REMOVAL OF LEAD FROM BATTERY MANUFACTURING WASTEWATER BY EGG SHELL

WANVISA KAEWSOMBOON

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ABSTRACT

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 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 statistically processed using Least Significant Difference (LSD) 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 that had 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. with a contact time of 90 minutes. The best adsorbent was natural duck egg shell, which had a significant difference ($p<0.05$) 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.

KEY WORDS : LEAD / WASTEWATER / BATTERY MANUFACTURING / EGG SHELL

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การบำบัดตะกั่วในน้ำเสียจากอุตสาหกรรมผลิตแบตเตอรี่โดยใช้เปลือกไข่
(REMOVAL OF LEAD FROM BATTERY MANUFACTURING WASTEWATER BY EGG SHELL)

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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาการบำบัดตะกั่วในน้ำเสียจากอุตสาหกรรมผลิตแบตเตอรี่ โดยใช้เปลือกไข่ ปัจจัยที่ใช้ในการศึกษา คือ ค่าความเป็นกรดด่าง ระยะเวลาสัมผัส ปริมาณเปลือกไข่ นอกจากนั้นทำการวิเคราะห์คุณลักษณะ และองค์ประกอบทางเคมีของเปลือกไข่ ส่วนปริมาณตะกั่วในตัวอย่างการทดลองวิเคราะห์โดยใช้ AAS และข้อมูลที่ได้จากการทดลอง ทำการวิเคราะห์ทางสถิติโดยใช้ Least Significant Difference (LSD) ที่ระดับความเชื่อมั่น 95 % ($p<0.05$)

จากผลการศึกษาแสดงให้เห็นว่า ค่า pH ที่เหมาะสมในการบำบัดตะกั่วโดยใช้เปลือกไข่ทั้ง 4 ชนิด ได้แก่ pH 6 แต่ที่ pH นี้พบว่า ค่าความเข้มข้นของตะกั่วที่เหลือต่ำเกินไป ไม่เหมาะสมที่จะนำมาทำการศึกษาเรื่อง Adsorption Isotherm ในการศึกษาครั้งนี้ จึงทำการทดลองโดยใช้น้ำเสียที่ไม่ผ่านการปรับ pH ซึ่งมีค่าความเข้มข้นของตะกั่วเริ่มต้นประมาณ 2.365 mg/L, pH เริ่มต้น 1.35-1.45 พบว่ามีข้อดี คือ ลดการใช้สารเคมีที่มีราคาแพงในการปรับ pH และลดสารเคมีตกค้างในสิ่งแวดล้อม เนื่องจากคุณสมบัติความเป็นเบสของเปลือกไข่ ที่ช่วยเพิ่ม pH ของสารละลายทันทีภายหลังการเติม ส่วนปริมาณเปลือกไข่ที่เหมาะสมเป็น 1.0 g และระยะเวลาในการสัมผัส 90 นาที เปลือกไข่ที่มีประสิทธิภาพในการบำบัดสูงสุด คือ เปลือกไข่เป็ดดิบ และมีความต่างอย่างมีนัยสำคัญทางสถิติ ($p<0.05$) จากเปลือกไข่ชนิดอื่นๆ ค่าความเข้มข้นของตะกั่วภายหลังการบำบัดในสภาวะที่เหมาะสม คือ 0.059 mg/L อยู่ในเกณฑ์มาตรฐานน้ำทิ้งของกรมโรงงาน

ในส่วนของแบบจำลองไอโซเทอม การบำบัดตะกั่วโดยใช้เปลือกไข่มีความสัมพันธ์กับแบบจำลองของ Freundlich จากการศึกษาครั้งนี้พบว่ากระบวนการตกตะกอนได้เข้ามามีส่วนร่วมในกระบวนการดูดซับด้วย โดยเฉพาะอย่างยิ่งเมื่อเติมเปลือกไข่ในปริมาณสูง จะทำให้ค่า pH ของสารละลายเพิ่มขึ้นอย่างมาก และจากการศึกษา Adsorption Isotherm พบว่าประสิทธิภาพการบำบัดตะกั่วจะลดลงตามลำดับดังต่อไปนี้ กล่าวคือ เปลือกไข่เป็ดดิบ , เปลือกไข่ไก่ดิบ , เปลือกไข่เป็ดต้ม และ เปลือกไข่ไก่ต้ม

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CHAPTER I
INTRODUCTION

1.1 State of Problem

Among various countries, Thailand is the one that suffer from water pollution due to reduction of water quality. It is harmful to the ecosystem especially to those aquatic organisms. Moreover, it can cause nuisances and hazards to people who use the water for their daily consumption. An important source of water pollutants is industrial discharged water. Most of industrial wastewater are discharged directly into natural water system without proper management process. In Thailand, lead is one of major pollutants in wastewater. It is used as a major raw material in battery manufacturing and wastewater from this industry can contain high concentration of lead about 0.50-25.00 mg/L (1).

In general, there are mainly three techniques for the removal of heavy metal i.e., physical, chemical, and physico-chemical techniques. Each technique is difference in the optimum conditions, efficiency, chemical residues, and operation cost. For example, the chemical precipitation and reverse osmosis result in complete of metal removal but use a large amount of chemical reagents and energy. It's also generate toxic sludge (2).

The adsorption is a physico-chemical technique for the removal of heavy metal, which adsorps between liquid and solid phase (2). This process uses a few chemical reagents, so it can reduce chemical residues in wastewater. However, this technique use synthetic resin, which is quite expensive and it is non-biodegradable substance so it is obvious to use agricultural waste as the adsorbent , such as rice straw, egg shell, fruit residues, fish scale, and water hyacinth, etc., for generate many visual and decrease environmental problem.

Egg shell has a good adsorptive properties i.e., pores structure , $CaCO_3$ and protein acid mucopolysaccharide that can develop to the adsorbent. Important functional group of protein acid mucopolysaccharide are carboxyl (COO^-) , amine (NH_2^-) and sulfate (SO_3^-) that can bind heavy metal ion to form ionic bond (3). Moreover, egg shell is neutralizing agent, any aqueous solution equilibrated with egg shell become more basic (4) so heavy metal can precipitate and deposit on egg shell particles.

Thai people consume high amount of eggs so that have many waste egg shells about 58,020 tons / year (3). Therefore it should be considered to study the removal of lead using egg shell. Other studies removed lead from synthetic wastewater but this study removed lead from battery manufacturing wastewater that advantage to apply for treatment. The optimum condition, efficiency and adsorption isotherm are investigated in-depth. The results will be the guideline of alternative techniques for the removing heavy metal, reducing chemical residues, decreasing operation cost, and recycling agricultural waste or by-product.

1.2 Objectives

1.2.1 To study the optimum condition for the removal of lead using natural and boiled hen and duck egg shell.

1.2.2 To study adsorption isotherm of egg shells.

1.2.3 To compare the lead removal efficiency using four types of egg shells.

1.3 Hypothesis

1.3.1 Removal efficiency of lead using four types of egg shells varies according to pH value, contact time , and dose of egg shell.

1.3.2 The best adsorbent depends on adsorption isotherm.

1.3.3 There are differences on the removal efficiency of lead between natural and boiled hen and duck egg shell.

1.4 Scope of study

This study is batch experiment design which conducted in the laboratory at Faculty of Environment and Resource Studies, Mahidol University.

1.4.1 Use of natural and boiled hen and duck egg shells as adsorbents.

1.4.2 Wastewater is obtained from Battery Organization (Bangna , Bangkok) and adjust pH at 5, 6 and 7.

1.4.3 Dose of egg shell is 0.05, 0.2, 0.5, 1.0 and 1.5 g.

1.4.4 Contact Time is 30, 60, 90 ,120 and 150 min.

1.4.5 Determine final concentration of Heavy Metal by Atomic Absorption Spectrophotometer (AAS)

1.5 Conceptual Framework

Independent Variables

- Types of egg shell (hen and duck)
- Forms of egg shell (natural and boiled)
- Doses of egg shell (0.05, 0.2, 0.5, 1.0 & 1.5 g)
- pH values (5, 6 and 7)
- Contact times (30, 60, 90 ,120 and 150 min)

Control Variables

- Room temperature
- Speed rate of shaker (200 rpm.)
- Particle size of egg shell (60-100 mesh)

Dependent Variables

- Efficiency of egg shell for removal of lead

1.6 Definitions

1.6.1 Adsorption : the process in which a substance is accumulated at an interface between two phases, such as liquid- liquid, liquid-solid, liquid-gas, and solid-gas. The substance being adsorbed is called the adsorbate or solute and the adsorbing phase is the adsorbent (5).

1.6.2 Adsorption isotherm : the present of the amount of solute adsorbate per unit of adsorbent as a function of the equilibrium concentration in bulk solution, at constant temperature (6).

1.6.3 Wastewater from battery manufacturing : leads contaminated with wastewater from battery manufacturing derive from the cleaning process of raw materials, such as tube lead, electrodes, washing instruments and equipments since production process of battery never require water usage (1).

1.6.4 Batch operation : The technique involves placing the adsorbent and wastewater in to tank and mixing the samples for a prescribed time period.

1.6.5 Removal efficiency : capability of egg shell for removal of heavy metal from wastewater (7).

$$\text{Removal efficiency (\%)} = \frac{(A-B)*100}{A}$$

Then, A = Initial concentration (mg/l)

B = Final concentration (mg/l)

1.7 Expected Results

1.7.1 Utilization of egg shells and decrease waste in the environment.

1.7.2 Decreasing operation cost for the removal of heavy metal.

1.7.3 Know optimum condition for removal of lead using natural and boiled hen and duck egg shells that varies according to pH value, contact time and dose of egg shell.

