ADSORPTION OF LEAD IONS FROM SYNTHETIC WASTEWATER USING OYSTER SHELL
การดูดซับไอออนตะกั่วจากน้ำเสียสังเคราะห์ด้วยเปลือกหอยนางรม

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Abstract

The objective of this work was to study the adsorption ability of various Pb^{2+} ion concentrations by oyster shell *(Crassostre commercialis)* Oyster shells were prepared by 2 different methods. For the first method, oyster shell was washed with distilled water, dried in the oven at 105°C, then, crushed and sieved to particle size of 75-106 μm in diameter. This was called OS-A. For the second method, oyster shell was crushed and burnt in furnace at 850°C for 2 hr, then, sieved to particle size of 75-106 μm in diameter. This was called OS-B. The results of the adsorption experiment showed that adsorption reached equilibrium within 120 min with eighty four percent of Pb^{2+} was removed from 100 mg/L initial concentration. Moreover, Langmuir and Freundlich adsorption isotherms were used to fit the experimental data. The results showed that both Langmuir and Freundlich adsorption isotherms fitted the experimental data very well with high correlation coefficient (R^2). The high K_F value implied that the Pb^{2+} ions adsorption capacities of both OS-A and OS-B were high. The maximum Pb^{2+} adsorption capacity (qm) of OS-A and OS-B obtained from Langmuir adsorption isotherm were 196 and 233 mg-metal/g-adsorbent, respectively.

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาความสามารถในการดูดซับความเข้มข้นต่างๆของไอออนตะกั่ว (Pb^{2+}) ด้วยเปลือกหอยนางรมสายพันธุ์ *Crassostre commercialis* โดยเตรียมเปลือกหอยนางรม 2 วิธี คือ วิธีแรก ล้างเปลือกหอยนางรมด้วยน้ำกลั่น อบแห้งในตู้อบที่อุณหภูมิ 105°C บดและแยกขนาดให้ได้อนุภาคที่มีเส้นผ่าศูนย์กลาง 75-106 มคม. เรียกว่า OS-A วิธีที่สองบดเปลือกหอยนางรมเผาในเตาเผาที่ 850°C 2 ชม. แยกขนาดให้ได้อนุภาคที่มีเส้นผ่าศูนย์กลาง 75-106 มคม. เรียกว่า OS-B จากผลการทดลองพบว่าการดูดซับเข้า

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สู่สมดุลภายในเวลา 120 นท. โดยมีเปอร์เซ็นต์การกำจัด
ไอออนตะกั่วสูงถึง 84 % ที่ความเข้มข้นของสารละลาย
เริ่มต้น 100 มก./ล. นอกจากนี้ยังใช้สมการไอโซเทอร์ม
การดูดซับของแลงเมียร์ (Langmuir adsorption isotherm)
และไอโซเทอร์มการดูดซับของฟรุนด์ลิช (Freundlich
adsorption isotherm) มาใช้ทำนายผลการทดลอง พบว่า
สมการไอโซเทอร์มการดูดซับของแลงเมียร์และฟรุนด์ลิช
สามารถใช้ทำนายผลการทดลองได้ดี ค่า K_f ที่สูง แสดง
ให้เห็นถึงความสามารถสูงดูดซับไอออนตะกั่วของเปลือก
หอยนางรม OS-A และ OS-B ปริมาณไอออนตะกั่วที่ถูก
ดูดซับสูงสุด (q_m) ของ OS-A และ OS-B ที่ได้จากสมการ
ไอโซเทอร์มการดูดซับของแลงเมียร์ มีค่าเป็น 196 และ
233 มก.โลหะ/ก. วัสดุดูดซับ ตามลำดับ

คำสำคัญ: การดูดซับ, ตะกั่ว, เปลือกหอยนางรม,
สมการไอโซเทอร์มการดูดซับ

Introduction

Wastewater containing heavy metal ions
is often encountered in chemical industries such
as electroplating, tannery and textile dyeing, etc.
Heavy metals such as lead, cadmium and
mercury are highly toxic and not biodegradable.
When accumulating in living organisms, they
cause diseases[1]. Heavy metal ions treatment
techniques such as chemical precipitation,
solvent extraction, electrolytic processes,
membrane separation and ion-exchange, etc. are
not suitable for low contaminated heavy metal
ions in wastewater because of high operating
cost[2].

