ORIGINAL ARTICLE

Removal of lead from battery manufacturing wastewater by egg shell

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Abstract

**Arunlertaree, C., Kaewsomboon, W., Kumsopa, A., Pokethitiyook, P. and Panyawathanakit, P.
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This research was carried out to investigate the removal of lead from battery manufacturing wastewater by egg shells. The effect of operating parameters i.e., initial pH, contact time, types of egg shell and dose of egg shell were investigated. The characteristics and chemical compositions of egg shells were also investigated and experimental samples were analyzed using AAS, then the data was statistically processed using least significant difference at a 95% confidence level ($p<0.05$).

The results indicated that the optimum pH for lead removal using 4 types of egg shell was at pH 6, but at this pH final concentration of lead was too low for study of adsorption isotherm. Therefore, unadjusted pH wastewater was used with an initial lead concentration of about 2.365 mg/L, initial pH of 1.35-1.45. Unadjusted pH wastewater decreased the use of expensive chemical reagent for adjusting pH and reduced chemical residues in the environment due to basic properties of egg shell which immediately increased the pH of solution. The optimum dose of egg shell was 1.0 g/100 ml of wastewater with a contact time of 90

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minutes. The best adsorbent was natural duck egg shell, which had a significant difference from the other types of egg shell. The final concentration of lead was 0.059 mg/L which was lower than the wastewater quality standard.

Equilibrium modeling of the adsorption isotherm showed that removal of lead by 4 types of egg shells were able to be described by the Freundlich model. From this study, precipitation might take part in the adsorption process, especially at the high doses of egg shell which increased the high final pH of solution. Finally, the result of the adsorption isotherm demonstrated that the descending lead removal efficiency was natural duck egg shell, natural hen egg shell, boiled duck egg shell and boiled hen egg shell, respectively.

Key words : lead, egg shell, battery manufacturing, wastewater

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บทคัดย่อ

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การบำบัดตะกั่วในน้ำเสียจากอุตสาหกรรมผลิตแบตเตอรี่โดยใช้เปลือกไข่

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งานวิจัยนี้เป็นการศึกษาการบำบัดตะกั่วในน้ำเสียจากอุตสาหกรรมการผลิตแบตเตอรี่โดยใช้เปลือกไข่ ปัจจัยที่ใช้ในการศึกษา คือ ค่าความเป็นกรด-เบส (pH) ชนิดของเปลือกไข่ ระยะเวลาสัมผัส และปริมาณเปลือกไข่ นอกจากนั้นทำการวิเคราะห์คุณลักษณะ และองค์ประกอบทางเคมีของเปลือกไข่ ส่วนปริมาณตะกั่วในตัวอย่างการทดลองวิเคราะห์โดยใช้ AAS และข้อมูลที่ได้จากการทดลอง ทำการวิเคราะห์ทางสถิติโดยใช้ least significant difference ที่ระดับความเชื่อมั่น 95% ($p<0.05$)

จากผลการศึกษาแสดงให้เห็นว่า ค่า pH ที่เหมาะสมในการบำบัดตะกั่วโดยใช้เปลือกไข่ทั้ง 4 ชนิด ได้แก่ ที่ pH 6 แต่ ณ สภาวะนี้พบว่า ค่าความเข้มข้นของตะกั่วที่เหลือต่ำเกินไป ไม่เหมาะสมที่จะนำมาทำการศึกษา ในงานวิจัยครั้งนี้ จึงทำการทดลองโดยใช้น้ำเสียที่ไม่ผ่านการปรับค่า pH ซึ่งมีค่าความเข้มข้นของตะกั่วเริ่มต้นประมาณ 2.365 มก./ลิตร ค่า pH เริ่มต้น 1.35-1.45 พบว่ามีข้อดีคือ ลดการใช้สารเคมีที่มีราคาแพงในการปรับ pH และลดสารเคมีตกค้างในสิ่งแวดล้อม เนื่องจากสมบัติความเป็นเบสของเปลือกไข่ที่ช่วยเพิ่ม pH ของสารละลายทันทีภายหลังการเติม ส่วนปริมาณเปลือกไข่ที่เหมาะสมเป็น 1.0 กรัม/100 มล.ของน้ำเสีย และระยะเวลาในการสัมผัส 90 นาที เปลือกไข่ที่มีประสิทธิภาพในการบำบัดสูงสุดคือ เปลือกไข่เป็ดดิบ และมีความต่างอย่างมีนัยสำคัญทางสถิติ ($p<0.05$) จากเปลือกไข่ชนิดอื่น ๆ ค่าความเข้มข้นของตะกั่วภายหลังการบำบัดในภาวะที่เหมาะสมคือ 0.059 มก./ลิตร อยู่ในเกณฑ์มาตรฐานน้ำทิ้งของกรมโรงงานอุตสาหกรรม