CHAPTER II
LITERATURE REVIEW

The removal of lead from battery manufacturing wastewater is important to study the concept, theory and relevant research, as following ;

2.1 Lead

2.1.1 Chemical and physical properties (8)

Lead is soft , bluish-white, silvery, gray metal. It is the element in Group IV, Period VI of periodic table of the elements. The chemical symbol is Pb and the atomic weight is 207.2 . It has four naturally occurring isotopes : 208, 206, 207, and 204, in order of abundance. The isotopic ratios for various mineral sources are sometimes substantially different. This property has been used to carry out non-radioactive tracer environmental and metabolic studies. The usual oxidation state of lead in inorganic compounds is, therefore, +2 rather than +4. The inorganic compounds of lead are generally poorly soluble, with the exception of nitrate, the chlorate. Some of the salts formed with organic acids, e.g., lead oxalate, are also insoluble.

2.1.2 Uses of Lead (8)

The uses of lead commonly occurring in industry are divided into 2 groups namely;

2.1.2.1 Inorganic Lead

(1.) Metallic lead

It is widely used in lead-sheathed cables, lead batteries electrical vehicles, emergency light, lead solder, bullets and other projectiles for guns.

(2.) Oxide of lead

- Lead monoxide (PbO). This form is used in the manufacture of storages batteries, compounding rubber.

- Lead dioxide (PbO_2). This form is used in the manufacture of electrodes in batteries, pigments.

- Lead tetraoxide or red lead (Pb_3O_4). This form is used as rust inhibitor for iron and steel.

(3.) Salt of lead

- Lead chromate ($PbCrO_4$) or chrome yellow. This form is used as pigment in paints and dyes.

- Lead arsenate ($PbHAsO_4$). This form is used as constituent of various insecticides.

- Lead acetate [$Pb(CH_3COO)_2$]. This form is used chiefly in the manufacture of other lead compounds.

- Lead sulphate ($PbSO_4$). This form is used in white paints and in the rubber industry.

2.1.2.2 Organic lead

(1.) Tetraethyl lead [$Pb(C_2H_5)_4$] and Tetra methyl lead [($Pb(CH_3)_4$]. These forms are used as anti-nock agent in many gasolines.

2.1.3 Lead in the Environment

Wide use of lead cause the releasing of waste mix with lead into the surrounding environment, such as airs, soils and waters which are essential for human as well as other living organisms, thus concentrating in consumer goods that eventually affect to human beings.

2.1.3.1 Lead in the air (1)

Lead dust in the atmosphere originate from gases and lava steam shooting out from the volcanic cone or diffuse volcanic dusts from the earth's crust, testing nuclear bombs and melted radiation. Currently, sharp rising of lead in the air was caused by combustion of gas mixed with lead from exhaust pipe of vehicles that mostly contained 0.2-0.4 µm. of lead as the dust particles passing through the air sac into the lung and then the blood stream.

2.1.3.2 Lead in the soil (1)

Lead concentration in soil usually increase along with traffic jam. Some amount of lead from exhaust pipe which diffuse in air is accumulated on the ground near the roadside and seeping to underground water when it is raining while lead accumulate on the surface of the soil is consumed eaten by animals or bacteria.

2.1.3.3 Lead in the water

Lead concentration is high in agricultural as well as communities and industrial areas. Standard drinkable water is not more than 50 µg/L (9).

2.1.3.4 Lead in foods and consumer goods

Foods contaminate with lead are the major cause for lead entering the body, including lead in cosmetics and frequent used skincare. The maximum level of lead entering the adult's body from foods and beverages is not more than 500 µg/kg of those foods and beverages daily (10).

2.1.4 Lead hazardous to human's health (11)

2.1.4.1 There are 3 pathways for lead absorption into human body.

(1) Respiratory system : lead can be absorbed into the body from breathing air with dust, vapor of lead. Lead which is smaller than 0.75 µm. can enter into air sac in lung and bloodstream. Approximately, 40 % of lead entering through respiratory system in adult are absorbed by the body.

(2) Indigestive system : most of the times when lead entering the body through indigestive system, it usually contaminate with foods and waters which the body absorb about 5-10 %. Factors that affect to the absorption of lead into body are the amount of Ca^{2+} which will prevent lead from attaching to mucosal cell while PO_4^{3-} will combine with insoluble lead phosphate so that decrease absorbtion of lead into body.

(3) Skin absorption : lead which easily absorb through skin is inorganic lead, such as, tetramethyl lead which can be dissolved well in fat. Therefore, lead usually accumulates in the organs contain fats, such as, nervous system.

2.1.4.2 Lead dissemination, accumulation and bodily excretion

When lead enter the bloodstream, it will be carried all over the body. 95 % remain in the bones; tongue, heart and brain contain 0.05-0.09 µg/g ; thyroid, muscles, lung, stomach and intestines contain 0.14-0.19 µg/g. As for kidney, spleen and pancreas, the presence of lead indicate 0.65-0.80 µg/g.

Most lead expel from the body through excretes. It is lead that the body fail to absorb. In a day, the body can expel the most lead about 2 mg. When the lead concentration in the bloodstream reach 80 mg, toxic symptoms will start to show. When the lead has been over that level, the brain and liver may be severely damage.

2.1.4.3 Lead Toxins

Lead is unnecessary metal for the body which has no involvement of metabolism. Furthermore, lead can be intense poisoning to the body if consume in large amount. Lead toxins cause by the attempt to block hemoglobin in the body . Besides, lead will block the work of some enzyme, such as, Coenzyme A.

2.1.5 Two types of lead allergic reaction (11)

2.1.5.1 Sudden lead allergic reaction : usually cause by accidentally consume large amount of inorganic lead, the general symptoms will be severe thirst accompanied by painful burnt feeling in the stomach, vomiting, diarrheas, constipations, which can induce death within 2-3 days. As for allergic reaction to organic lead, most violent symptoms appear in the nervous systems.

2.1.5.2 Chronic lead allergic reactions : cause by small amount of lead that enter the body and accumulate until it is unable excrete the toxic lead. Most common symptoms are as follows :

First stage : Silent period by having faded skins and unstable body.

Display primary symptoms : losing appetite, easily irritate, insomnia and constipation.

Intense stage : severe stomach pain together with feeling nausea and paralyzing in certain part of the brain.

Critical stage : disturbing functions of the nervous system in the brain as well as increasing parasites.

2.1.6 Lead concentration in wastewater from industrial factories

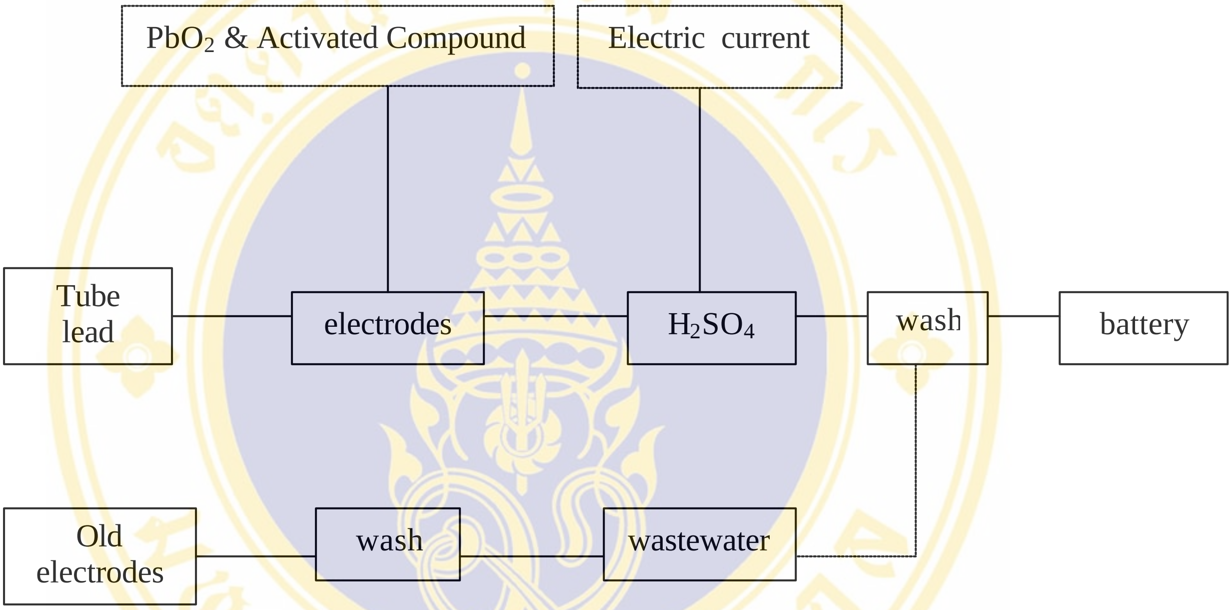
At present, there are many factories use leads as a raw materials in manufacturing which cause tremendous lead contamination in the wastewater. The lead concentration from industrial factories are shown in Table 2-1.

Table 2-1 Lead concentration in wastewater from various industrial factories

Type of Factory	Lead concentration (mg/L)
- Battery Manufacturing	
status of lead : suspended solid	-
: solution	-
- Metal plating	-
- Television bulb manufacturing	-
- Printing form manufacturing	
- Glass manufacturing	-
- Porcelain manufacturing	
- Ore mine working	-
- Explode manufacturing	
- Oil distillation	
: Organic lead	-
: Inorganic lead	-
- Paint manufacturing	-
- Steel manufacturing	-
- Metal casting	-
- Piston ring manufacturing	

Source : Jatesumrit U. ,1992 (12)

Leads contaminated with wastewater from industrial factories derive from the cleaning process of raw materials from battery manufacturing , such as tube lead, electrodes, washing instruments and equipments since production process of battery never require water usage.



Digrame 2-1 The Production Process of Battery (13)

2.1.7 Solubility of Lead

At pH 7-10 , $PbCO_3$ (Cerussite) is in stable form which slightly solubility. $Pb_3(CO_3)_2(OH)_2$ is almost in stable form. In oxidation condition, limitation of lead solubility is about $10^{-6.5}$ that is shown in Figure 2-1.

