

REMOVAL OF LEAD BY USING Na-A ZEOLITE SYNTHESIZED
FROM SPENT SILICA – ALUMINA

การกำจัดตะกั่วโดยใช้ซีโอไลต์สังเคราะห์จากซิลิกา-อะลูมินาใช้แล้ว

Pimonpan Uttapan¹, Petchporn Chawakitchareon^{1*} and Dawan Wiwattanadate²

¹ Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok
10330, Thailand

² Department of Mining and Petroleum Engineering, Faculty of Engineering, Chulalongkorn University,
Bangkok 10330, Thailand

พิมลพันธ์ อุดทาพันธ์¹, เพ็ชรพร เชาวกิจเจริญ^{1*} และ ดาววัลย์ วิวรรณเดชะ²

¹ ภาควิชาวิศวกรรมสิ่งแวดล้อม คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

กรุงเทพมหานคร 10330 ประเทศไทย

² ภาควิชาวิศวกรรมเหมืองแร่และปิโตรเลียม คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

กรุงเทพมหานคร 10330 ประเทศไทย

received : April 29, 2011

accepted : October 6, 2011

Abstract

This research was carried out in order to investigate the adsorption efficiency of lead removal using sodalite and Na-A zeolite synthesized from spent silica–alumina. The starting material composition used in this experiment was: Al₂O₃: 1.926 SiO₂: 3.165 Na₂O: 128 H₂O. The optimum condition used to synthesize zeolite was at 90 °C for 4 hr. The experiment was carried out by using sodalite and Na-A zeolite as an adsorbent for removing lead from aqueous solution. The adsorption was carried out in batch experiment. The results indicated that the optimum condition of sodalite and Na-A zeolite for lead adsorption was at the concentration of 30 ppm, pH 4 with the contact time of 60 min for sodalite and 30 min for Na-A zeolite. The efficiency of lead removal was about 98-99%. The adsorption isotherm of sodalite and Na-A zeolite was shown to be in a linear form and related to the Langmuir isotherm. The adsorption phenomenon was monolayer. The maximum lead adsorption capacity for sodalite was at 224 mg lead/g. While the maximum lead adsorption capacity for Na-A zeolite was only 46 mg lead/g.

Keywords: spent silica-alumina, sodalite, Na-A zeolite, adsorption process, lead

*

corresponding author

E-mail : petchporn.c@chula.ac.th

Phone : +66-2218-6674, Fax : +66-2218-6666

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาความสามารถในการกำจัดตะกั่วในน้ำเสียสังเคราะห์โดยใช้โซดาไลต์และซีโอไลต์เอ ซึ่งสังเคราะห์จากซิลิกา-อะลูมินาที่ใช้แล้ว โดยใช้องค์ประกอบเริ่มต้นตามสัดส่วนโดยโมลดังนี้ $Al_2O_3 : 1.926 SiO_2 : 3.165 Na_2O : 128 H_2O$ สภาวะที่เหมาะสมในการสังเคราะห์ซีโอไลต์เอ คืออุณหภูมิ 90 °C เป็นเวลา 4 ชม. ทำการทดลองโดยใช้โซดาไลต์และซีโอไลต์เอไปทดสอบความสามารถในการกำจัดตะกั่วในน้ำเสียสังเคราะห์ โดยทำการทดลองแบบที่ละเท ซึ่งสภาวะที่เหมาะสม คือ ความเข้มข้นเริ่มต้น 30 มก./ล. พีเอช 4 ระยะเวลาสัมผัส 30 นาที ส่วนโซดาไลต์ระยะเวลาสัมผัส 60 นาที มีประสิทธิภาพการกำจัดตะกั่วอยู่ที่ร้อยละ 98-99 การดูดซับของโซดาไลต์และซีโอไลต์เอสอดคล้องกับไอโซเทอมการดูดซับแบบแลงเมียร์ ลักษณะการดูดซับเป็นแบบชั้นเดียว โซดาไลต์มีความสามารถในการดูดซับตะกั่วสูงกว่าซีโอไลต์เอ โดยมีค่าปริมาณตะกั่วที่ถูกดูดซับสูงสุด เท่ากับ 224 มก./ก. ส่วนซีโอไลต์เอมีค่าปริมาณตะกั่วที่ถูกดูดซับสูงสุดเพียง 46 มก./ก.