ในส่วนของแบบจำลองไอโซเทอร์ม การบำบัดตะกั่วโดยใช้เปลือกไข่มีความสัมพันธ์กับแบบจำลองของ Freundlich จากการศึกษาครั้งนี้พบว่า กระบวนการตกตะกอนได้เข้ามามีส่วนร่วมในกระบวนการดูดซับด้วย โดยเฉพาะอย่างยิ่งเมื่อเติมเปลือกไข่ในปริมาณสูง จะทำให้ค่า pH ของสารละลายเพิ่มขึ้นอย่างมาก และจากการศึกษาการดูดซับไอโซเทอร์ม พบว่าประสิทธิภาพการบำบัดตะกั่วจะลดลงตามลำดับดังต่อไปนี้ กล่าวคือ เปลือกไข่เป็ดดิบ เปลือกไข่ไก่ดิบ เปลือกไข่เป็ดต้ม และเปลือกไข่ไก่ต้ม

An important source of water pollutants is industrial discharge water. Most industrial wastewaters are discharged directly into natural water systems without proper management process. In Thailand, lead is one of major pollutants in wastewater. It is used as a major raw material in battery

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manufacturing and wastewater from this industry can contain high concentration of lead about 0.50-25.00 mg/L (Phomun, 2002).

Adsorption is a physico-chemical technique which involves mass transfer between liquid and solid phase (Eckenfelder, 1980). This process can reduce chemical residues. However, the frequently used sorbent solid is a synthetic resin which is quite expensive and a non-bio-degradable substance, so it is more suitable to use agricultural waste as the adsorbent. For example, egg shell that has a good adsorptive properties i.e., pore structure, $CaCO_3$ and protein acid mucopolysaccharide that can be developed into the adsorbent. Important functional groups of protein acid mucopolysaccharide are carboxyl, amine and sulfate that can bind heavy metal ion to form ionic bond (Surasen, 2002). Moreover, egg shell is neutralizing agent, any aqueous solution equilibrated with egg shell becomes more basic (Brown and Lemay, 1985) so heavy metal can precipitate and deposit on egg shell particles.

Other researchers removed lead from synthetic wastewater but this study removed lead from battery manufacturing wastewater and therefore has the advantage of direct application to real treatment. The main objectives of this study were; 1) to study the optimum condition for the removal of lead using natural and boiled hen and duck egg shell 2) to study lead adsorption isotherm by the egg shells 3) to compare the removal efficiency using four types of egg shell. The results will be the guideline for the removing heavy metal, reducing chemical residues, decreasing operation cost, and recycling waste or by-product.

Materials and Methods

Wastewater preparation and wastewater characteristic analysis

Wastewater from the Battery Organization (Bang Na, Bangkok) was kept in polyethylene bottle and stored at 4°C in acid condition (pH < 2) (Pollution Control Department, 1997) for precipitation at least 1 day. The wastewater characteristic included pH value, total dissolved solids (TDS) and total solids (TS) were analyzed according to the standard methods. Lead was digested using nitric acid - hydrochloric acid digestion methods and its concentration determined by Atomic Absorption Spectrophotometer (AAS; GBC 932 Plus) using the standard method (APHA *et al.*, 1995).

Egg shell preparation

Natural and boiled hen and duck egg shells were washed with tap water several times then air-dried and incubated in hot air oven at 40°C for 30 minutes (because protein component in egg shell can denature at high temperature; > 40°C). Consequently, egg shells were ground to a powder in a grinder, and sieved to obtain between 60-100 mesh (0.25-0.104 mm) size particles.

The removal of lead from battery manufacturing wastewater using egg shells

1. The optimum pH value analysis

1.1 The pH values of wastewater were controlled at 5, 6 and 7 by using 1 M. NaOH.

1.2 100 ml of sample was added into Erlenmeyer flask and lead concentration was analyzed. Then 0.05 g of egg shell was added in each sample and the rotary shaker was adjusted at 200 rpm, 90 minutes.

1.3 Treated wastewater was filtered through filter paper No.4, then the lead concentration was determined.

2. The optimum contact time analysis

2.1 0.05 g of egg shell was added into optimum pH wastewater (from step 1) and the rotary shaker was adjusted at 200 rpm with 30, 60, 90, 120 and 150 minutes.

2.2 Treated wastewater was filtered through filter paper No.4, then the lead concentration was determined.

3. The optimum dose of egg shell analysis

3.1 100 ml of optimum pH wastewater was added into Erlenmeyer flask, then lead concentration was analyzed.

3.2 0.05, 0.2, 0.5, 1.0 and 1.5 g of egg shell was added into each sample and the rotary shaker was adjusted at 200 rpm with optimum contact time (from step 2).