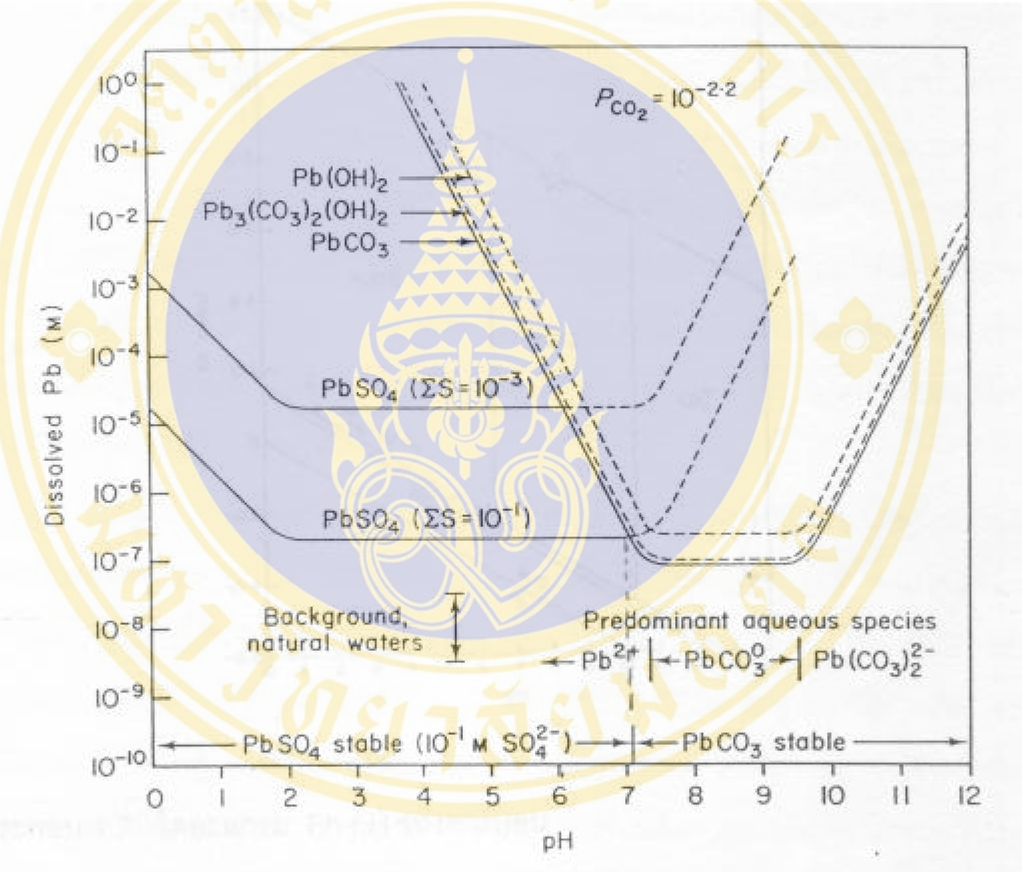


Figure 2-1 Mineral solubility in Pb-O-H-S-C system at 25 °C, 1 atm (14)

2.1.8 Standard of Lead

Standard of lead in effluent wastewater from industrial factories must lower than 0.2 mg/L (15).

2.2 Egg Shell

By nature, egg shell act as the air passages to prevent bumping and outside germs from harming the unborn chick. Most fowl eggs, including ducks and hens contain the same elements and structures that can be separated into 3 parts : egg yolks, albumens and egg shells, only differences in proportions and quantities depend on sizes and types of fowls. A single egg average 58 g in weight with albumen, egg yolk and egg shell at 32.9 g, 18.7 g and 6.4 g, respectively. (albumen and egg yolk occupied 89 % of total weight for one egg , 11 % is waste egg shell).

Component of egg shell is $CaCO_3$ 94 %, $Ca_3(PO_4)_2$ 1 %, $MgCO_3$ 1 %, organic matter 4 % (16).

Table 2-2 Average component of egg shell

Component	Weight (g)	Percent
Water	0.1	1.6
Dry matter	6.0	98.4
1. Organic matter	0.2	3.3
- protein	0.2	3.27
- fat	scarcely	0.03
2. Inorganic matter	5.8	95.1
Total	**6.1**	**100**

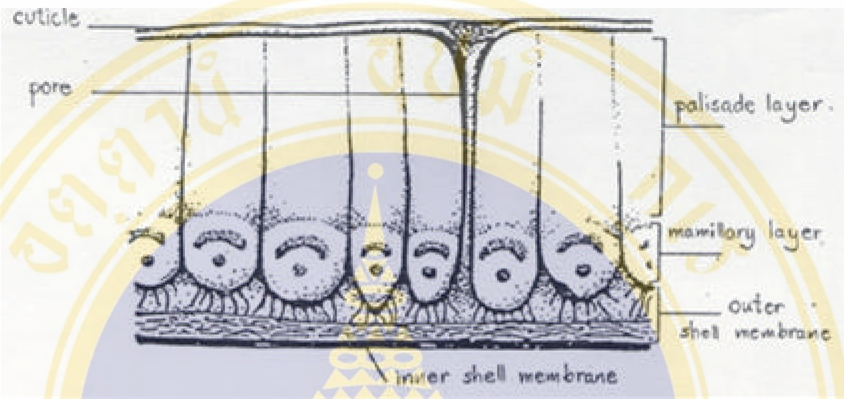
Source : Kasetsuwan K , (16)

2.2.1 Structure of egg shell

Two parts of egg shell (16)

2.2.1.1 Organic matter : joint cells together as collagen-like.

2.2.1.2 Inorganic matter : major component is $CaCO_3$.



Figture 2-2 Cross section of Egg shell (17)

2.2.2 Component of egg shell

In general, the egg shell consists of several mutually through-growing layers of $CaCO_3$. The innermost layer – mamillary layer (≅ 100 µm.) grows on the outer egg membrane and creates the base on which the palisade layer constitutes the thickest part (≅ 200 µm.) of the egg shell. The top layer is the vertical layer (≅ 5-8 µm.) covere by the organic cuticle (18).

More details of egg shell can be explained as follows :

2.2.2.1 Cuticle is the surface outside the egg shell with the thickness about 1.5-12.8 µm. When magnifying with SEM, many cracks are appeared on the surface since the cuticle act as the porous sealers to prevent loss of water and invasion of bacteria. Cuticle contain proteins 85.87 %, carbohydrates 3.5-4.4 %, fats 2.5-3.5 % and ashes 3.5 % (19). Besides, the top level of cuticle found pigment which originate from porphyrins spreading all over. Palisade layer contain more pigments than mamillary layer and shell membrane (16).

2.2.2.2 Pores are open spaces on the surface of egg shell founded from 10-30 µm. In general, an egg contain about 7,500 -1,7000 pores (20). Duck egg shell has pore per square-centimeter more than hen egg shell (16).

2.2.2.3 Spongy or Palisade layer is the layer with calcium carbornate tightly pack as calcite and vertically arrange on organic matrix as part of protein acid mucopolysaccharide complex. It contain protein 70 %, polysaccharide 11 % consist of chondroitin sulfate A and B 35 % , hyaluronic acid 20 % (21) in figure 2-3 and 2-4.

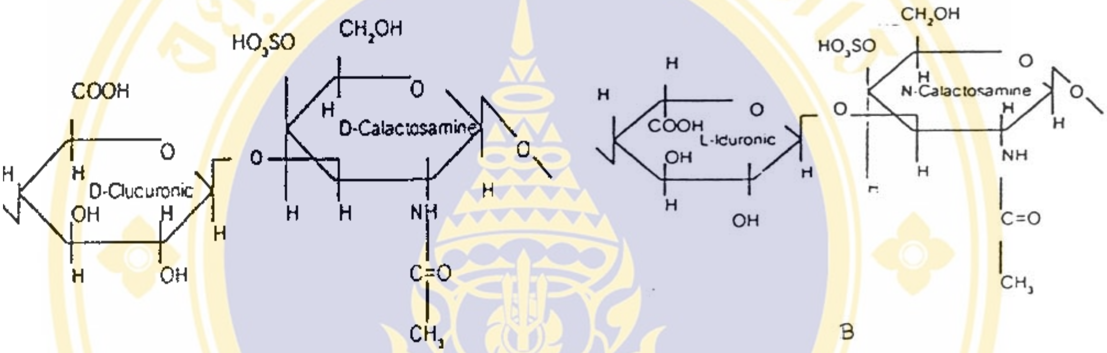


Figure 2-3 A : Structure of chondroitin sulfate A (22)

B : Structure of chondroitin sulfate B (22)

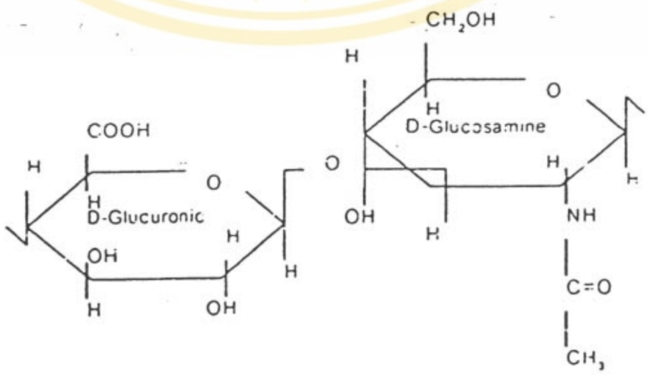


Figure 2-4 Structure of hyaluronic acid (22)

Organic matrix contain COO^-, NH_2^- and SO_3^- which can bind heavy metal (23). Normally, organic matrix consist of fine fibrils with the thickness of 0.01 µm and the length of 10 µm (17). Palisade layer has the features similar to sponges because it contain many porous, starting from 7,000 to 17,000 with uneven numbers per square centimeter. For an obtuse, middle and protrude sides, there were 125.6, 106.1-113.4 and 73.7 pores per square centimeters, respectively (20).

2.2.2.4 Mamillary layer with mamillary core inside which contain tiny organic matters and being the start of manufacturing seeding sites that comprise of protein acid mucopolysaccharide complex with neutral sugar and neutral mucopolysaccharide surrounding by sialomucin (17).

2.2.2.5 Shell membrane is formed as two thin layers clinging to each other, except the obtuse side that is separated with air sac. This layer consist of protein 95 %, carbohydrate 2 % & fat 3 % (24). Shell membrane is protein fiber such as keratin, collagen and elastin (25).