คำสำคัญ: ซิลิกา-อะลูมินาที่ใช้แล้ว, โซดาไลต์, ซีโอไลต์เอ, กระบวนการดูดซับ, ตะกั่ว

Introduction

During the manufacturing process of hydrogen peroxide, spent silica-alumina was generated as an industrial waste. Spent silica-alumina is currently treated at landfill sites, but its daily output and the limited landfill capacity have induced social and environmental problems. Previous researches on the spent silica-alumina have concentrated on using the alumina-silica waste as a component in construction materials such as making pavement ⁽¹⁾, ceramic tiles production ⁽²⁾, concrete blocks ⁽³⁾, etc. One possible and effective alternative is to convert the spent silica-alumina to Na-A zeolite adsorbents. Zeolites are a suitable choice as they have a large cation exchange capacity and an affinity for heavy metals. They are widely used as sorbents, catalysts and cation exchangers. Aim of this study is to investigate the applicability of synthetic Na-A zeolite for the removal of lead (Pb) ions from aqueous solutions and to examine the effects of various parameters such as initial metal concentration, pH, and contact time on the adsorption percentage. The obtained optimal parameters have been applied to wastewater from the industrial zone in order to remove lead in the effluents. The equilibrium isotherms of lead ions sorption are also evaluated using Langmuir and Freundlich models. Objectives of this study are as following.

- To study the characteristic of synthetic Na-A zeolite as an adsorbent material for the removal of lead ion from aqueous solutions.

- To study the maximum condition of the adsorption capacity for the removal of lead ion from aqueous solutions.

Materials and Methods

Preparation of zeolite

The spent silica-alumina generated from hydrogenperoxide process was used as raw material. It was pretreated mechanically and thermally. In the mechanical treatment, the spent silica-alumina was milled and sieved to obtain particles smaller than 200 mesh. The waste was then calcined at 700 °C for 3 hrs in the thermal treatment. The chemical composition of the calcined spent silica-alumina was determined by using a X-ray Fluorescence Spectroscopy. The waste was found rich in Al_2O_3 , while the SiO_2 content was low. Hence, there was a need to add SiO_2 (water glass) in the reaction mixture. Next step, weigh each substance to the required molar ratio which was 3.98 g of alumina-silica waste : 8.16 g of water glass : 10.67 g of NaOH and 67.19 g of H_2O . The solution and sodium hydroxide solution were added to silica-alumina. Finally, the whole mixture was stirred at 60 °C and kept over 24 hrs for incubation. The preparation of Na-A zeolite was performed in the same conditions. The gels were hydrothermally reacted in Teflon-lined stainless steel autoclaves at 90 °C for 4 hrs. Thereafter, the products were recovered by filtration, washed with distilled water and dried at 100 °C overnight ⁽⁴⁾.

Characterization of Zeolite

The chemical compositions of the raw and the pre-treated alumina-silica waste were determined by using XRF analyzer at The Scientific and Technology Research Equipment Centre (STREC), Chulalongkorn University, Bangkok, Thailand.

Crystallinity and X-ray diffraction (XRD) pattern of the Na-A zeolite were performed by a X-ray diffractometer (Rigaku D/MAX-220 Ultima⁺). The experiments were carried out by using $CuK\alpha$ radiation and the diffraction angle (2θ) in the range 5-50 °.

The shape and the size of the synthetic Na-A zeolite were observed microscopically by using Scanning Electron Microscope (SEM, JEOLJSM-35) at the Science Service Department, Chulalongkorn University, Bangkok, Thailand.

Preparation of synthetic solutions of metal

The chemicals used were of analytical reagent grade. Doubly distilled water was used throughout the experimental studies. Stock Pb solutions (1000 mg/L) were prepared by dissolving $Pb(NO_3)_2$ in 1000 ml of doubly distilled water. Working standards were prepared by progressive dilution of stock Pb solutions using doubly distilled water.