Adsorption is one of the most efficient
methods for the removal of heavy metal ions
from low-contaminated industrial effluents. The
research for low-cost adsorbents that have high
adsorption capacities has intensified and
materials locally available in large quantities
such as natural materials, agricultural waste or
industrial by products can be utilized as low-cost
adsorbents.

The objective of this work was to study
the adsorption ability of various Pb^{2+} ion
concentrations by oyster shell (*Crassostre
commercialis*).

Materials and Methods
Preparation of synthetic Pb^{2+} ion solution

The synthetic Pb^{2+} ion solution at
concentration of 1,000 mg-metal/L was prepared
by dissolving $Pb(NO_3)_2$ in deionized water and
adding 5 ml of concentrated nitric acid (concHNO$_3$)
for 1 L of solution. The stock solution was kept
in refrigerator at 4°C and was diluted to the
concentrations of 50, 60, 70, 80, 90, 100 ppm
to be used for the experiment.

Preparation of adsorbent

Crassostre commercialis was collected
from Chonburi province, Thailand. Oyster shells
were prepared by 2 different methods. For the
first method, oyster shell was washed with
distilled water, dried in the oven at 105°C,
then, crushed and sieved to particle size of
75-106 μm in diameter. This was called OS-A.
For the second method, oyster shell was crushed
and burnt in furnace at 850°C for 2 hr, then, sieved
to particle size of 75-106 μm in diameter. This
was called OS-B.

Adsorption experiment

The experiments were performed by mixing 0.1 g oyster shell in 500 ml erlenmeyer flasks containing 200 ml of Pb^{2+} ion solution. The Pb^{2+} ion solution was prepared by dilution of stock solution to the concentration 50, 60, 70, 80, 90, 100 ppm and adjustment with 0.1 mol NaOH solution for pH 6. The mixtures were mixed in a shaker at the rate of 200 rpm. The 2 ml mixtures was collected at each time (0, 5, 10, 15, 30, 60, 120 and 180 min) and filtered with filter paper (Whatman No. 1), immediately. The filtrates were added with 0.05 ml conc HNO_3. The amount of lead ions in filtrates were determined by Flame Atomic Absorption Spectrophotometer (AAS) following standard methods : 3111B[3].

Calculation for percentage of removal and adsorption capacity

The percentage of lead ion removal was calculated as follows :

$$\% \ Removal = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

where,

C_i = initial concentration (mg / L)

C_e = equilibrium concentration (mg / L)

The amount of Pb^{2+} ion uptake per unit mass of adsorbent (Adsorption capacity, q_e) was calculated as follows:

$$q_e = \frac{(C_i - C_e)v}{w} \tag{2}$$

where,

q_e = The amount of Pb^{2+} ions uptake per unit mass of adsorbent at equilibrium (mg/g)

C_i = initial concentration (mg/ L)

C_e = equilibrium concentration (mg /L)

v = volume of solution (L)

w = amount of adsorbent (g)

Adsorption isotherm

Langmuir and Freundlich adsorption isotherm were used to fit the experimental data. Langmuir adsorption isotherm was presented in Equation 3[4].

$$q_e = \frac{K_L \, q_m \, C_e}{1 + K_L C_e} \tag{3}$$

The linear form of this model is given below:

$$\frac{C_e}{q_e} = \frac{1}{K_L \, q_m} + \frac{1}{q_m} C_e \tag{4}$$

where,

q_e = The amount of Pb^{2+} ions uptake per unit mass of adsorbent at equilibrium (mg/g)

C_e = equilibrium concentration (mg /L)

q_m = The maximum amount of Pb^{2+} ions uptake per unit mass of adsorbent at equilibrium (mg/g)

K_L = the Langmuir constant related to energy of adsorption (L/mg)

Freundlich adsorption isotherm was presented in Equation 5[5].

$$q_e = K_F C_e^{(1/n)} \tag{5}$$

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The linear form of this model is given below:

$$\log qe = \log KF + \left(\frac{1}{n}\right) \log C_e \qquad (6)$$

where,

K_F = the Freundlich constant related to the adsorption capacity of the sorbent (mg/g (L/mg)$^{1/n}$)

1/n = the Freundlich constant related to the energy heterogeneity of the system and the size of the adsorbed molecule.