Figure 2-5 Scanning electron micrographs of egg shell membrane (26)

Shell membrane can be divided into 2 layers (24)

(1) Outer shell membrane : connect with true shell with some thin fibers protrude into the base of inner shell to form mammillary core which has the largest diameter of 3 µm and 15 µm in length.

(2.) Inner shell membrane : smooth thin surfaces have fibers longer than 23 µm , the largest diameter of 1.5 µm, averaging 0.9 µm. Both layers which separate albumen from the shell is called "Limiting membrane" contain many porous at the surface. The porous function as the air passages in higher numbers at the inner shell membrane than outer shell membrane.

Table 2-3 Component in each part of egg shell

1. Cuticle		
1.1 Protein		Unspecified
1.2 Carbohydrate	Hexosamines	Glucosamine, Galactosamine, Sialic acid
	Neutral sugars	Galactose, Glucose, Mannose, Fucose
	Pentoses	Xylose, Unspecified pentose
1.3 Fat	Neutral lipids	Mono-, di, and tri-glyceride Free fatty acid, Cholesterol ester
	Phospholipids	Lysolecithin, Lecithin, Cephalin Sphingomyelin
1.4 Porphyrins		
2. Egg shell matrix		
2.1 Protein		Unspecified but non-collagenous
2.2 Calcium-binding		Unspecified except for ovocacin component
2.3 Carbohydrate	Hexosamines	Glucosamine, Galactosamine, Sialic acid
	Neutral sugars	Galactose, Glucose, Mannose, Fucose, Xylose
	Hexuronic acid	Glucuronic acid, Iduronic acid
	Mucopolysaccharides	Hyaluronic acid, Chondroitin Sulphate A, Chondroitin Sulphate B

Source : Tullet S.G., 1992 (17)

Table 2-3 Component in each part of egg shell (continued)

3. Mammillary cores	Neutral mucopolysaccharide	
	Sialomucins	
4. Shell membrane		
4.1 Protein	Keratin	
	Collagen	
	Elastin	
4.2 Carbohydrate	Hexosamines	Glucosamine, Galactosamine, Sialic acid
	Neutral sugars	Galactose, Glucose, Mannose, Fucose
	Aldopentoses	Xylose
4.3 Fat	Neutral lipids	Mono-, di-, and tri-glyceride, Free fatty acid, Cholesterol, Cholesterol ester
	Phospholipids	Lysolecithin, Lecithin, Cephalin, Sphingomyelin

Source : Tullet S.G., 1992 (17)

2.2.3 Component of egg shell that affected to removal of lead

This study used natural and boiled hen and duck egg shell. Egg shell has suitable chemical and physical properties for removal of heavy metal such as $CaCO_3$, pore structure and functional group.

Detail of each component that affected to lead removal

2.2.3.1 Egg shells are mainly composed of $CaCO_3$ that occur displacement reaction (26,27). Lead ion displace calcium ion in $CaCO_3$ because K_{sp} (Solubility Product constant) of $CaCO_3$ is higher than K_{sp} of $PbCO_3$ (K_{sp} of $CaCO_3$ = 4.8×10^{-9}, K_{sp} of $PbCO_3$ = 1.5×10^{-13}). Formation of $PbCO_3$ (s) and calcium ion in solution as shown in this equation.

$$\text{Egg shell } (CaCO_3) + Pb^{2+} + 2\ H_2O \longrightarrow \text{egg shell} - (PbCO_3 \cdot 2H_2O) + Ca^{2+} \quad (28)$$

2.2.3.2 Protein acid mucopolysaccharide complex : 4 % was part of total weight of egg shell that consist of protein 7 %, polysaccharide 11 % (chondroitin sulfate A & B 35 % , hyaluronic acid 20 %). Important functional group is carboxyl (COO^-), sulfate (SO_3^-), amine (NH_2^-) that can bind heavy metal to form complex (27).

2.2.3.3 Pore structure : numerous studies have reported that the pore structure of adsorbent is particulary affected to the adsorption capacity (3,27).

Moreover, egg shell is neutralizing agent, any aqueous solution equilibrated with egg shell become more basic so heavy metal can precipitate and deposit on egg shell particles that confirmed with following mechanism (4).

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

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

Hydrolysis reaction of $CaCO_3$ occurred basic solution because Ca^{2+} and OH^- increased pH of solution.

2.3 Method for the Removal of Heavy Metal in Wastewater

The heavy metals in the wastewater can be removed by chemical precipitation , ion exchange , electrodialysis , reverse osmosis and adsorptive process. The guidelines for the removal of heavy metal techniques is considerable significance from a characteristic of water , quantity of water , operation cost , efficiency , and effect to the environment.

2.3.1 Chemical precipitation (29,30)

The usual method for the removal of heavy metals is the chemical precipitation. The metal will be precipitated at various pH levels , which depends on the solubility of metal ions. The choice of reactant is the first consideration in the precipitation process. For example , hydroxide (lime), carbonate , silicate, and sulfide (sodium sulfide or sodium bisulfate) can precipitate with heavy metals. The second consideration is the solubility of heavy metal and the finally factor is the liquid or solid state of waste.

2.3.2 Ion Exchange (2,30,31,32)

Ion Exchange is the reversible interchange of ions between a liquid and solid phase , which employs for the removal or exchange of dissolved inorganic substance in the water or wastewater, such as hardness (Ca^{2+}) or metal ion (Cr^{6+} , Zn^{2+} and Fe^{2+}), etc.

Most ion exchange materials for the wastewater treatment are synthetic resin, which made by the polymerization of organic compounds in to a porous three dimensional structure. The ion exchange resins are often classified by nature of the functional group as strong acid ,weak acid, strong base, and weak base.

The ionic species can be removed from solution, which are an important properties of an ion exchange resin and metal ion. The selectivity refers to the relative preference of resins for the different types of ions. The main factors influencing selectivity are ionic charge (valences), atomic number, and ionic concentration.

2.3.3 Electrodialysis (32)

The heavy metal is transferred through the membrane with a direct electric current field (D.C.). The electrodialysis system consists of cation and anion exchange membranes placed between two electrodes. An electric field is applied across the membrane and moved the cations as Mg^{2+} through the cation selective membrane and anions as Cl^{-} through anion selective membranes. In the electrodialysis, the solute ions and other charged material are mobile molecules and cross membranes in contrast to reverse where the water is forced through the membrane.

2.3.4 Reverse Osmosis (30,33)

Reverse Osmosis is a solvent flows through a semi-permeable membrane from a less concentrated to a more concentrated solution by osmotic pressure. The pressure applied exceeds osmotic pressure of the salt solution against a semi-permeable membrane , thereby forcing pure water through membrane and leaving salts behind.

2.3.5 Adsorption (24)

Adsorptive process is a substance involves its accumulation at interface between two phases. The atoms at a surface are subject to the unbalanced forces of attraction normal to surface plane. The molecule, accumulates at the interface, is called adsorbate and solid phase is adsorbent.

In this study investigated the removal of lead in wastewater from battery manufacturing by adsorptive process. Therefore, it should be studied the process and adsorptive factors for design the appropriate technique for the heavy metal removal.

2.4 Theory of Adsorption

2.4.1 Adsorptive Process (34,35)

2.4.1.1 The process of adsorption may be classified as physical and/or chemical force. The physical adsorption is the van der waals force and dispersion force, while chemical adsorption involves the transfer of electron and formation of chemical bonding.

2.4.1.2 The process depends on capillary action. The rate of adsorption is controlled by the rate of diffusion of adsorbate molecules within the capillary pores of adsorbent.

2.4.1.3 The surface charge on the adsorbent can adsorb the opposite charge. This condition is similar to the ion exchange process.

2.4.2 Adsorptive Mechanism (33)

The removal of heavy metal using adsorptive process involves a number of steps :

2.4.2.1 Adsorptive Transport : The molecules are transported from solution to the boundary layer of water surrounding adsorbent. This transport occurs by turbulent mixing or water transportation.

2.4.2.2 Film Diffusion Transport : The adsorbates are transported by molecular diffusion the layer of water, which surrounds the adsorbent particles.

2.4.2.3 Pore Diffusion Transport : The adsorbent has many pores in the particles. After passing through the film of water , the adsorbates are transported through the adsorbent's pore to available adsorptive sites.

2.4.2.4 Adsorptive Process : The adsorptive bond is formed between the adsorbate and adsorbent , after transport to an available site. This reaction is occurred by physical adsorption, which is very rapid. However, it can occurred by chemical reaction, which is slower than the diffusion reaction.

2.4.3 Type of Adsorbents (33,35)

2.4.3.1 Inorganic substances, such as magnesium oxide, bone char, and activated carbon, etc., have the surface density of 50-200 m^2/g.

2.4.3.2 Activated carbon can adsorb ions better than the inorganic substance. The surface density is 600-1,000 m^2/g. Although the activated carbon can be regenerated reused, the regeneration of activated carbon must use of high temperature and expensive operation cost.

2.4.3.3 Synthetic resin has functional group, which has been used for the adsorption of opposite ions. A few resins are called macroporous resin or adsorbent resin, such as styrene divinylbenzene (SDVB) resin and phenol-formaldehyde (PF) resin, etc. The surface density is 300-500 m^2/g that less than the activated carbon. However, the synthetic resin can be regenerated and lower operation cost than the activated carbon.

2.4.3.4 Organic substance produced from natural material, such as bark, fiber, shell, and peel, etc., which has a functional group for adsorption of opposite ions similar to the synthetic resin.

2.4.4 Adsorptive factors

2.4.4.1 Properties of Adsorbent (27)

(1.) Surface area and pore structure

Surface area and pore structure related to adsorptive efficiency. Many surface area and pore structure increase adsorptive efficiency because adsorption process always occurs on surface area.

(2.) Particle size of adsorbent

When particle size of adsorbent decreases, adsorptive efficiency increases. If adsorbent has many pores, important position for adsorption is pore so that capability of adsorption doesn't depend on particle size of adsorbent.