Batch adsorption

1. Optimum initial concentration

Batch adsorption experiments were conducted using 0.1 g zeolites in 100 ml solutions containing lead metal ions with different concentrations between 10-50 mg/L for lead metals at constant pH 5.0 in 250 ml glass bottles. The bottles were shaken in a rotary shaker at 200 rpm for 120 min⁽⁵⁾ at room temperature. Solutions containing lead metals were filtered through Whatman filter paper (No. 42). The concentration of lead metals was determined by using an atomic absorption spectrometer (AAS).

2. Optimum pH

Batch adsorption experiments were conducted using 0.1 g zeolites in 100 ml solutions containing lead metal ions with optimum concentrations for lead r metals at different pH 3.0-7.0 in 250 ml glass bottles. The bottles were shaken in a rotary shaker at 200 rpm for 120 min. ⁽⁵⁾ at room temperature. Solutions containing lead metals were filtered through Whatman filter paper (No. 42). The concentration of lead metals was determined by using AAS.

3. Optimum contact time

Batch adsorption experiments were conducted using 0.1 g zeolites in 100 ml solutions containing lead metal ions with optimum concentrations for lead metals and optimum pH in 250 ml glass bottles. The bottles were shaken in a rotary shaker at 200 rpm for different contact time of 15-180 min. at room temperature. Solutions containing lead metals were filtered through Whatman filter paper (No. 42). The concentration of lead metals was determined by using AAS.

4. Adsorption isotherm

The adsorption isotherm of lead metals ions on zeolite experiments were conducted using different dose of zeolites (0.01-0.25 g) in 100 ml of solutions containing lead metal ions in 250 ml glass bottles with all other optimum parameters. The bottles were shaken in a rotary shaker at 200 rpm for the optimum contact time at room temperature. Solutions containing lead metals were filtered through Whatman filter paper (No. 42). The concentration of lead metals was determined by using AAS. The adsorption percentage was calculated following Equation (1). The Langmuir and Freundlich isotherm was calculated as in Equations (2) and (3), respectively.

$$\text{Removal (\%)} = \frac{(C_i - C_e) 100}{C_i} \quad (1)$$

where C_i and C_e are the initial and final concentrations of metal ion in its aqueous solution (mg/L) , respectively

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2)$$

where q_e is equilibrium uptake per mass of zeolite (mg/g), q_{\max} is the maximum equilibrium uptake per mass of zeolite (mg/g), b (L/g) (sorption equilibrium constant) is constants.

$$q_e = k C_e^{1/n} \quad (3)$$

where k (L/g) and $1/n$ are Freundlich constants.

Result and Discussion

Characterization of zeolite

1. Chemical composition

Chemical components of spent silica-alumina before and after burning at 700 °C is shown in Table 1. It was apparent that the weight ratio of alumina to silica increased in the calcined spent silica-alumina, which was appropriate for the synthesis of Na-A zeolite. Moreover, the burning process also removed 26.15 % by weight organic compounds. The spent silica-alumina burnt at 700 °C for 3 hrs had an amorphous structure. The burning process caused restructuring that was appropriate for the synthesis of Na-A zeolite. The dissolution step was carried out under conditions of 60 °C for 24 hrs with a filter. The sodalite structure, which was the primary structure of Na-A zeolite, was found (Figure 1). During the synthesis, the formation step of Na-A zeolite was fixed at 90 °C for 4 hrs in the autoclave ⁽⁶⁾. The structure of Na-A zeolite was found (Figure 2). It could be summarized that the suitable time used in the formation of Na-A zeolite was at 4 hrs with 100 % crystallinity ⁽⁷⁾.

Table 1 Chemical composition of silica-alumina

Chemical composition (%wt)	Al ₂ O ₃	SiO ₂	SO ₃	Na ₂ O	CaO	Fe ₂ O ₃	K ₂ O	Cl	Organic
Raw	54.02	11.70	4.41	3.17	0.42	0.05	0.08	-	26.15
Calcined 700 °c	74.68	14.74	5.71	4.13	0.52	0.09	0.03	0.01	0.09

