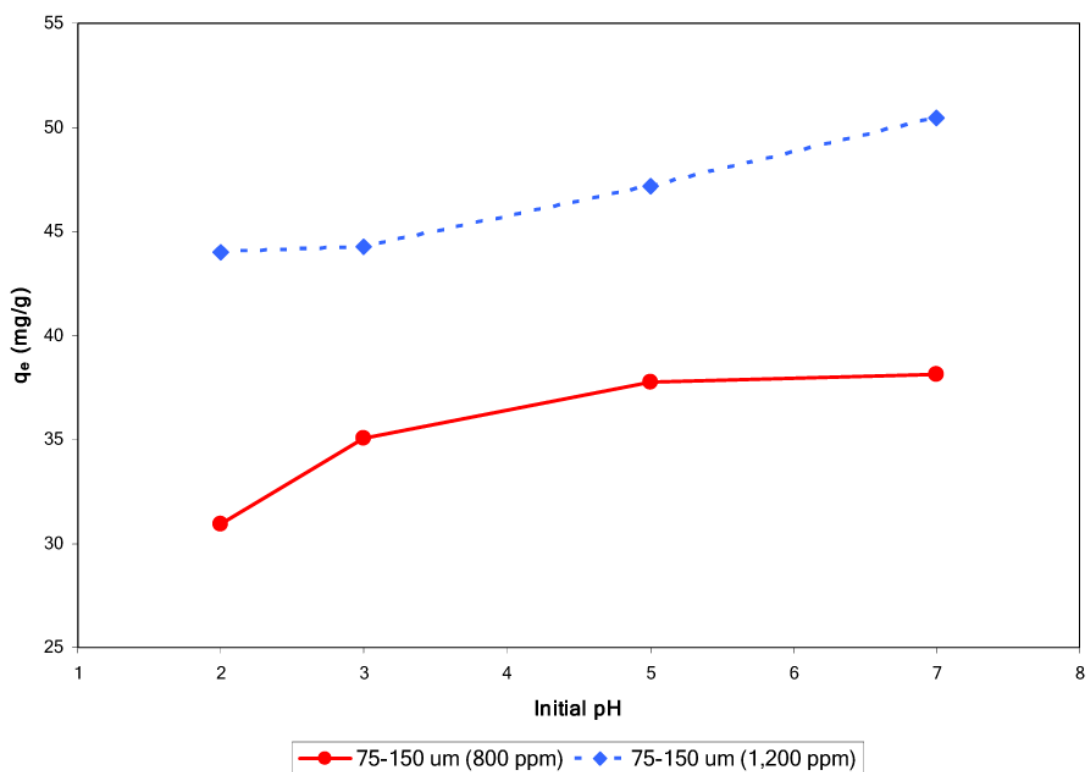


Figure 3. Effect of initial pH on the removal of Pb(II) by clinoptilolite.

3.5 Effect of Temperature

From Figure 4, the amounts of adsorbed lead onto the zeolite increase with an increase in the temperature of heavy metal solution. Raising the temperature from 30 to 60 °C increases the value of q_e 50 and 58 mg/g for initial concentration of 1,200 ppm. The maximum adsorption capacities was calculated as 58.73 mg Pb(II)/g zeolite at 75 °C, showed

that this adsorbent was suitable for heavy metals removal from aqueous media.

Concerning the effect of temperature on the adsorption process, the metals uptake is favored at higher temperatures, since a higher temperature activates the metal ions for enhancing adsorption at the coordinating sites of the minerals [13]. Also, it is mentioned that cations move faster with increasing

temperature. Likely explanation for this is that retarding specific or electrostatic, interactions

become weaker and the ions become smaller, because solvation is reduced [14].