3.3 Treated wastewater was filtered through filter paper No.4, then the lead concentration was determined.

Study of adsorption isotherm

Data from step 3 were used to study adsorption isotherm for determining the best adsorbent. Langmuir's and Freundlich's adsorption isotherms are the most commonly used for the description of the adsorption data (Samuel and Osman, 1987).

Statistical analysis

The removal efficiency (%)

$$= \frac{(A-B)}{A} \times 100 \qquad \text{(Kosayothin, 2002)}$$

Then, A = Initial concentration (mg/L), B = Final concentration (mg/L)

The results were investigated by using the least significant difference at a 95% confidence level by SPSS.

Results and Discussion

Characteristics of wastewater

The wastewater sample was collected from battery manufacturing Bang Na, Bangkok. The characteristics of wastewater were presented in Table 1. The pH of wastewater was strongly acid and initial lead concentration was higher than wastewater quality standard control of Thailand Industrial Work Department in 1992.

Table 1. Characteristics of wastewater from battery manufacturing

Parameter	Value of each parameter*	Industrial effluent standard**
Lead (mg/L)	2.365	< 0.2
Cadmium (mg/L)	N.D.	< 0.03
Copper (mg/L)	N.D.	< 1.0
SS (mg/L)	18.13	< 30
TS (mg/L)	2,245.60	-
TDS (mg/L)	2,227.47	< 2000 or < 5000
pH	1.35-1.45	5.0-9.0

*** The Battery Manufacturing from Bangna, Bangkok**
**** Wastewater quality standard control of Thailand Industrial Work Department, 1992**

Chemical and physical properties of egg shells

The chemical composition of all egg shells were examined by x-ray fluorescence spectrometer (XRF; S4-Explorer) and the results were shown in Table 2. It was demonstrated that all egg shells had similar chemical contents which mainly composed of $CaCO_3$ and a few of other elements; i.e. S, Mg, P, Al, K and Sr.

The surface structure of 4 types of egg shells were observed by scanning electron microscope (SEM) as shown in Figure 1. It showed that egg shell surfaces were irregular shape. Pore sizes of

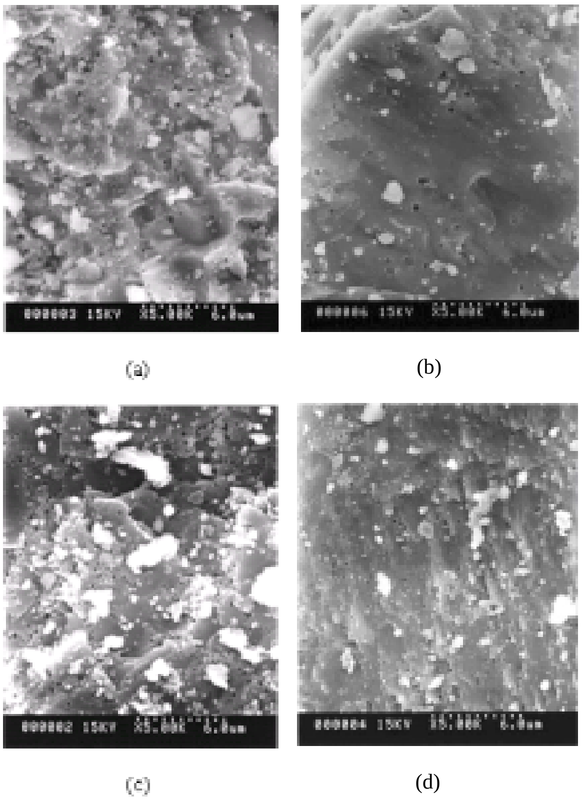

Figure 1. Morphology of 4 types of egg shell with magnification of x 5,000
(a) Natural hen egg shell
(b) Boiled hen egg shell
(c) Natural duck egg shell
(d) Boiled duck egg shell

Table 2. Chemical compositions of egg shells

Element	Weight (%)			
	Natural hen egg shell	**Boiled hen egg shell**	**Natural duck egg shell**	**Boiled duck egg shell**
$CaCO_3$	96.48	96.48	96.48	95.99
S	2.31	3.59	1.24	1.92
Mg	0.404	0.440	0.996	0.927
P	0.501	0.469	0.508	0.481
Al	-	-	-	0.309
K	-	-	0.0839	0.00957
Sr	0.0737	0.0734	0.118	0.093

natural and boiled hen egg shells were between 0.3-0.6 µm while those of natural and boiled duck egg shells were between 0.2-0.4 µm.

Numerous studies have reported that the pore structure particulary affects by adsorption capacity (Surasen, 2002; Polamesanaporn, 2001); pictures from scanning electron microscope (SEM; HITACHI S-2500) showed that natural and boiled duck egg shells had more pores per square-centimeter than natural and boiled hen egg shells. This result was inconsistent with Kasetsuwan (1979). Moreover, amount and distribution of protein fiber in natural hen and duck egg shells were higher than in boiled hen and duck egg shells, as shown in Figure 1.