(3.) Functional group of adsorbent

Functional group on surface of adsorbent effects to the adsorptive efficiency because functional group can bind heavy metal to form complex.

2.4.4.2 Properties of Adsorbate (27)

(1.) Solubility of adsorbate

Capability of adsorption related to solubility of adsorbate. If adsorbate has high solubility so that is difficult for attaching of adsorbate on surface of adsorbent then adsorptive efficiency decreases.

(2.) Molecular weight and particle site of adsorbate

When molecular weight and particle site of adsorbate increase, the adsorptive efficiency increase because solubility of adsorbate decrease so it is easy for move to surface of adsorbent.

2.4.4.3 Condition of adsorption

(1.) pH of solution (27)

The pH of solution relates to the molecular precipitation , as show in figure 2-1. Furthermore, pH affected to functional group. Low adsorptive efficiency occur at low pH (acid condition) because functional group on surface of adsorbent can bind H^+ ion so surface of adsorbent has positive charge that resist to bind with heavy metal ions.

(2.) Contact time (35)

Increasing contact time effects to the increasing efficiency of heavy metal adsorption. Until, its will be an equilibrium.

(3.) Mixing of Solution (36)

The efficiency of heavy metal adsorption relates to the film diffusion and pore diffusion. The column experiment uses low mixing , so the film diffusion determines the adsorptive efficiency. On the other hand, high mixing is used for the batch experiment, so the adsorptive efficiency is determined by pore diffusion.

(4.) Temperature (36)

The adsorptive efficiency is related to the temperature. The increasing temperature effects to the increasing efficiency of heavy metal adsorption, until its will be an equilibrium.

2.4.5 Adsorption Isotherm (6)

The presentation of the amount of solute adsorbed per unit of adsorbent as a function of the equilibrium concentration in bulk solution, at constant temperature, is termed the adsorption isotherm.

Several models can be used for the description of the adsorption data, and Langmuir's and Freundlich's adsorption isotherms are the most commonly used.

2.4.5.1 Langmuir's adsorption isotherms

The basic assumptions underlying Langmuir's model, which is also called the ideal localized monolayer model are :

(1.) The molecules are adsorbed on definite sites on the surface of the adsorbent.

(2.) Each site can accommodate only one molecule (monolayer).

(3.) The area of each site is a fixed quantity determined solely the geometry of the surface.

(4.) The adsorption energy is the same at all sites.

$$X = \frac{X_m b C_e}{1+bC_e} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.1)$$

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 (also called monolayer capacity)

B = a constant related to the heat of adsorption

C_e = equilibrium concentration of the solute

For linearization of the data, Equation (2.1) can be written in the form :

$$\frac{C_e}{X} = \frac{1}{bX_m} + \frac{C_e}{X_m} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.2)$$

When C_e/X is plotted against C_e, a straight line, having a slope $1/X_m$ and an intercept 1/bXm should result. Another linear form can be obtained by dividing Equation (2.2) by C_e .

$$\frac{1}{X} = \frac{1}{Xm} + \left(\frac{1}{Ce}\right)\left(\frac{1}{bX_m}\right) \qquad \text{(2.3)}$$

Plotting 1/X against $1/C_e$ a straight line, having a slope $1/bX_m$ and intercept $1/X_m$ is obtained.

2.4.5.2 Freundlich's adsorption isotherms

The Freundlich's adsorption equation is perhaps the most widely used mathematical description of adsorption in aqueous systems. The Freundlich equation is expressed as :

$$\frac{x}{m} = KC_e^{1/n} \qquad \text{(2.4)}$$

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

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. For linearization of the data, the Freundlich equation is written in logarithmic form.

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_e \qquad \text{(2.5)}$$

According to the theory of adsorption, adsorptive process should be applied to the removal of heavy metals. The investigation for heavy metals removal should be used agricultural waste or by product because the agricultural waste or by product has an efficiency for heavy metal removal and low operation cost.

2.5 Relevant Research

The relevant research consists of two parts :

2.5.1 The removal of lead in wastewater from battery manufacturing

Wesarujtragul S. (11) studied the efficiency of *Eichhornia crasspes* (Mart.) Solms (Water hyacinth) in removal of lead from battery manufacturing wastewater. Water hyacinth was packed in colums at a height of 30 and 60 cm. , this water sample was adjusted to a pH of around 5-6 and was continuously run through each column with a flow rate of 10,20 and 30 mL/min. Filtrated samples were collected every hour for 7 hours. The results showed that the highest percentage was 98.81 % with a flow rate of 10 mL/min and a 60 cm. high treatment column. The lowest percentage was 93.08 % with a flow rate of 30 mL/min and a 30 cm. high treatment column.

Aungudornpukdee J. (37) studied the efficiency of *Typha augustifolia L.* and Rice straw in removing lead from battery factory wastewater that was prepared at 2 concentration levels, 8 and 15 mg/L. The pH was adjusted to over 5. Continuous wastewater at flow rates of 7 and 14 ml/min. were passed through columns with 30 or 60 cm. When flow rate is 7 ml/min , bed depth is 60 cm., initial concentration is 8 and 15 mg/L , after 12 hours, efficiency of lead removal was 99.41 % and 99.10 % respectively. This showed that when initial lead concentration was 8 mg/l, the efficiency was better than when initial lead concentration is 15 mg/L.

Poomngam C. (38) studied the removal of lead from wastewater by cockle shells and mussel shells. The non-continuous or batch test was used to evaluate the adsorption efficiency under various factors. The continuous study column was applied in order to evaluate the performance of shells. Study of efficiency of the shells using various size of shells dried at different temperature showed that cockle shells of 20-60 mesh size dried under sunshine in summer had the best of lead removal The optimum pH for the lead adsorption was between 6.3-8.8 and the adsorption decreased with pH. The continuous adsorption column test has been performed for breakthrough curve construction using lead-contaminated water collected from battery factory. The lead concentration of the water was 5.98 mg/L. The column with a diameter of 1.9 cm. packed with cockle shells of 2.3 cm. high could treat the lead contaminated water up to 6 litres.

Naksawas S.(39) studied the optimum conditions for the use of ground fish scales for removing lead and nickel from battery wastewater. The experiment was conducted using the jar test by various ground fish scale doses of 30, 40, and 50 g with pH levels of 8.0, 9.0, 10.0, and the settling times of 2, 3, and 4 hours. The optimum removal conditions were at ground fish scales dose of 30 g., pH level of 8.0, and the settling time of 2 hours. Under these conditions the lead and nickel removal efficiencies were 99.20 % and 98.47 % and suspended solids generated was 28.67 mg/L.

Phomun N. (1) studied the efficiency of lead removal from battery manufacturing wastewater by rice husk ash. The first stage was the study in term of lead removal from synthetic wastewater. Rice husk ash in column at the heights of 30 and 60 cm. The filter rates were 0.4, 0.6, and 0.8 m^3/m^3-hr. These parameters were also applied to the next test on actual wastewater from battery manufacturing process. The optimum condition for lead removal from synthetic wastewater were pH 3 , height of rice husk ash 60 cm. and filter rate 0.4 m^3/m^3.hr and 8 hours of filtration time. The efficiency was more than 99.85 %. The result of actual wastewater has been shown that the optimal pH was 4. The efficiency of lead removal was higher with the height of rice husk ash 60 cm. and filter rate 0.4 m^3/m^3-hr.

2.5.2 The Removal of Heavy Metal in Wastewater using Waste or By-product

The previous report in the literature for removal of heavy metal used of bagasse, crab shell, egg shell and fruit residues, bentonite; etc.

Tangaromsuk J., Pokethitiyook P., Kruatrachue M., Upatham E.S. (40) studied the biosorption properties for cadmium of bacterial biomass and the effects of environmental factors (i.e., biosorbent type, initial pH and biosorbent concentration). Microorganisms isolated in Bangkok, the gram-negative bacterium *Sphingomonas paucimobilis* exhibited the greatest cadmium tolerance and it was able to survive in the medium containing cadmium as high as 200 mg/L. The results showed that the cadmium removal capacity of living cells was markedly higher than that of nonliving cells. Cadmium biosorption by *S. paucimobilis* biomass was also affected by the initial pH and biosorbent concentration.

Kosayothin K. (7) studied the removal of heavy metal from wastewater using bagasse in a water quality analysis laboratory. The results indicated that the optimum conditions for the removal of heavy metal using bagasse was pH 9 and 25 g/L of bagasse with a contact time of 90 min. The best adsorbent was activated bagasse (0.045-1.00 mm). The final concentration of Cd, Cr, Fe, Hg, Mg, Mn and Ag was 0.021 mg/L, 0.053 mg/L, 0.078 mg/L, 3.010 mg/L, 35.920 mg/L, 77.100 mg/L and N.D.(non-detectable) respectively. The concentration of Cr and Cd were lower than the wastewater quality standard, while the concentration of Hg and Mn were higher than the wastewater quality standard.

Rangsayatorn N., Pokethitiyook P., Upatham E.S. and Lanza G.R.(41) studied the biosorption of Cd by immobilized *Spirulina platensis* on alginate gel and silica gel. The maximum biosorption capacities for alginate immobilized cells and silica immobilized cells were 70.92 and 36.63 mg-Cd/g biomass, respectively. Temperature did not have an influence on metal sorption, whereas an initial pH solution did. Sorption occurred in a wide pH range (pH 3-8). The highest adsorption of alginate immobilized cell was at pH 6, while silica immobilized cell adsorption was not affected at pH between 4 and 7. The results showed that immobilized cells could be repeatedly used in the sorption process up to five times.

Moo-Yeal Lee, Sung-Ho Lee, Hyun-Jae Shin, Toshio Kajiuchi and Ji-Won Yang (42) studied the removal efficiency of lead by crab shell that depend on contact time, initial solution pH , crab shell dose, ionic strength, co-ion concentration and settling time. The removal efficiency was slightly affected by initial solution pH over 3.0. In addition, when the crab shell dose increased from 0.5 to 1.5 g/litre, 84 % removal efficiency improved to 99.8 % at initial pH 2.0. Maximum uptake of lead was 870 mg Pb/g crab shell at initial pH 3.0. Removal efficiency was not affected by ionic strength up to 1.0 M of $NaNO_3$. Co-ions as Cd^{2+}, Cu^{2+}, Fe^{2+} and Zn^{2+} did not decrease the removal efficiency significantly.