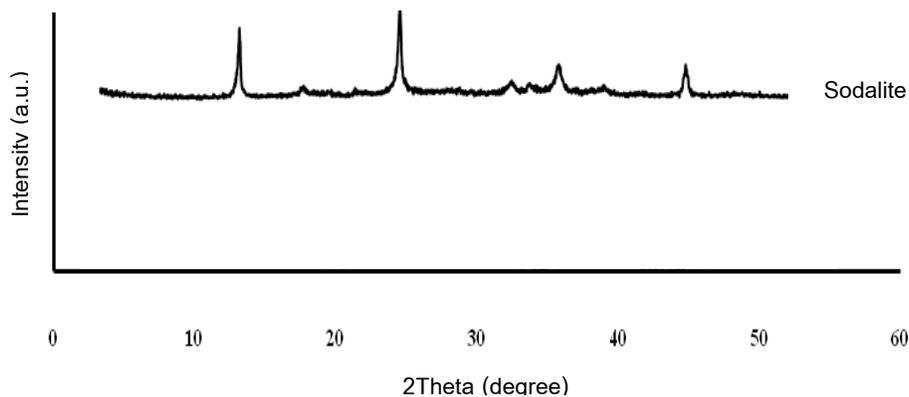


Figure 1 The diffractograms of sodalite

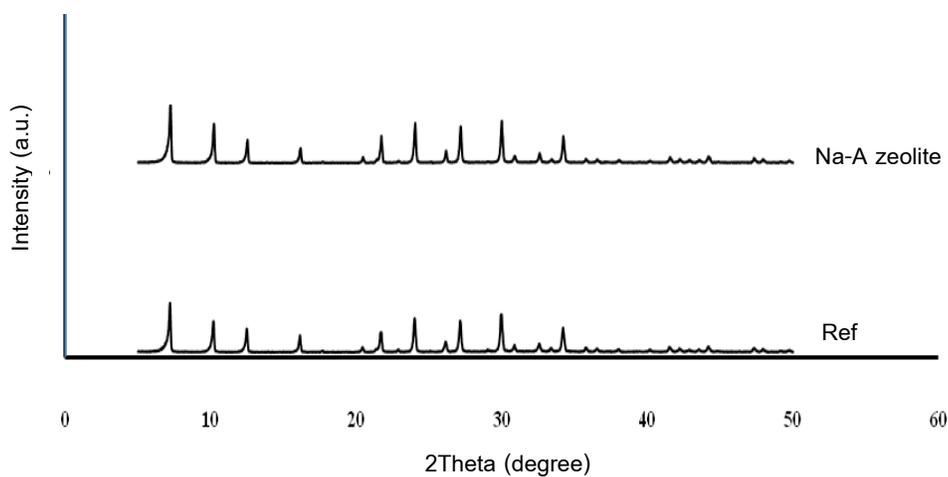


Figure 2 The diffractograms of Na-A zeolite

2. Physical composition

The physical composition such as the surface area, micropore volume and pore size, was important to the capacity of the adsorption by sodalite and Na-A zeolite. The BET surface area of sodalite and Na-A zeolite was 109.64 and 28.59 m^2/g , the micropore volume was 0.213 and 0.054 cm^3/g and the pore size was 7.78 and 7.62 nm., respectively. It is interesting that sodalite and Na-A zeolite showed an increase of BET surface area and micropore volume compared to the spent silica-alumina. This is mainly due to the presence of sodium hydroxide, which has larger surface area compared to the spent silica-alumina. Figure 3 shows that the

crystallites of spent silica-alumina, sodalite and Na-A zeolite. Figure 3(a) shows that crystallized spent silica-alumina forms no amorphous gels, no micropore, and its surface is crowded. Figure 3(b) shows that crystallized sodalite forms amorphous cubic particles with clearly visible facets. Figure 3(c) shows that the structure of Na-A zeolite is generally cubic, the crystals are obviously complete in cubic forms, and they are larger than sodalite. The outer structure has significant feature relevant to the crystallinity (%) of the Na-A zeolite. In other word, the outer structure of the crystals is clear cubic in accordance with the increasing of crystallinity (%). From these pictures, they explain the rather high surface diffusion coefficients for sodalite which makes the exchange fast. This indicates that sodalite may be more efficient in lead ion removal than another.