Result and Discussion
Characterization of the adsorbent

Characterization of the adsorbent was investigated by X-ray Fluorescence Spectrometer (XRF), BET (Brunauer, Emmetl, and Teller) surface area analysis and Scanning Electron Microscopy (SEM) investigations.

The OS-A has a high percentage of calcium carbonate ($CaCO_3$) about 80%. The latter, which is OS-A, has silica oxide (SiO_2) and alumina oxide (Al^2O_3). The OS-B has a high percentage of calcium oxide (CaO) about 69%. The latter, which is OS-B, has 18% of silica oxide (SiO_2) and 2.4% of magnesium oxide (MgO) (Table 1). The OS-B has a high percentage of CaO because $CaCO_3$ was converted to CaO at 850°C in pretreatment process. The calcination reactions were shown in Equation 7.

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g) \qquad (7)$$
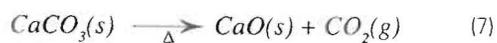
The BET surface area of the OS-A (9.47 m^2/g) was higher than that of the OS-B (1.73 m^2/g). Moreover, the pore size of OS-A and OS-B were 10.08 and 9.89 μB, respectively (Figure 1).

The chemical composition and surface area affect on the adsorption capacity of adsorbent. High percentage of CaO and high surface area of adsorbent provided high adsorption capacities, accordingly.

Table 1. Chemical composition of OS-B

Chemical composition	Wt. %
SiO_2	17.67
Al_2O_3	1.10
CaO	68.99
MgO	2.43
Fe_2O_3	0.29
TiO_2	0.01
MnO_2	0.01
K_2O	0.04
Na_2O	0.53

Table 2. BET surface area of adsorbent

	OS-A	OS-B
Surface area (m^2/g)	9.47	1.73
porosity (%)	70.83	75.96
Pore size (μm)	10.08	9.89
Loss on incineration	8.93	

(OS-A)   (OS-B)
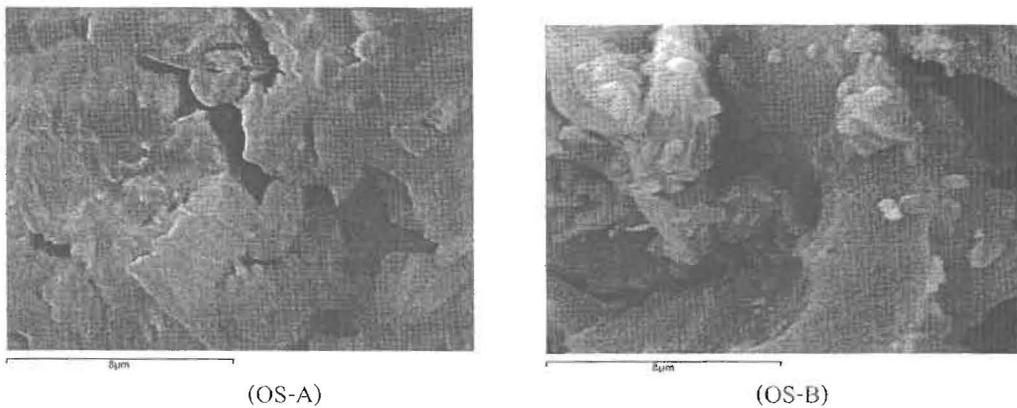
Figure 1. SEM micrograph of the particles of adsorbent (1,000 x)

Effect of reaction time

The variation of adsorbed amount of Pb^{2+} ion on OS-B according to time was examined by using 0.5 g/L adsorbent dosage and 100 ppm Pb^{2+} ions synthetic wastewater. At the initial stage of adsorption, The removal rate of Pb^{2+} was high during the first 5 min. After 5 min, the removal rates of Pb^{2+} slowly declined and adsorption reached equilibrium within 120 min with 84 % Pb^{2+} removed from 100 mg/L initial concentration (Figure 2). Initially, the active adsorption sites is open and the metal ions interacts easily with the sites and hence a higher rate of adsorption is observed. Further, the driving force for adsorption (the concentration difference between the bulk solution and the solid-liquid interface) is higher initially and this results a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent[6].
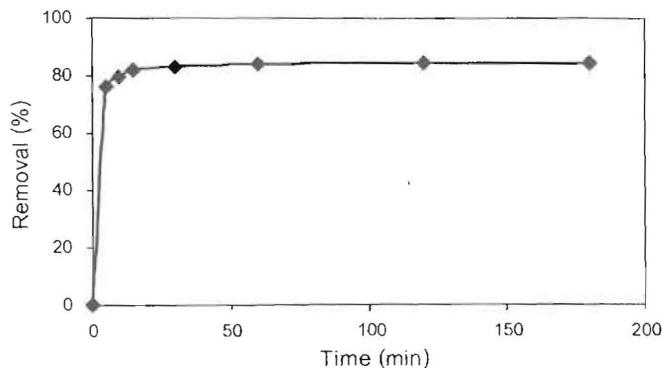
Figure 2. The percentage on the removal of Pb^{2+} ions OS-B according to time