Optimum conditions for lead removal by egg shells

1. Effect of pH (0.05 g egg shell/100 ml of wastewater, 90 mins of contact time)

The results were shown in Table 3 and Figure 3. Lead removal efficiency changed significantly at different pH. Optimum removal efficiency of all types of egg shells was at pH 6 but unadjusted pH wastewater was conducted in the next step of the experiment because the final concentration of lead at pH 6 was too low for study of adsorption isotherm. Unadjusted pH wastewater decreased the use of expensive chemical reagent for adjusting pH and reduced chemical residues in the environment due to basic properties of egg shell which immediately increased the pH of solution. Chemical precipitation was the main process in adjusted pH wastewater (pH 5, 6 and 7), when pH level reached the optimum point, lead will precipitate as confirmed in Figure 2. Solubility of lead continuously decreased from pH 4 until it was in stable form at pH 7.

2. Effect of contact time (Unadjusted pH wastewater, 0.05 g egg shell /100 ml of wastewater)

The results were shown in Table 4 and Figure 4. Removal efficiency for all types of egg shell at the contact time of 90, 120 and 150 mins was not significantly different, whereas the results obtained at contact time 30, 60 and 90 mins were

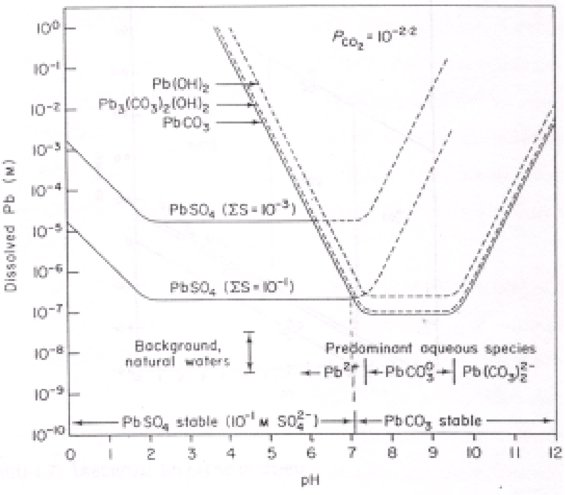

Figure 2. Mineral solubility in Pb-O-H-S-C system at 25°C, 1 atm (Rose *et al.*, 1979)

Table 3. Effect of pH on lead removal

pH	Initial conc. (mg/L)	Natural Hen egg shell		Boiled hen egg shell		Natural duck egg shell		Boiled duck egg shell	
		Final conc. (mg/L)	Removal Efficiency (%)	Final conc. (mg/L)	Removal Efficiency (%)	Final conc. (mg/L)	Removal Efficiency (%)	Final conc. (mg/L)	Removal Efficiency (%)
5	1.063	0.587±0.015^{a}	44.78	0.650±0.014^{a}	38.82	0.546±0.013^{a}	48.67	0.630±0.014^{a}	40.70
6	0.349	0.077±0.005^{b}	78.03	0.094±0.006^{b}	72.97	0.073±0.004^{b}	79.18	0.086±0.005^{b}	75.36
7	N.D.	N.D.^{c}	100	N.D.^{c}	100	N.D.^{c}	100	N.D.^{c}	100

Remark: Differences of superscripts in each column indicate statistically significant differences with the confidence of 95% by LSD

Table 4. Effect of contact time on lead removal

Contact time (mins)	Initial conc. (mg/L)	Natural Hen egg shell		Boiled hen egg shell		Natural duck egg shell		Boiled duck egg shell	
		Final conc. (mg/L)	Removal Efficiency (%)	Final conc. (mg/L)	Removal Efficiency (%)	Final conc. (mg/L)	Removal Efficiency (%)	Final conc. (mg/L)	Removal Efficiency (%)
30	2.365	2.017±0.005^{a}	14.70	2.179±0.007^{a}	7.86	1.456±0.009^{a}	17.28	2.117±0.008^{a}	10.48
60	2.365	1.831±0.015^{b}	22.58	2.003±0.014^{b}	15.29	1.661±0.014^{b}	29.76	1.936±0.011^{b}	18.15
90	2.365	1.637±0.006^{c}	30.79	1.819±0.008^{c}	23.10	1.544±0.006^{c}	34.73	1.747±0.004^{c}	26.13
120	2.365	1.634±0.012^{c}	30.92	1.821±0.016^{c}	22.99	1.536±0.007^{c}	35.07	1.734±0.015^{c}	26.70
150	2.365	1.631±0.011^{c}	31.03	1.821±0.013^{c}	22.99	1.535±0.013^{c}	35.09	1.733±0.013^{c}	26.74