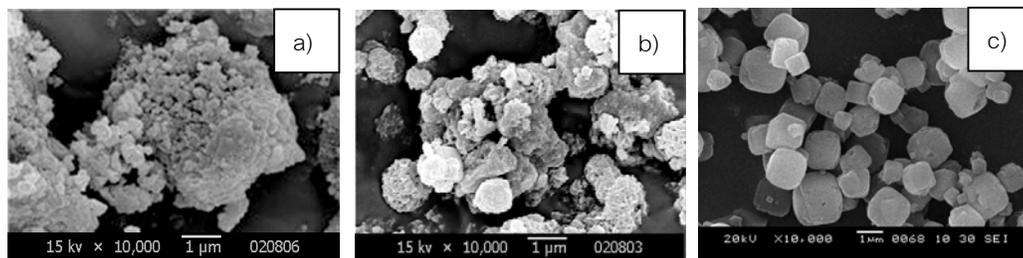


Figure 3 Scanning electronic micrographs of a) Spent silica-alumina b) Sodalite c) Na-A zeolite

Effect of experimental condition on lead adsorption

1. The optimum concentration on lead adsorption

The adsorption of the lead ions onto sodalite and Na-A zeolite as a function of the initial lead concentrations was studied by varying the lead ion concentrations from 10, 20, 30, 40 to 50 mg/L with all other parameters kept constant. Figure 4 shows that the uptake of lead decreases with the increasing concentration indicating that fewer favorable sites become involved when the concentration rises. The lead uptake on sodalite was similar to that 98.0 % with the increase in the concentration of lead metal. While, the uptake of lead on Na-A zeolite decreases from 88.84 % to 81.34 % and 81.54 % with an increase of lead concentration from 30, 40 to 50 mg/L, while the uptake decrease for both sodalite and Na-A zeolite with the increase of initial lead concentration indicating that less favourable media when the solution concentration increases⁽⁸⁾. Similar experiment using zeolite synthesized from fly ashes for the adsorption of lead metal indicated the ion exchange on zeolite increases when lead concentration decreased⁽¹⁰⁾. Their adsorption decreased with increasing initial concentration. This may be due to their larger ions and high hydration energy. It is more difficult for large ions

to diffuse through the pores of zeolite, and they may block outside the pores. This resulted in a decreasing of the metal ions passing through the pore and, thus, less adsorption.

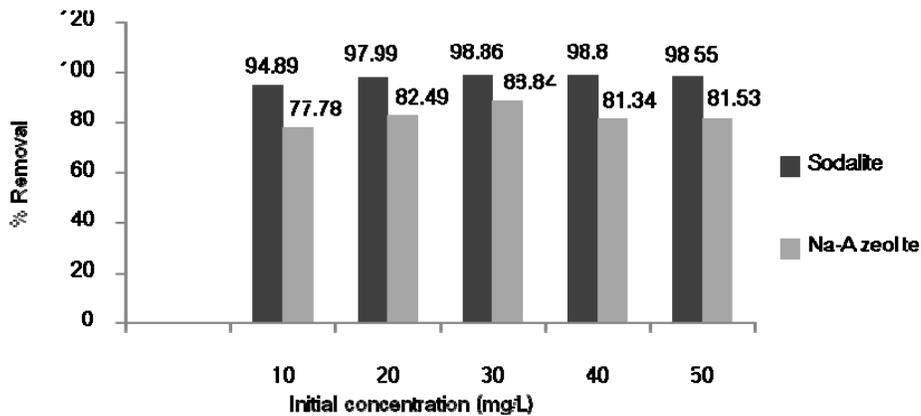


Figure 4 Variation of adsorption uptake of lead on sodalite and Na-A zeolite with the initial concentration.