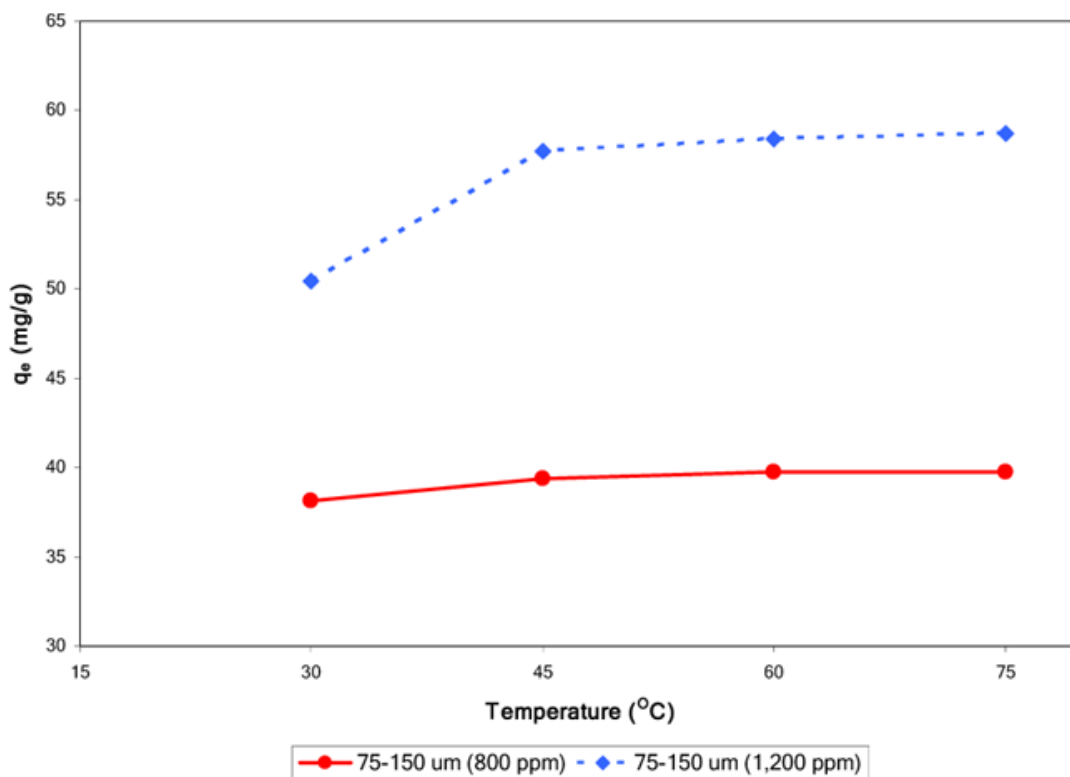


Figure 4. Effect of temperature on the removal of Pb(II) by clinoptilolite.

3.6 Comparison of Adsorption Isotherms

In this study, the relationship between the adsorbed and the aqueous concentrations at equilibrium has been described by two-parameter isotherm models (Langmuir and Freundlich). In addition to the experimental data, plotting the experimental data using Eqs. (3) and (4) indicated that these models give good fit for the data. It was determined that the equilibrium removal of Pb(II) by the clinoptilolite can be represented by the following equations:

...(5)

...(6)

The experimental data for metal ions fit

well with the linearized Langmuir and Freundlich isotherms. The values of isotherm parameter obtained from the Langmuir model were $K_L = 7.01$ L/g and $a = 0.153$ L/mg. The empirical constants from Freundlich model were $K_F = 13.6$ mg/g and $n = 0.168$ g/L. The comparisons of the experimental values with the values of q_e obtained by both models are shown in Figure 5. They are seen from this figure, Langmuir isotherms was well fitted with the experimental data rather than Freundlich isotherms for Pb(II) removal by zeolite. The correlation coefficients for Langmuir isotherm ($R^2 = 0.96$) and Freundlich isotherm ($R^2 = 0.92$) indicating that the Langmuir and Freundlich model can be applied to these sorbent systems and shown good adsorption [8].