Remark: Differences of superscripts in each column indicate statistically significant differences with the confidence of 95% by LSD

Table 5. Effect of dose of egg shell on lead removal

Dose of egg shell (g)	Initial conc. (mg/L)	Natural Hen egg shell		Boiled hen egg shell		Natural duck egg shell		Boiled duck egg shell	
		Final conc. (mg/L)	Removal Efficiency (%)	Final conc. (mg/L)	Removal Efficiency (%)	Final conc. (mg/L)	Removal Efficiency (%)	Final conc. (mg/L)	Removal Efficiency (%)
0.05	2.365	1.637±0.006^{a}	30.80	1.819±0.009^{a}	23.04	1.544±0.004^{a}	34.74	1.747±0.005^{a}	26.15
0.20	2.365	0.698±0.009^{b}	70.50	0.950±0.008^{b}	59.83	0.513±0.006^{b}	78.31	0.884±0.005^{b}	62.62
0.50	2.365	0.359±0.011^{c}	84.83	0.548±0.018^{c}	76.83	0.271±0.006^{c}	88.53	0.441±0.012^{c}	81.37
1.00	2.365	0.082±0.004^{d}	96.53	0.122±0.005^{d}	94.84	0.059±0.005^{d}	97.51	0.099±0.008^{d}	95.81
1.50	2.365	0.088±0.009^{d}	96.42	0.120±0.006^{d}	94.94	0.051±0.003^{d}	97.56	0.097±0.013^{d}	95.76

Remark: Differences of superscripts in each column indicate statistically significant differences with the confidence of 95% by LSD

significantly different. Therefore, the optimum contact time for all types of egg shell should be at 90 mins. This result was consistent with Pawebang and Sukcharoen (1999), who reported that the equilibrium time to remove lead in synthetic wastewater by egg shell could be reached at about 80 min. Similary the study of Lee *et al.* (1998) on the removal of lead by crab shell particle showed that

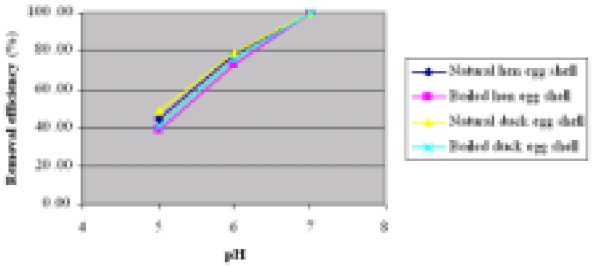

Figure 3. Effect of pH on lead removal by 4 types of egg shell

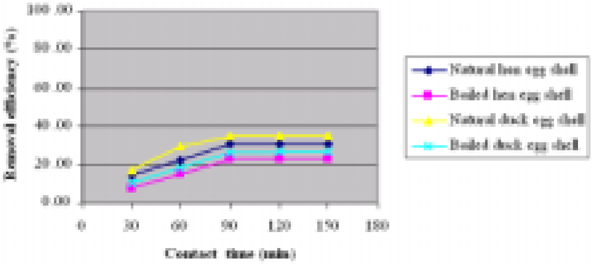

Figure 4. Effect of contact time on lead removal by 4 types of egg shell

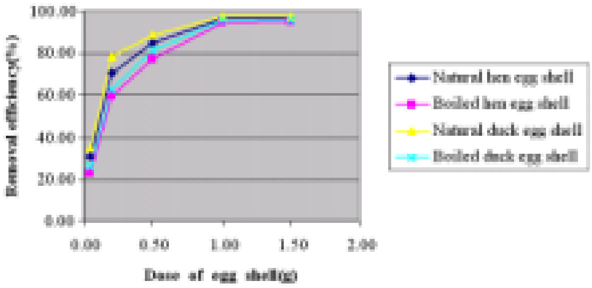

Figure 5. Effect of dose of egg shell on lead removal by 4 types of egg shell

the necessary contact time to reach equilibrium was about 90-120 mins.

3. Effect of dose of egg shell (Unadjusted pH wastewater, 90 mins of contact time)

The results were shown in Table 5 and Figure 5. Removal efficiency for the doses of all types of egg shell of 0.05, 0.2, 0.5, and 1.0 g were significantly different whereas the results obtained from using 1.0 and 1.5 g. were not significantly different. Therefore, an appropriate dose for all types of egg shell should be 1.0 g. Dose of egg shell affected the removal of lead, because the removal efficiency of solutes increased with increasing dose of adsorbent (Eamsiri *et al.*, 2005). The removal efficiency increased according to the increasing dose of egg shell at an appropriate level.