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Effect of initial concentration

In Figure 3, when the initial Pb^{2+} ions concentration increased from 50 to 100 mg/L, Pb^{2+} adsorption removal of OS-A and OS-B decreased from 78% to 65.7% and 92% to 84%, respectively. The higher percentage of removal at low concentration is attributed by the availability of greater surface area with active centers on the adsorbent for lesser amounts of adsorb ate ions[7].
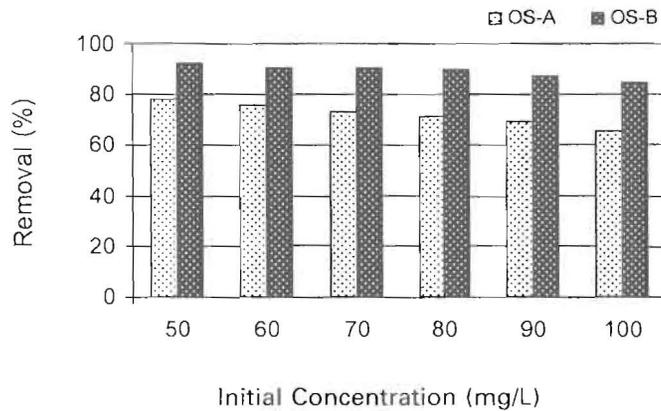
Figure 3. Effect of initial concentration to removal efficiency (adsorbent dosage 0.5 g/L)

In Figure 4, when the initial Pb^{2+} ion concentration increased from 50 to 100 mg/L, The adsorption capacity of OS-A and OS-B increased from 71 to 124.6 mg/g and 84 to 160 mg/g, respectively. The higher initial concentration provided increasing driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases resulting in higher probability of collision between Pb^{2+} ions and sorbents. This results in higher metal uptake[8].
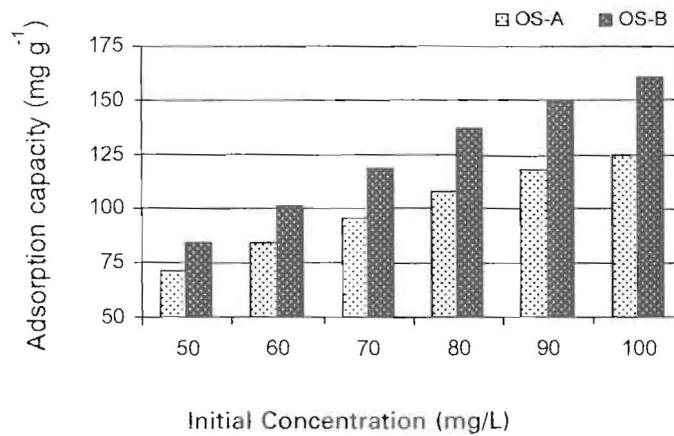
Figure 4. Effect of initial concentration on the adsorption capacity (adsorbent dosage 0.5 g /L)