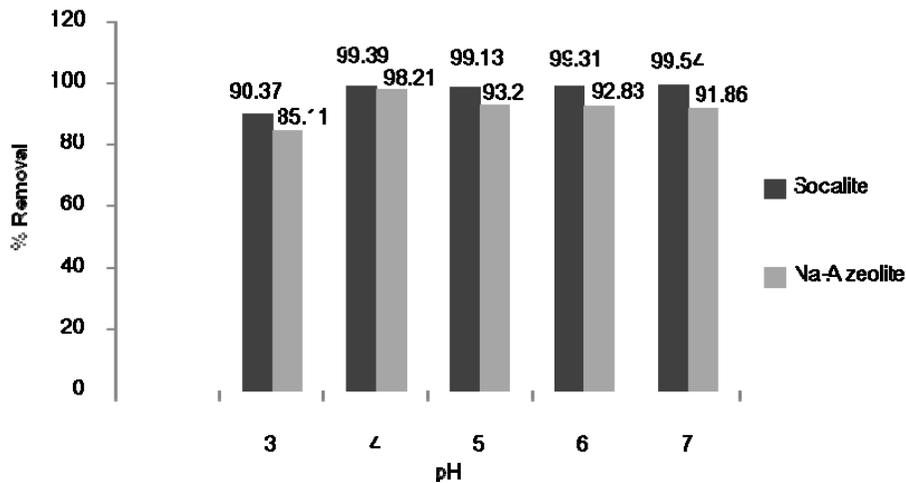


Figure 5 Variation of adsorption uptake of lead on sodalite and Na-A zeolite with the pH.

2. pH optimum on lead adsorption

In order to study the dependence of the removal efficiency on pH, experiments were conducted on pH range of 3-7 and the results are illustrated in Figure 5. The uptake adsorption of the lead by sodalite and Na-A zeolite increases with an increase in pH value. It can be explained by their point zero charge (pzc). Each adsorbent has its pzc. The pzc of an adsorbent is the pH of the adsorbent suspension at which its surface has zero net charge⁽¹⁰⁾. If the

measured pH of the colloid system is lower than the pzc, the net charge of the surface is positive. If the pH is higher than pzc, the net charge is negative. Hence, positively charged surface ($\text{pH} < \text{pH}_{\text{pzc}}$) tends to repulse with cations in the solution, and lower metal adsorption on the surfaces. Therefore, at low pH, adsorptions of cations tend to be low. The sodalite and Na-A zeolite used in this study have pzc values of 9.0 and 9.8, respectively. Therefore, at pH above their pzc, the net charge on the zeolite surface becomes positive, the positive charges increase with the increase of the solution pH. The pzc of sodalite is lower than that of Na-A zeolite, at the same pH solution above their pzc, the positive charges on the surface of sodalite would be expected to be greater than Na-A zeolite. Hence, cation adsorption onto sodalite is expected to be higher than Na-A zeolite at the same pH. The uptake of the lead by sodalite which is optimum at pH 4 was 99.39% and 98.21% for Na-A zeolite. Similar experiment using zeolite synthesized from fly ashes for the adsorption of lead gave the optimum condition at pH 5. In the subsequent investigations, experiments were performed at pH solution value of 4 to avoid any possible hydroxide precipitation⁽¹¹⁾.

3. Optimum contact time on adsorption of lead

Figure 6 shows that the adsorption of lead has gradual increase with 30 min contact time. Then the % removal became constant for Na-A zeolite. Sodalite shows the same trend since it attained equilibrium after 60 min. After 60 - 180 min, it showed a slight increase in % removal. From the calculated % removal, the efficiency of sodalite and Na-A zeolite were almost equal, They have nearly equal % removal ($\geq 99\%$) at optimum contact time, although sodalite has higher pore diameter than Na-A zeolite. This may be attributed to the fact that zeolites can act as ion exchanger. Accordingly, the pore diameter is not effective but the operating capacity depends on other parameters such as the concentration of adsorbent, contact time, particle size and pH⁽¹²⁾.

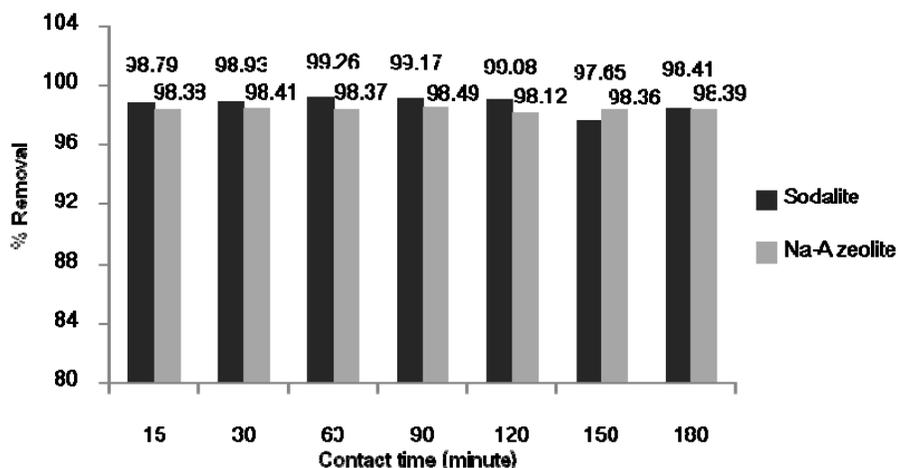


Figure 6 Variation of adsorption uptake of lead on sodalite and Na-A zeolite with the contact time.