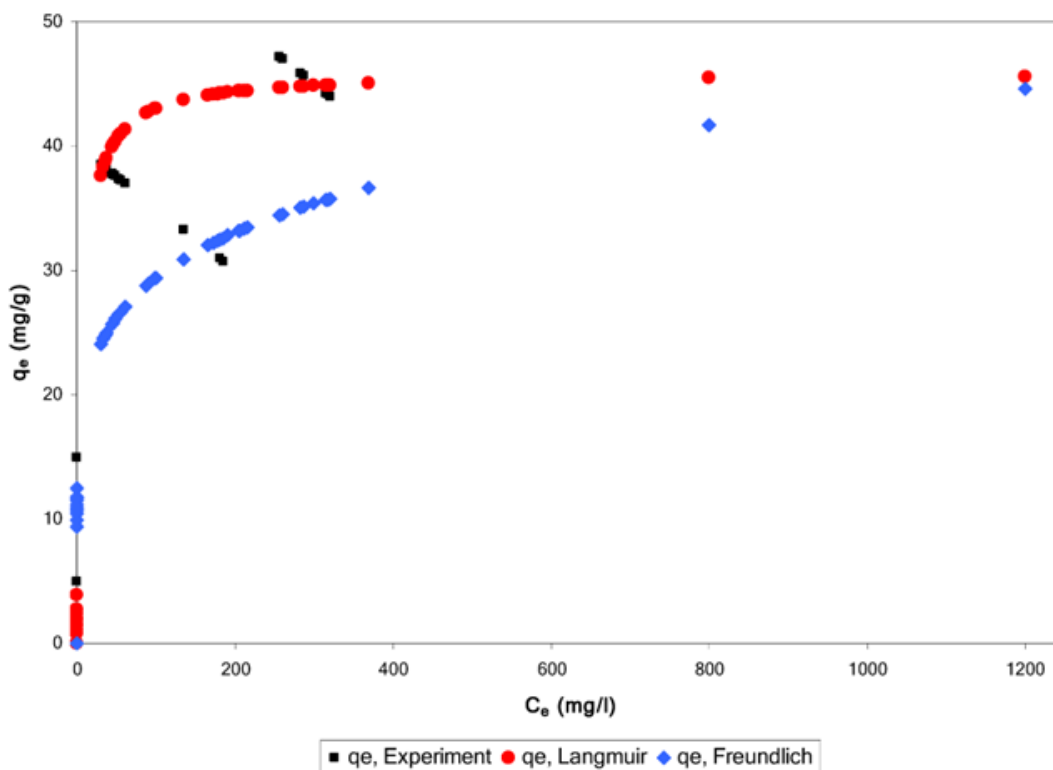


Figure 5. Comparison of the experimental results with the q_e values obtained by Langmuir and Freundlich isotherms for Pb(II) removal by clinoptilolite.

Table 2. Values of maximum adsorption capacities of some adsorbents of Pb(II).

Adsorbent	q_e (mg/g)	Source
Chitosan	16.36	Babel and Kurniawan [13]
Clay (Bentonite)	1-20	Babel and Kurniawan [13]
Zeolite	62-175	Babel and Kurniawan [13]
Activated Carbon	30	Babel and Kurniawan [13]
Phillipsite	104	Ali and El-Bishtawi [19]
Clinoptilolite	58.73	This Study

It was determined that best fitted adsorption isotherm models considering the relative errors were obtained for two-parameter isotherms to be in the order of prediction precision: Temkin, Dubinin-Radushkevich, Langmuir and Freundlich

isotherms. Three-parameter isotherms have higher regression coefficients (>0.99) and lower relative errors ($<5\%$) than two-parameter isotherms. Comparing the values of SSE, Δq , and r^2 obtained from the adsorption models shows that the fitness

between the experimental values and the predicted values using the models were generally very good for all three-parameter isotherm models. However, the Sips and Toth isotherms provided the best correlation for raw and pretreated clinoptilolite, respectively [15].

The values of maximum experimental adsorption capacity of some adsorbents for Pb(II) were also given in Table 2 [13,19]. It can be seen from the table, clinoptilolite used in this study show a good adsorption capacity for Pb(II) ion in water.

4. CONCLUSIONS

In this study, the interaction between lead ions and zeolite has been investigated. The results indicated that several factors such as particle size, solution concentration, pH, temperature and contact time affect the adsorption process. The physico-chemical characteristics of wastewaters from varying sources can be much more complex compared to the aqueous metal solution used in this study. Because of this, the effects of other components of wastewaters on commercial metal adsorption process should be determined. However, this work can be considered a preliminary study to conclude that clinoptilolite is suitable and efficient material for the adsorption of Pb(II) from aqueous solution. The experimental results were a good fit with the adsorption isotherm models.

ACKNOWLEDGEMENTS

The authors acknowledge sincerely the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials and Center of Materials for Energy and Environment, Department of Materials Science and Engineering (MSE), Faculty of Engineering and Industrial Technology, Silpakorn University for the financial support

of this study and thanks are due to the Pesticide Free Agriculture Association of Thailand for the zeolite samples and relative information.