According to the chemical composition analysis in Table 2, egg shell mainly composed of $CaCO_3$. Major alkaline contributors in egg shell was $CaCO_3$ so it was expected that any aqueous solution equilibrated with egg shell became more basic that confirmed by following mechanism (Brown and Lemay, 1985).

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^{-} + OH^{-}$$

Hydrolysis reaction of $CaCO_3$ gave basic solution because Ca^{2+} and OH^- increased the pH of the solution as well as in this experiment, adding various doses of egg shell into wastewater increased the pH of solution as shown in Table 6.

This basic property of egg shells, which increased the pH of solution, was of advantage to decrease the use of expensive chemical reagent for adjusting pH of wastewater (decreasing operation cost) and reduced chemical residues in the environment. At optimum condition (1.0 g of egg shell/ 100 ml of wastewater), the final pH and final concentration of lead were lower than wastewater quality standard control of Thailand Industrial Work Department, 1992

Adsorption isotherm

Experiments were conducted to determine the adsorption isotherm of lead using egg shells at 0.05, 0.2, 0.5, 1.0 and 1.5 g in 100 ml of unadjusted pH wastewater (pH 1.35-1.45). Initial lead concentration was approximately 2.365 mg/ L. The experimental datas were calculated to determine the adsorption isotherm by using the Langmuir and Freundlich models.

The Langmuir equation was expressed as :

Table 6. Final pH at various doses of egg shell

Dose of Egg shell (g)	Final pH at various doses of egg shell			
	Natural hen egg shell	Boiled hen egg shell	Natural duck egg shell	Boiled duck egg shell
0.05	1.45±0.01	1.43±0.02	1.45±0.02	1.44±0.04
0.20	1.75±0.02	1.74±0.01	1.76±0.02	1.73±0.02
0.50	4.48±0.03	4.44±0.03	4.52±0.01	4.44±0.02
1.00	5.85±0.01	5.80±0.02	5.89±0.03	5.82±0.02
1.50	5.88±0.02	5.85±0.02	5.92±0.02	5.84±0.01

$$Q_e = \frac{X_m b C_e}{1 + b C_e} \quad \text{(Samuel and Osman,1987)}$$

where;

X = the amount of solute adsorbed per unit weight
X_m = amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage of the surface
B = a constant related to the heat of adsorption
C_e = equilibrium concentration of the solute

For linearization of the data, Equation could be written in the form :

$$\frac{C_e}{Q_e} = \frac{1}{bX_m} + \frac{C_e}{X_m}$$

Plotting C_e/Q_e against C_e, a straight line, slope was $1/X_m$ and an intercept is $1/bX_m$. The b value was the ratio between adsorption rate and desorption rate. X_m could be used to compare the removal efficiency of each adsorbent.

The Freundlich equation was expressed as :

$$\frac{x}{m} = KC_e^{1/n} \quad \text{(Samuel and Osman,1987)}$$

where;

x = the amount of solute adsorbed
m = the weight of adsorbent
C_e = the solute equilibrium concentration
K and 1/n = constants characteristic of the system

For linearization of the data, the Freundlich equation was written in logarithmic form :

$$Log\ Q_e = \log K + \frac{1}{n}\log C_e; \quad (Q_e = \frac{x}{m})$$

Plotting Log Q_e against log C_e, a straight line, slope was 1/n and intercept was log K. The calculated n value was qualitative related to the distribution of site bonding energies. K values could be used to compare the removal efficiency of each adsorbent.

The final concentrations (C_e) of lead, as shown in Table 7, were plotted as C_e/Q_e versus C_e for the Langmuir model as shown in Figure 6, and log Q_e versus log C_e for the Freundlich model (Figure 7), and values of the constants for each type of egg shells were determined after linearizing the equations through linear regression analysis.

The K values and all constant values in Langmuir (X_m,b) and Freundlich (K,1/n) equations were also presented in Table 8. In our experimental ranges, the results of all egg shells tended to be described by the Freundlich model, because the regression line obtained from the Freundlich curve fit better than the Langmuir curve. K values in Freundlich equation could be used to compare the removal efficiency of each adsorbent. It was shown that the descending lead removal efficiency on K value of each egg shell was natural duck egg shell (K = 1.2362), natural hen egg shell (K = 0.9889), boiled duck egg shell (K = 0.7901) and boiled hen egg shell (K = 0.6834), respectively. The n values obtained from this study were higher than 1, which may indicate that the energies of adsorption were decreased with increasing surface area of egg shell that bind with the heavy metal ion. The results were consistent with Polamesana-

Table 7. Final concentration of lead at various doses of egg shell and adsorption capacity