4. The adsorption isotherm

Langmuir and Freundlich isotherm models were used to analyze the equilibrium data by means of sodalite and Na-A zeolite sorbents. The Langmuir adsorption isotherms of lead on sodalite and Na-A zeolites are shown in Figure 7 and the Freundlich adsorption isotherms of lead on sodalite and Na-A zeolites are shown in Figure 8. The model parameters and the statistical fits the sorption data to these equations given in Table 2. The results show that Langmuir model is better than Freundlich model because it describes sorption data with a correlation factor R^2 values > 0.9 . According to the saturated monolayer sorption capacity q_e (mg/g) and b (L/g), the prepared sodalite adsorbs better than Na-A zeolite. The adsorption capacity of sodalite and Na-A zeolite were at 223.88 and 45.80mg lead /g, respectively. On the other hand, the equilibrium data were analyzed using Freundlich isotherm model and the R^2 values were estimated for sodalite (0.855) and Na-A zeolite (0.891). The value of $1/n < 1$ generally indicates that the adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the zeolites by the lead ions; thus infinite surface coverage is expected to occur indicating multilayer adsorption on the surface⁽¹²⁾. It can be concluded from Table 2 that the Langmuir isotherm was more suitable than the Freundlich as in most cases the correlation coefficient was higher as seen in Table 2. Thus, the applicability of lead on the adsorbents surface in monolayer coverage. This can be explained by the fact that zeolites have a large surface area for metal adsorption. Therefore, only monolayer adsorption occurred on their surfaces, in spite of any surface modification.