In 2001, H.K. An, B.Y. Park and D.S. Kim (43) studied ability of crab shell to remove heavy metals from aqueous solution that comparing with that of several sorbents (cation exchange resin, zeolite, granular activated carbon , powder activated carbon). All experiments were conducted using several heavy metal ion solutions (Pb, Cd, Cu, Cr). The orders of heavy metal removal capacity and initial heavy metal removal rate were found as crab shell > cation exchange resin > powder activated carbon = granular activated carbon. Therefore, crab shell is satisfactory as a good biosorbent for the heavy metal removal.

Pawebang P. and Sukcharoen O.(44) compared the efficiency of lead removal by egg shell and fish scale at various condition such as pH values , initial concentration and contact time. At 100 mg/L of initial concentration and 2.5 g. of adsorbent (particle size 40-60 mesh), the results showed that optimum pH values was 4.5 and optimum contact time was 80 min. Egg shell (2.5 g.) could adsorb lead 11.25 mg/g, fish scale (2.5 g.) could adsorb lead 13 mg/g so that the fish scale had more potential for lead adsorption than the egg shell.

In 1997, Kruitsanasup S. (45) studied lead removal using column of egg shell. Particle size are 20-40, 40-60, 60-80 mesh; flow rate are 0.5, 1.5, 2.5, & 3.5 ml/min; pH are 3, 5, 7 and 9. The result showed that egg shell could remove lead at all condition of experiment (99 %) because egg shell has $CaCO_3$ and specific functional group (COO^- , NH_2^-, SO_3^-) for binding of lead.

In 2001, Polamesanaporn Y.(27) studied the cadmium adsorption capability of two types of egg shell, i.e. natural egg shell and protein-removed egg shell. There are two experiment studies : (1) adsorption at equilibrium conditions with three sizes of egg shell (20-40, 40-60, 60-80 mesh) and (2) kinetic adsorption. The best adsorption results, at equilibrium conditions (120 min) in case of 60-80 mesh, showed that the maximum amount of cadmium adsorped by natural and protein-removed egg shell per gram (q_{max}) are 1.6028 and 1.3170 millimole/g, respectively. The adsorption capability of the small size egg shell was greater than the large size egg shell.

In 2002, Surasen C. (3) studied the efficiency and suitable condition of cadmium removal in synthetic wastewater by egg shell filter the results showed that suitable pH range for Cd removal were 4-6. The size of egg shell granul was 0.300-0.850 mm.. And the filter rate was 1.5 m^3 / m^2-hr. The efficiency of Cd removal decreased as the Cd concentration increased. The highest efficiency , more than 99.99 % of Cd removal for this study was at the 50 cm. height of egg shell , Cd concentration of 5 mg/L for 24 hours of filtration time.

Senthikumaar. S. Bharathi, D. Nithyanandhi and V. Subburam (46) studied the removal of toxic heavy metals (Hg, Pb, Cd, Cu, Zn and Ni) by biowaste obtained from the fruit juice industry (FR). Phosphated FR (P-FR) was prepared by treatment of FR with phosphorous (V) oxychloride. Biosorption of a metal was dependent on the initial pH of the aqueous solution. An efficient removal was obtained with P-FR at low pH.

Han R. , Zhang J. , Zou W., Shi J., and Liu H. (47) studied lead removal by cereal chaff. Variables of the system include biosorption time, chaff dose and solution temperature. The experimental results were fitted to Langmuir model. According to the elution using the Langmuir equation, the maximum biosorption capacities of lead ion onto chaff was 12.5 mg/g at 293 K.

Maria Martines, Nuria Miralles, Soraya Hidalgo, Nuria Fiol, Isabel Villacscusa and Jordi Poch (48) studied the sorption of lead and cadmium by grape stalk waste (by product from wine production). The effects of contact time, pH, ionic medium, initial concentration, other metal ions present and ligands were studied in batch experiments at 20^{o}C. Maximum sorption for both metals was found to occur at an initial pH of around 5.5. The equilibrium process was described well by Langmuir model, with maximum grape stalk sorption capacities of 0.241 and 0.248 mmol/g for Pb and Cd , respectively.

Eamsiri A., Arunlertaree C. and Datchaneekul K.(49) studied the removal of heavy metals in synthetic wastewater by adsorption on bentonite, initial pH and co-metal ions competition on heavy metals adsorption capacity and removal efficiency were investigated. The contact time of adsorbent reached equilibrium with in 1 hour and the optimum amout of bentonite was 2 g. The maximum adsorption capacity of nickel occurred at pH 4, and pH 5 for Zinc and Mn including mixed heavy metals solution. The adsorption efficiency of Ni, Zn and Mn from the single heavy metal solution was higher than the mixed heavy metals solution. Equilibrium modeling of the adsorption isotherm showed that adsorption of those heavy metals was able to be described by the Freundlich model, the ability for heavy metal was in the order of Ni > Zn > Mn.

These studies have previous been shown that the removal of heavy metal by waste or by-product is an appropriate technique, because it does not use the chemical reagents. This technique is conducted under the various condition, i.e. pH of solution, dose of adsorbent, contact time, and type of adsorbents. Therefore, the removal of lead in wastewater from battery manufacturing using egg shells should be investigated the optimum condition , removal efficiency and adsorption isotherm. The advantage of report is a guideline for the removal of lead using egg shells. This process can reduce the chemical residue and recycling waste or by-product.

For this study, natural and boiled hen and duck egg shells were used for the adsorbents. pH of solution was varied at 5, 6 and 7 because they are under wastewater quality standard control of Industrial Works Department. From the experiment of Pawebang P. and Sukcharoen O.(44), optimum dose of egg shell was 2.5 g, optimum contact time was 80 min for the removal of lead in synthetic wastewater which had 100 mg/L of lead concentration. Applied for the removal of lead from battery manufacturing wastewater, lead concentration was about 2 mg/L and taked 100 mL of water sample so that dose of egg shell for this studied should vary at 0.05, 0.2, 0.5, 1.0 and 1.5 g. On the other hand, contact time should vary at 30, 60, 90, 120 and 150 min. From the experiment of Kruitsanasup S.(45) and Polamesanaporn Y. (27) showed that the optimum particle size of egg shell was 60-80 mesh but in this study , 60-100 mesh size particle of sieved ground egg shells were conducted and speed rate of shaker of Polamesanaporn Y. (27) was 200 rpm so that will be used in this study.

CHAPTER III
MATERIALS AND METHODS

3.1 Study Plan

3.1.1 Collecting data and relevant research concerning heavy metal (lead), wastewater from battery manufacturing, egg shell and adsorption isotherm.

3.1.2 Experimental planning

3.1.3 Set up the experiment

3.1.4 Analyzing the results

3.1.5 Conclusion

3.2 Study Pattern

This research was conducted as batch experimental design in the laboratory at Faculty of Environment and Resources Studies, Mahidol University. Natural and boiled hen and duck egg shell were used for the removal of lead from battery manufacturing wastewater.

3.3 Materials

3.3.1 Pipette

3.3.2 Erlenmeyer flask

3.3.3 Beaker

3.3.4 Dropper

3.3.5 Filter paper no.4

3.3.6 Watch glass

3.3.7 Volumetric flask

3.3.8 Cylinder

3.3.9 Sterring rod

3.3.10 Glass Funnel

3.3.11 Suction Flask and Buchner Funnel

3.3.12 Evaporating dish

3.4 Apparatus

3.4.1 Weighting balance

3.4.2 Hot Air Oven (Contherm 260 M)

3.4.3 pH meter (Horiba F-22A)

3.4.4 Atomic Absorption Spectrophotometer (GBC 932 Plus)

3.4.5 X-ray Fluorescence Spectrometer (S4-Explorer)

3.4.6 Scanning Electron Microscope (HITACHI S-2500)

3.4.7 Sieve no. 60 and 100 mesh

3.4.8 Rotary Shaker

3.4.9. Grider

3.5 Chemical Reagents

3.5.1 Conc. Nitric Acid 65 % (Conc. HNO_3)

3.5.2 Conc. Hydrochloric Acid 37% (Conc. HCl)

3.5.3 1 M. Sodium Hydroxide (1M. NaOH)

3.5.4 Heavy metal standard solution (Pb)

3.6 Variables

3.6.1 Independent Variables

3.6.1.1 Types of egg shell (Hen and Duck)

3.6.1.2 Forms of egg shell (Natural and Boiled)

3.6.1.3 Doses of egg shell (0.05 , 0.2 , 0.5 ,1.0, and 1.5 g.)

3.6.1.4 pH of wastewater (5, 6 and 7)

3.6.1.5 Contact times (30, 60, 90, 120 and 150 mins)

3.6.2 Dependent Variables

3.6.2.1 Efficiency of egg shells for removal of lead

3.6.3 Control Variables

3.6.3.1 Room temperature

3.6.3.2 The shaker was operated at 200 rpm.

3.6.3.3 Size of egg shells were 60-100 mesh

3.7 Equipment Preparation

The instruments were calibrated and prepared following to the manufacturer recommended procedure using calibration standard and glasswares were washed down using 1:1 nitric acid for reducing interference.