Types of egg shell	Dose of egg shell (g) m	Final Conc. (mg/L) C_e	Solute Adsorbed (mg) x	Adsorption capacity (mg/g) Q_e, x/m	C_e/Q_e	Log C_e	Log Q_e
Natural hen egg shell	0.05	1.637	0.073	1.457	1.124	0.214	0.163
	0.20	0.698	0.167	0.834	0.837	-0.156	-0.079
	0.50	0.359	0.201	0.401	0.895	-0.445	-0.397
	1.00	0.082	0.228	0.228	0.359	-1.086	-0.641
	1.50	0.088	0.228	0.152	0.580	-1.056	-0.819
Boiled hen egg shell	0.05	1.819	0.055	1.092	1.665	0.260	0.038
	0.20	0.950	0.950	0.708	1.343	-0.022	-0.150
	0.50	0.548	0.201	0.363	1.508	-0.261	-0.440
	1.00	0.122	0.224	0.224	0.544	-0.914	-0.649
	1.50	0.120	0.225	0.150	0.802	-0.921	-0.825
Natural duck egg shell	0.05	1.544	0.082	1.643	0.940	0.189	0.216
	0.20	0.513	0.185	0.926	0.554	-0.290	-0.033
	0.50	0.271	0.201	0.419	0.647	-0.567	-0.378
	1.00	0.059	0.231	0.231	0.256	-1.229	-0.637
	1.50	0.051	0.231	0.154	0.331	-1.292	-0.812
Boiled duck egg shell	0.05	1.747	0.062	1.236	1.414	0.242	0.092
	0.20	0.884	0.148	0.741	1.194	-0.054	-0.130
	0.50	0.441	0.192	0.385	1.146	-0.356	-0.415
	1.00	0.099	0.227	0.227	0.437	-1.004	-0.645
	1.50	0.097	0.227	0.151	0.642	-1.013	-0.820

Table 8. Constants and correlation coefficients for lead removal with 4 types of egg shell

Type of egg shell	Langmuir model			Freundlich model		
	X_m	b	R^2	K	1/n	R^2
Naturalhen egg shell	2.5602	0.7297	0.7283	0.9889	0.6923	0.9553
Boiled hen egg shell	1.7908	0.7207	0.6829	0.6834	0.6453	0.9423
Natural duck egg shell	2.5094	1.1347	0.8250	1.2362	0.6600	0.9680
Boiled duck egg shell	1.9547	0.8095	0.7467	0.7901	0.6441	0.9570

porn (2001), who found that the Cd removal efficiency of natural hen egg shell was higher than protein - removed hen egg shell.

From this experiment, natural hen and duck egg shells have more protein fiber than boiled hen and duck egg shells when observed by SEM. Thus protein fiber which comprising of carboxyl and amine groups may promote the natural duck and