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Adsorption isotherm

The adsorption of Pb^{2+} ions was carried out at different initial Pb^{2+} ion concentrations ranging from 50 to 100 mg/L, at equilibrium time (120 min). The linearized Freundlich and Langmuir adsorption isotherm of each sorbent were shown in Figures 5 and 6. Langmuir and Freundlich adsorption isotherm parameters were shown in Table 3.
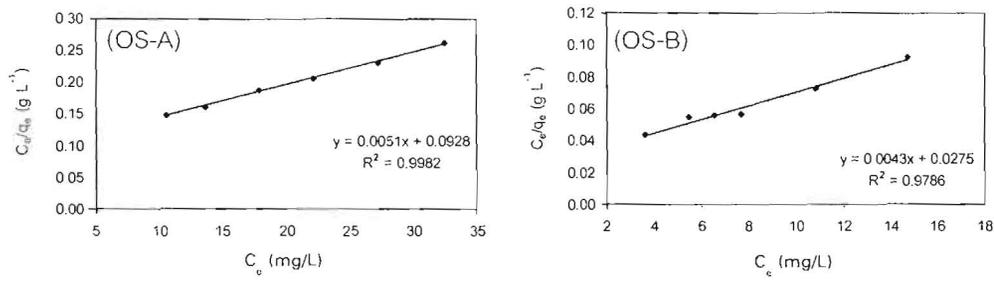
Figure 5. Langmuir adsorption isotherm of OS-A and OS-B
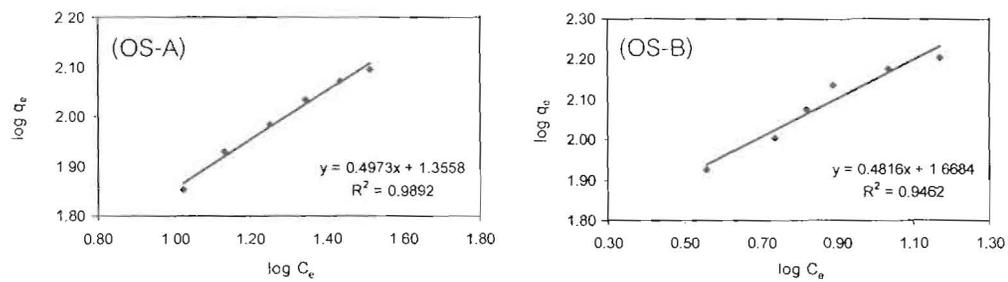
Figure 6. Freundlich adsorption isotherm of OS-A and OS-B

The both Langmuir and Freundlich adsorption isotherm fitted the experimental data very well with high correlation coefficient (R^2). Freundlich parameters (K_F and n) indicates whether the nature of adsorption is either favorable or unfavorable[9]. The intercept is an indicator of adsorption capacity and the slope is an indicator of adsorption intensity. A high value of the intercept, K_F, is indicative of a high adsorption capacity. A relatively slight slope 1/n indicates that adsorption intensity is good (or favorable) over the entire range of concentrations studied, while a steep slope (n > 1) means that adsorption intensity is good (or favorable) at high concentrations but much less at lower concentrations[10]. The K_F value of OS-A and OS-B were 22.68 and 46.60, respectively.

The K_L parameter is the adsorption equilibrium constant, which not only gives information on adsorption rate compared to desorption rate of the system, but also was used to the heat of adsorption. For exothermic reaction, K_L should decrease with increasing temperature of the system[11]. The maximum Pb^{2+} adsorption capacity (q_m) of OS-A and OS-B obtained from Langmuir adsorption isotherm were 196 and 233 mg-metal/g-adsorbent, respectively (Table 3). The maximum Pb^{2+} adsorption capacity (q_m) of various adsorbents (30-796 mg/g) were shown in Figure 7[12-15].

Table 3. Langmuir and Freundlich adsorption isotherm parameters

Type of adsorbent	Langmuir Adsorption Isotherm			Freundlich Adsorption Isotherm		
	q_m (mg/g)	K_L (L/g)	R^2	K_F	n	R^2
OS-A	196	18.20	0.9982	22.68	2.01	0.9892
OS-B	233	6.40	0.9786	46.60	2.08	0.9462
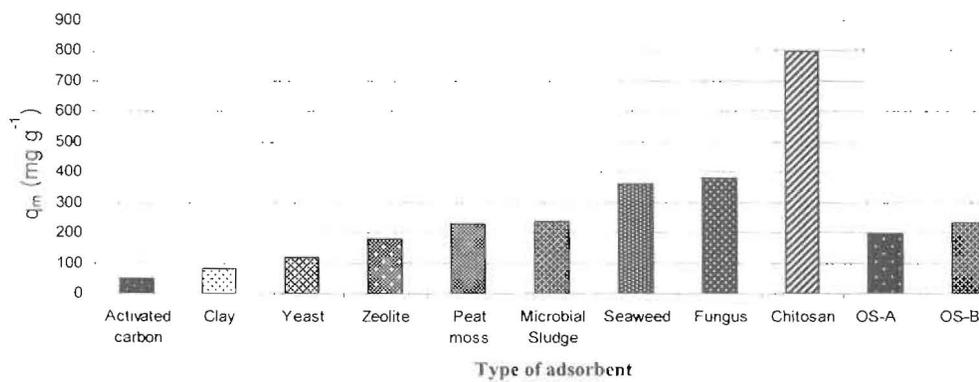
Figure 7. The maximum adsorption capacity (qm) of various adsorbent