3.8 Procedures

3.8.1 Wastewater preparation

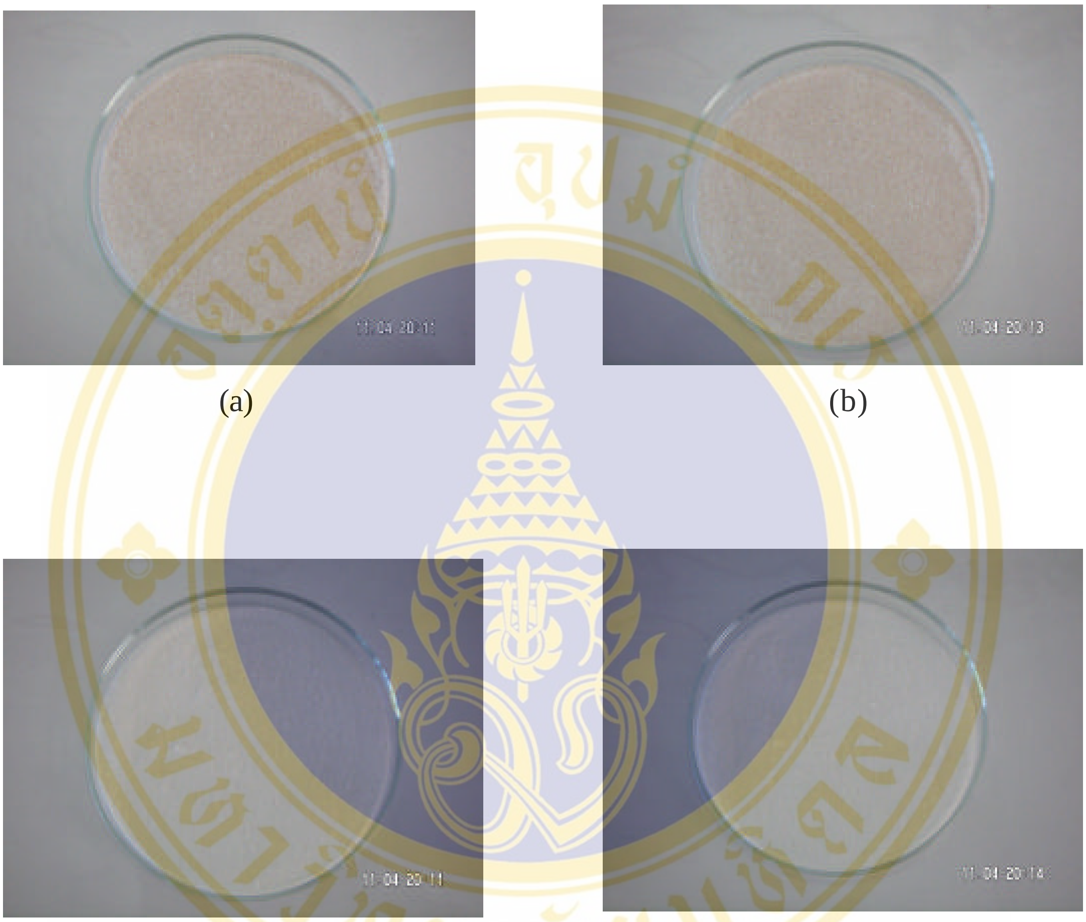
Wastewater from Battery Organization (Bangna , Bangkok) was kept in polyethylene bottle and stored at 4 ^{o}C in acid condition (pH < 2) (50) for precipitation at least 1 day.

3.8.2 Wastewater characteristic analysis

The wastewater characteristic included pH value, Total Dissolved Solids (TDS) and Total Solids (TS) were analyzed according to the standard method. The concentration of lead was digested using nitric acid - hydrochloric acid digestion method and determined using Atomic Absorption Spectrophotometer (AAS), as described in Table 3-1 and Appendix B.

3.8.3 Egg shell preparation

Natural and boiled hen and duck egg shells were washed with tap water for several times then air-dried and incubated in hot air oven at 40 ^{0}C for 30 minutes. Consequently, egg shells were grounded to powder by grinder, and sieved between 60-100 mesh size particles. The sieved ground egg shells (4 types) are shown in Figure 3-1.



(a) (b)

(c) (d)

Figure 3-1 Sieved ground egg shells

(a) Natural hen egg shell

(b) Boiled hen egg shell

(c) Natural duck egg shell

(d) Boiled duck egg shell

3.8.4 The removal of lead from battery manufacturing wastewater using egg shells

The Egg shell was classified into four types :

Type 1 (A) : Natural hen egg shell

Type 2 (B) : Boiled hen egg shell

Type 3 (C) : Natural duck egg shell

Type 4 (D) : Boiled duck egg shell

The optimum conditions for lead removal by egg shell type were carried out as follows :

3.8.4.1 The optimum pH analysis (see diagram 3-1)

(1.) The initial pH values of wastewater was adjusted to 5, 6 and 7 using 1 M. NaOH.

(2.) The 100 mL of sample was added to 250 mL of Erlenmeyer flask.

(3.) Analyzed initial lead concentration using method as described in Appendix B.

(4.) Added 0.05 g. of egg shell in each sample.

(5.) Adjusted the shaker at 200 rpm for 90 minutes and sample was filtrated through filter paper no. 4.

(6.) The lead concentration in treated solution was measured by method as described in Appendix B.

3.8.4.2 The optimum contact time analysis (see diagram 3-2)

(1.) 100 ml of optimum pH wastewater (from 3.8.4.1) was added to 250 mL of Erlenmeyer flask

(2.) Analyzed initial lead concentration using method as described in Appendix B.

(3.) Added 0.05 g. of egg shell in each sample.

(4.) Adjusted the shaker at 200 rpm for 30, 60, 90, 120 and 150 minutes and sample was filtrated through filter paper no. 4.

(6.) The lead concentration in treated solution was measured by method as described in Appendix B.

3.8.4.3 The optimum dose of egg shell analysis (see diagram 3-3)

(1.) 100 ml of optimum pH wastewater (from 3.8.4.1) was added to 250 mL of Erlenmeyer flask

(2.) Analyzed initial lead concentration using method as described in Appendix B.

(3.) Added 0.05, 0.2, 0.5, 1.0, and 1.5 g. of egg shell in each sample.

(4.) Adjusted the shaker at 200 rpm with optimum contact time (from 3.8.4.2) and sample was filtrated through filter paper no. 4.

(5.) The lead concentration in treated solution was measured by method as described in Appendix B.

Table 3-1 The method for wastewater characteristic and heavy metal (lead) analysis in wastewater from battery manufacturing

Parameter	**Method**
1. pH	pH Meter
2. Total Dissolved Solids (TDS)	25 mL of sample is filtered through glass-fiber filter and evaporate at 103-105 ^{0}C (constant weight). Cool in dessicator and weigh.
3. Total Solids (TS)	25 mL of sample is evaporated at 103-105 ^{0}C for 1 hour. Cool in dessicator and weigh.
4. Lead	Nitric acid-hydrochloric acid digestion

Source : APHA, AWWA and WPCF, 1995 (51)

3.8.5 Study Adsorption Isotherm

Data from 3.8.4.3 was used to study the adsorption isotherm for determined the best adsorbent. Several models can be used to describe the adsorption data, Langmuir's and Freundlich's adsorption isotherms are the most commonly used (6).