REFERENCES

- [1] Solmaz K., Abdülkerim K., Adil D., and Yuda Y., Batch Removal of Copper (II) and Zinc (II) from Aqueous Solutions with Low-Rank Turkish Coals, *Sep. Purif. Technol.*, 2000; **18**: 177-184.
- [2] Naseem R., and Tahir S.S., Removal of Pb(II) from Aqueous/Acidic Solutions by Using Bentonite as an Adsorbent, *Water Res.*, 2001; **33**, 3982-3986.
- [3] Misaelides P., Godelitsas A., Charistos V., Ioannou D., and Charistos D., Heavy Metal Uptake by Zeoliferous Rocks from Metaxades, Thrace, Greece: an Exploratory Study, *J. Radioanal. Nucl. Chem.*, 1994; **183**, 159-166.
- [4] Shanableh A., and Kharabsheh A., Stabilization of Cd, Ni and Pb in Soil Using Natural Zeolite, *J. Hazard. Mater.*, 1996; **45**, 207-217.
- [5] Arcoya A., González J.A., Llabre G., Seoane X.L., and Travieso N., Role of the Counteractions on the Molecular Sieve Properties of a Clinoptilolite, *Micropor. Mater.*, 1996; **7**, 1-13.
- [6] Doula M., Ioannou A., and Dimirkou A., Copper Adsorption and Si, Al, Ca, Mg, and Na Release from Clinoptilolite, *J. Colloid Interface Sci.*, 2002; **245**, 237-250.
- [7] Trgo M., Perić J., and Medvidović N.V., A Comparative Study of Ion Exchange Kinetics in Zinc/Lead-Modified Zeolite-Clinoptilolite Systems, *J. Hazard. Mater.*, 2006; **136**, 938-945.
- [8] Ali H.O., and Abidin K., Factors Affecting Adsorption Characteristics of Zn²⁺ on Two Natural Zeolites, *J. Hazard. Mater.*, 2006; **131**, 59-65.

- [9] Vassilis J.I., Marinos A.S., Despoina G., and Maria D.L., Removal of Pb(II) from Aqueous Solutions by Using Clinoptilolite and Bentonite as Adsorbents, *Desalination*, 2007; **210**, 248-256.
- [10] Sabriye D., and Ali C., Pb(II) and Cd(II) Removal from Aqueous Solutions by Olive Cake, *J. Hazard. Mater.*, 2006; **138**, 22-28.
- [11] Myroslav S., Boguslaw B., Artur P.T., and Jacek N., Study of the Selection Mechanism of Heavy Metal (Pb^{2+} , Cu^{2+} , Ni^{2+} and Cd^{2+}) Adsorption on Clinoptilolite, *J. Colloid Interface Sci.*, 2006; **304**, 21-28.
- [12] Sevgi K., Comparison of Amberlite IR 120 and Dolomite's Performances for Removal of Heavy Metals, *J. Hazard. Mater.*, 2007; **147**, 488-496.
- [13] Babel S., and Kurniawan T.A., Low-Cost Adsorbents for Heavy Metals Uptake from Contaminated Water: a Review, *J. Hazard. Mater.*, 2003; **97**, 219-243.
- [14] Inglezakis V.J., Loizidou M.D., and Grigoropoulou H.P., Ion Exchange Studies on Natural and Modified Zeolites and the Concept of Exchange Site Accessibility, *J. Colloid Interface Sci.*, 2004; **275**, 570-576.
- [15] Ahmet G., Ertan A., and İsmail T., Lead Removal from Aqueous Solution by Natural and Pretreated Clinoptilolite: Adsorption Equilibrium and Kinetics, *Journal of Hazardous Materials*, 2007; **146**, 362-371.
- [16] Langmuir I., The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum, *J. Am. Chem. Soc.*, 1918; **40**: 1361-1403.
- [17] Murat A., Abdulkarim K., Orhan A., and Yuda Y., Removal of Silver (I) from Aqueous Solutions with Clinoptilolite, *Micropor. Mesopor. Mater.*, 2006; **94**: 99-104.
- [18] Freundlich H.M.F., Over the Adsorption in Solution, *J. Phys. Chem.*, 1906; **57**: 385-470.
- [19] Ali A.H.H., and El-Bishtawi R., Removal of Lead and Nickel Ions Using Zeolite Tuff, *J. Chem. Technol. Biotechnol.*, 1997; **69**: 266-271.