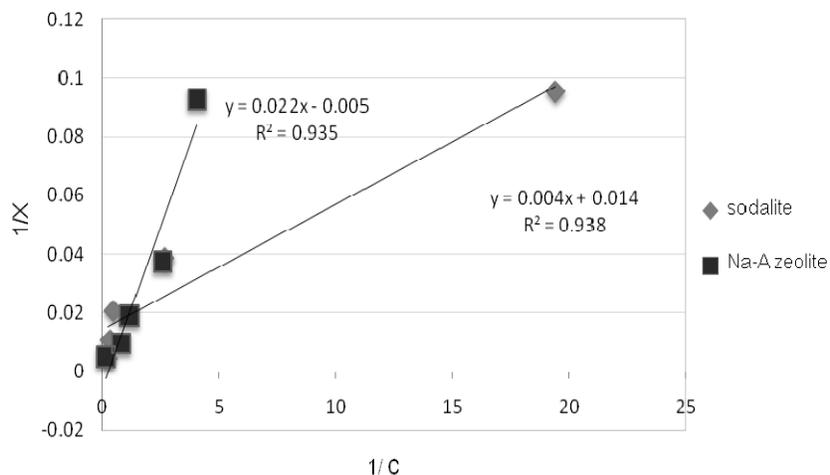


Figure 7 Langmuir isotherm for adsorption of lead on sodalite and Na-A zeolite

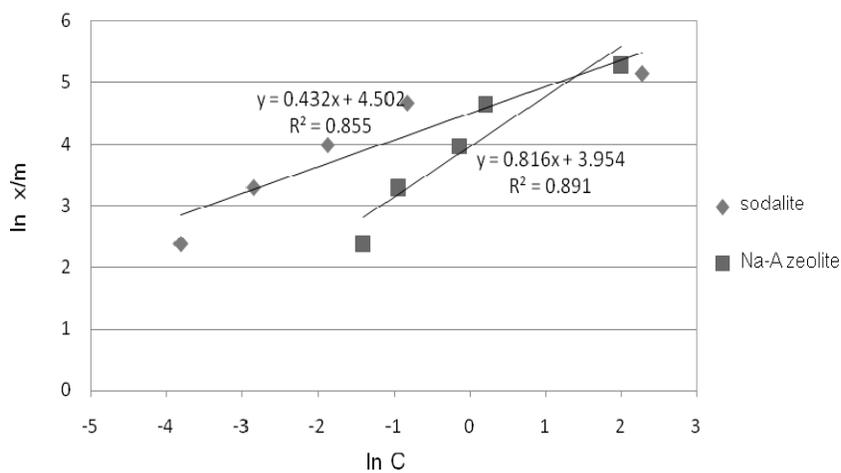


Figure 8 Freundlich isotherm for adsorption of lead on sodalite and Na-A zeolite

Table 2 Langmuir and Freundlich constant values of adsorbents.

Adsorbents	Langmuir constants			Freundlich constants		
	q_m (mg/g)	b (L/g)	R^2	K (L/g)	$1/n$	R^2
Sodalite	223.88	0.285	0.938	90.19	0.432	0.855
Na-A zeolite	45.80	4.400	0.935	52.14	0.816	0.891

Conclusion

Sodalite and Na-A zeolite prepared from spent silica-alumina were highly efficient for heavy metal removal due to the presence of nanometer pores. The optimum contact time for

sodalite was at 60 min and for Na-A zeolite was at 30 min. The removal was 98-99%. The adsorption capacity of sodalite and Na-A zeolite was at the optimum pH 4.0 and optimum concentration of 30 mg/L for both types of zeolite. The maximum adsorption capacity was at 223.88 and 45.80 mg lead/g, for sodalite and Na-A zeolites respectively. The adsorption isotherm of lead was related to Langmuir adsorption isotherm for both types of zeolite.

Acknowledgements

This research was supported financially by the 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund) no.14 (1-2554).

References

- (1) Apithamviriya, L. 1999. The utilization of spent silica-alumina for making pavement. Thesis for the degree of master of Environmental Engineering, Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University.
- (2) Patchotpong, S. 2002. Utilization of spent silica-alumina for making ceramic tiles production. Thesis for the degree of master, Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University.
- (3) Thitinan, H. 2003. Utilization of spent silica-alumina for making concrete block. Thesis for the degree of master, Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University.
- (4) Anuwattana, R. and Khummongkol, P. 2009. Conventional hydrothermal synthesis of Na-A zeolite from cupola slag and aluminum sludge. *J. Hazard. Mater.* 166: 227-232.
- (5) Nibou, D., Mekatel, H., Amokrane, S., Barkat, M., and TrarM, i. 2010. Adsorption of Zn²⁺ ions onto NaA and NaX zeolites: Kinetic, equilibrium and thermodynamic studies. *J. Hazard. Mater.* 173, 637-646.
- (6) Sampim, T. 2010. Synthesis of Na-A zeolite from spent silica-alumina. Thesis for the degree of master of, Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University.
- (7) Sampim, T, Chawakitchareon P. and Nuntasri D. 2010. Utilization of alumina-silica waste as for synthesis of zeolite NaA. The Proceedings of The 4th International Workshop and Conference on Earth Resources Technology, Phuket, Thailand, May 11-13, 2010
- (8) Hui, K.S., Chao, C.Y.H. and Kot, S.C. 2005. Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. *J. Hazard. Mater.* 127: 89-101.
- (9) Wei Qiu and Ying Zheng. (2009). Removal of lead, copper, nickel, cobalt, and zinc from water by a cancrinite-type zeolite synthesized from fly ash. *J. Chem. Eng.* 145: 483-488.

- (10) Chantawong, V. 2003. Synthesis of zeolites from Thai Clay for treatment of wastewater contaminated with heavy metals. The Degree of doctor of philosophy in Environmental Technology Department of Energy and Environment King Mongkut's University of Technology Thonburi.
- (11) Purna Chandra Raa, G., Satyavenia, S., Ramesha, A., Seshaiaha, K., Murthyb, K.S.N. and Choudary, N.V. 2006. Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite. *J. Environ. Manage.* 81: 265–272.
- (12) Tarek, S.J., Hanan, S.I., Abd El-Maksoud, I.H. and El-Wakeel, S.T. 2010. Application of zeolite prepared from Egyptian kaolin for removal of heavy metals: I. Optimum conditions. *Desalination.* 258: 34–40.