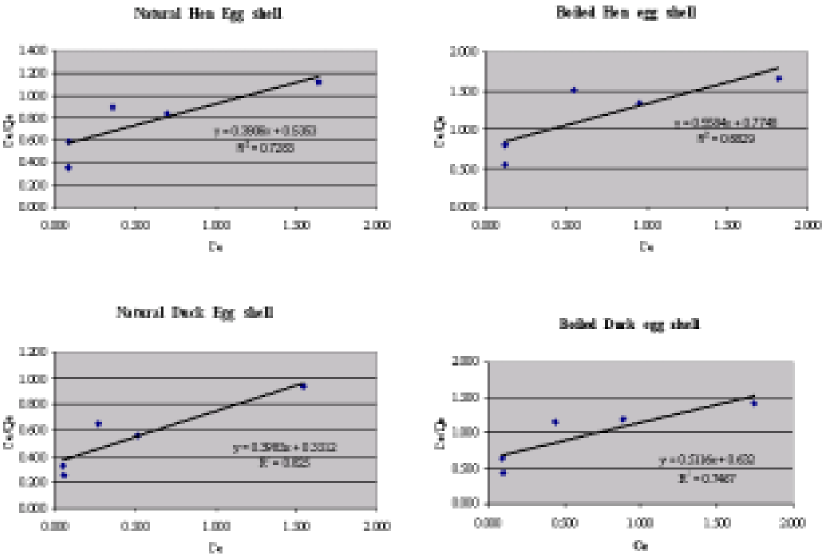

Figure 6. Langmuir adsorption isotherm on lead removal by 4 types of egg shells

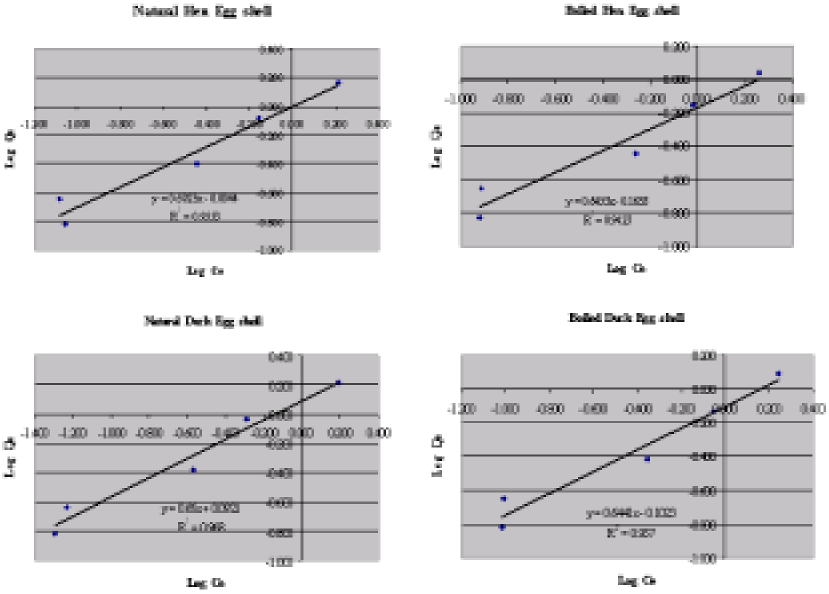

Figure 7. Freundlich adsorption isotherm on lead removal by 4 types of egg shell

hen egg shell to bind lead ions better than boiled duck and hen egg shell. Moreover, acid condition of wastewater may cause protein fiber in natural hen and duck egg shell to be contracted and tightly captured, blocking the reaction between H^+ and $CaCO_3$. This phenomenon resulted in decreasing solubility of natural hen and duck egg shell so that the amount of adsorbent increased. In addition, removal efficiency of duck egg shell was higher than that of hen egg shell because duck egg shells had more pores per square-centimeter than hen egg shells, that was consistent with Kasetsuwan (1979). Chemical composition analysis from XRF in Table 2 indicated that $CaCO_3$ in

4 types of egg shells may slightly affect the removal efficiency.

From this study, removal of lead might occur through more than one type of mechanism i.e., adsorption and precipitation, especially at the high doses of egg shell (0.5-1.5 g/100 ml of wastewater) which increased final pH more than 4 so precipitation might take part in the adsorption process. As confirmed with Figure 2, the solubility of lead continuously decreased from pH 4 until it was in stable form at pH 7; as a result lead might form complexes with OH^- as $Pb(OH)_2$, so lead hydroxyl species might participate in the adsorption and precipitate onto the egg shell structure. However, at low dose of egg shell (0.05-0.2 g/100 ml of wastwater), the final pH of solution was lower than 4 so adsorption was the main mechanism.

These results were consistent with other studies performed with basic adsorbent material i.e., fly ash and bentonite. The mechanism that influenced zinc removal characteristics of bentonite was adsorption, ion exchange and precipitation (at the high pH level i.e., pH 8), zinc might form complex with OH^- so zinc hydroxyl species might participate in the adsorption and precipitate onto the bentonite structure (Kaya and Oren, 2005). Moreover, the results were consistent with Boonpaniad (1998) who studied the removal of lead and zinc by fly ash. Hydroxide ion might participate in the adsorption process and increase the pH of solution so adsorption capacity was increased. Formation of $Pb(OH)_2$ on the surface of ash was presumably the mechanism followed by adsorption. Precipitation of some $Pb(OH)_2$ could be deposited on fly ash particles.

Conclusion

The results from this work showed that the optimum pH was at pH 6 but final concentration of lead was too low for study of adsorption isotherm, so unadjusted pH wastewater was used in this study. Unadjusted pH wastewater decreased the use of expensive chemical reagent for adjusting pH and reduced chemical residues in the environment due to basic properties of egg shell which immediately increased pH of solution. The optimum contact time and optimum dose of egg shell were 90 mins and 1.0 g/100 ml of wastewater, respectively. Final concentration of lead at optimum condition was lower than the wastewater quality standard.

The adsorption isotherm data tended to fit with the Freundlich model. From this research, precipitation might take part in the adsorption process, especially at the high doses of egg shell. The result of the adsorption isotherm demonstrated that the descending lead removal efficiency was natural duck egg shell, natural hen egg shell, boiled duck egg shell and boiled hen egg shell, respectively. (as discussed earlier). In the study of adsorption isotherm, final pH should be stable but in this experiment, final pH varied according to various doses of egg shell. This was the limitation of using real wastewater for uncontrolled final pH and it was different from synthetic wastewater. When fixed dose of egg shell was added into various initial concentration of synthetic wastewater, final pH was stable.

In summary, the egg shell could remove lead due to its physical and chemical properties such as $CaCO_3$ contents (95-96 %), pore structure and functional group i.e., carboxyl, amine and sulfate group. Moreover, egg shell was a neutralizing agent, any aqueous solution equilibrated with egg shell became more basic so heavy metals could precipitate and deposit on egg shell particles.

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