The maximum adsorption capacity of OS-B was higher than maximum adsorption capacity of OS-A because main composition of OS-B was calcium oxide (CaO) that removed Pb^{2+} ions well although surface area of OS-A was more than surface area of OS-B about 5.5 time. In this case, the result showed that chemical composition was important effect to adsorption.

Conclusion

Oyster shells were prepared with 2 different methods for using as low-cost adsorbents for removal of Pb^{2+} ions from aqueous solutions. The removal rate of Pb^{2+} was high during the first 5 min. At 5 min, Pb^{2+} ions were removed from 100 mg/L initial concentration by OS-B about 76% and adsorption reached equilibrium within 120 min with 84 % Pb^{2+} removal. Langmuir and Freundlich adsorption isotherm fitted the experimental data very well with high correlation coefficient (R^2). The K_F value of OS-A and OS-B were 22.68 and 46.60, respectively. The maximum adsorption capacity (q_m) of OS-A and OS-B obtained from Langmuir adsorption isotherm were 196 and 233 mg-metal/g-adsorbent, respectively. The maximum adsorption capacity of OS-A and OS-B were moderately high when compared with the maximum adsorption capacity of various adsorbents that were between 30 to 796 mg-metal/g-adsorbent[12-16].

References

(1) Wang, Y., Lin, S. and Juang, R. 2003. Removal of Heavy Metal Ions from Aqueous Solutions Using Various Low-cost Adsorbents. J. Hazard. Mater. B102 : 291-302.

(2) Gulnaz, O., Saygideger, S. and Kusvuran, E. 2005. Study of Cu(II) Biosorption by Dried Activated Sludge: Effect of Physico-chemical Environment and Kinetic Study. J. Hazard. Mater. B120 : 193-200.

(3) Clesceri, L. S., Greenberg, A. E. and Eaton. A. D. 2000. Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC

(4) Langmuir, I. 1918. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. J. Am. Chem. Soc. 40 : 1361-1403.

(5) Weber, W. J. Jr. 1972. Physicochemical Processes for Water Quality Control, Wiley, New York.

(6) Amarasinghe, B.M.W.P.K., Williams, R.A. 2007. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, Chem. Eng J. 132 299-309.

(7) Kuh, S. E. and Kim, D. S. 2000. Removal Characteristics of Zinc Ions by Waste Egg Shell. Environ. Technol. 21 : 883-890.

(8) N. Tewari, P. Vasudevan, B.K. Guha,. 2005. Study on biosorption of Cr(VI) by Mucor hiemalis, Biochem. Eng. J. 23(2) : 185-192.

(9) Frimmel, F.H. and Huber, L. 1996. Influence of humic substances on the aquatic adsorption of heavy metals on defined minerals phases. Environ. Int. 22(5) : 507-517.

(10) McKay, G. 1980. The removal of colour from effluent using various adsorbents. IV. Silica: equilibria and column studies, Water Res. 14(1) : 21-27.

(11) Mouflih, M., Aklil, A. and Sebti, S. 2005. Removal of lead from aqueous solutions by activated phosphate. J. Hazard. Mater. B119 : 183-188.

(12) Babel, S. and Kurniawan, T. A. 2003. Low-cost Adsorbents for Heavy Metals Uptake from Contaminated Water : a review. J. Hazard. Mater. B97 : 219-243.

(13) Volesky, B. and Holan, Z.R. 1995. Biosorption of Heavy Metals. Biotechnol. Prog. 11(2) : 235-250.

(14) Bailey, S. E., Olin, T. J., Bricka, R. M. and Adrian, D. D. 1999. A Review of Potentially Low-cost Adsorbents for Heavy Metals. Water Res. 33(11) : 2469-2479.

(15) Chayapat Tabtong. 2006. Removal of Lead Ions from Wastewater Using Microbial Sludge. J. Environ. Res. 28(1) : 1-12.