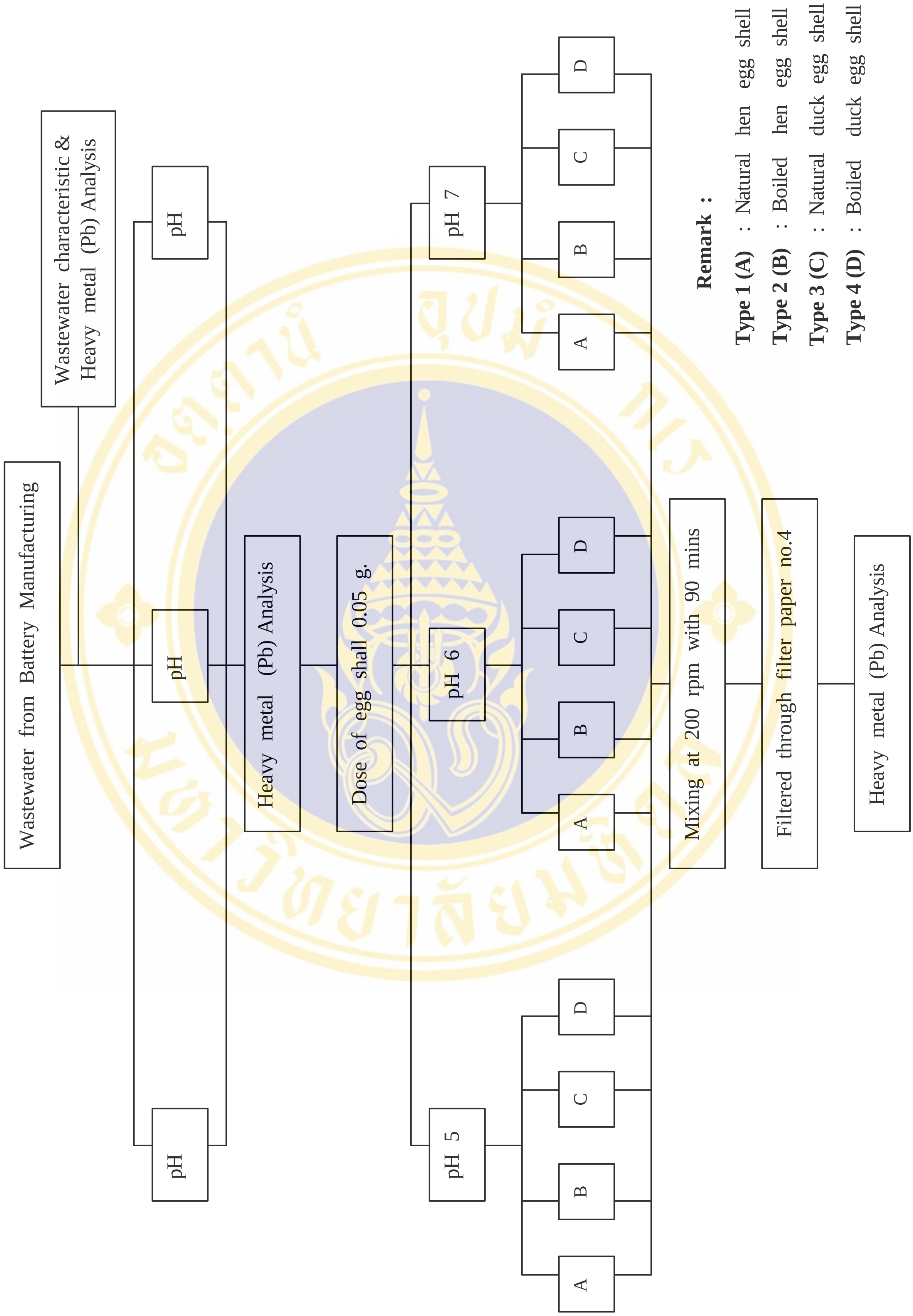


Diagram 3-1 The optimum pH value analysis

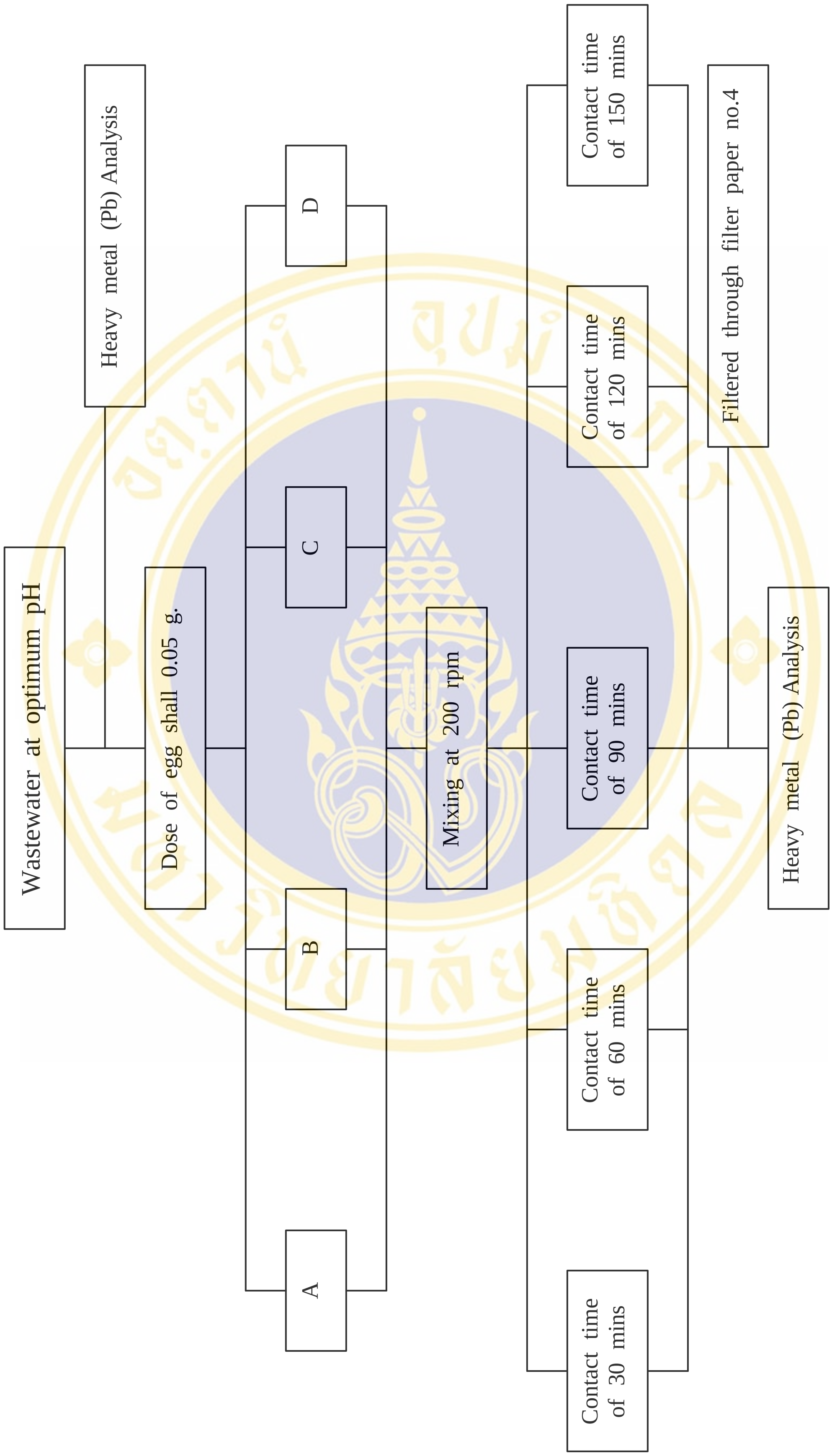


Diagram 3-2 The optimum contact time analysis

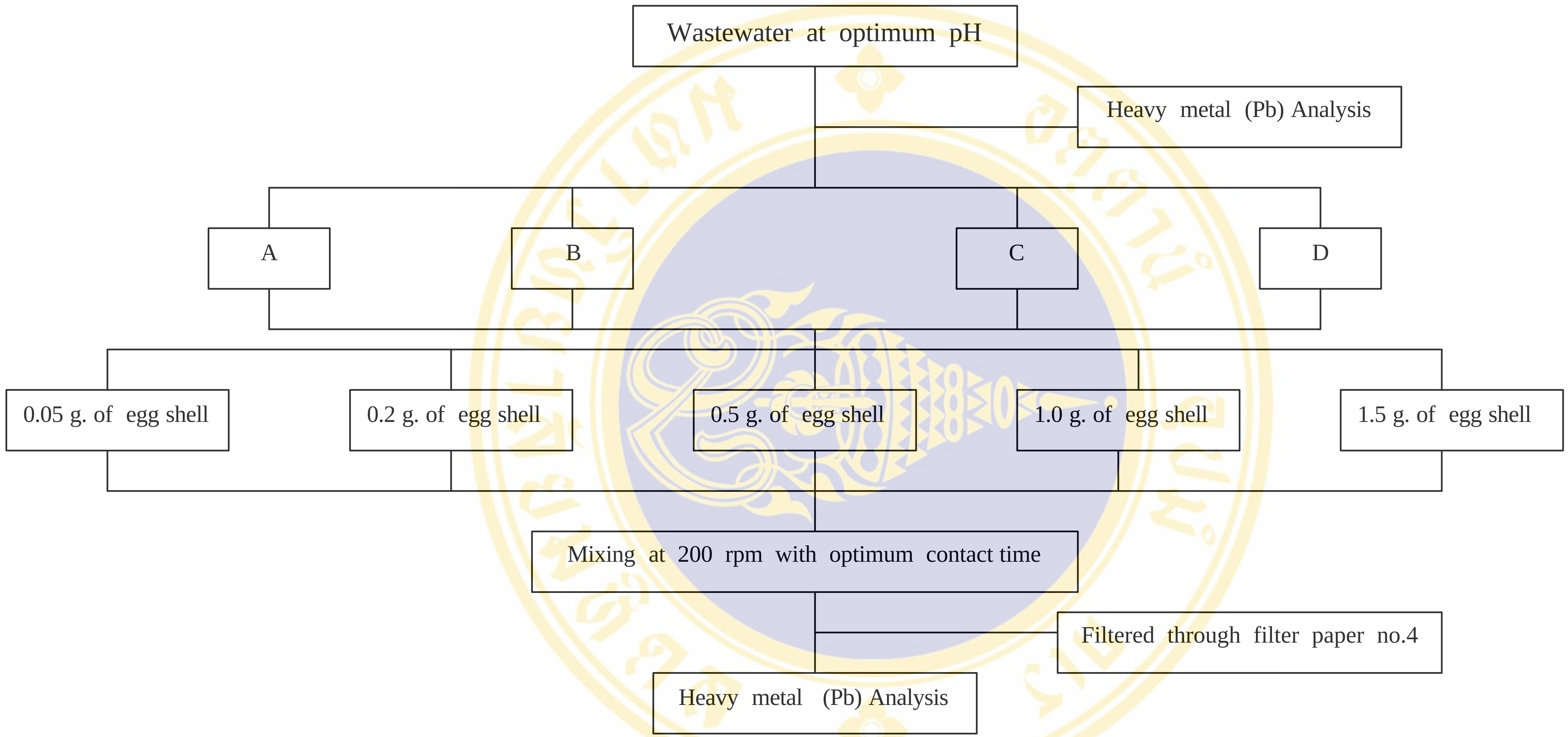


Diagram 3-3 The optimum dose of egg shell analysis

3.9 Statistical Analysis

3.9.1 Percent values

The concentration of lead was expressed in mg/L or ppm and the removal efficiency was calculated according to this formula : (7).

$$\text{The removal efficiency (\%)} = \frac{(A-B)x100}{A}$$

where, A = Initial concentration (mg/L)

B = Final concentration (mg/L)

3.9.2 Average removal efficiency

To determine average removal efficiency of 4 types of egg shell which obtained according to pH of wastewater, contact time and dose of egg shell.

3.9.3 Relation of the results

Relation of the results were investigated. Using the Least Significant Difference (LSD) at a 95 % confidence level by statistical package for the social sciences (SPSS) software performed the statistical validation of the results.

CHAPTER IV
RESULTS AND DISCUSSION

This chapter presents the results and discussion that obtain from the experiments in laboratory scale for the removal of lead from battery manufacturing wastewater using egg shell. The egg shells were classified into 4 types : natural hen egg shell , boiled hen egg shell , natural duck egg shell and boiled duck egg shell. The details are described as follows :

4.1 Characteristics of wastewater

The wastewater sample was collected from battery manufacturing Bangna, Bangkok. The characteristics of wastewater are presented in Table 4-1. The pH of wastewater was strong acid and initial lead concentration was higher than wastewater quality standard control of Thailand Industrial Work Department in 1992.

Table 4-1 Characteristic 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
Suspended Solids (SS) (mg/L)	18.13	< 30
Total Solids (TS) (mg/L)	2,245.60	-
Total Dissolved Solids (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

4.2 Chemical and physical properties of egg shells

The chemical composition of all egg shells were examined by X-ray Fluorescence Spectrometer and the results are shown in Table 4-2. 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.

$CaCO_3$ and P in natural duck and hen egg shell were higher than boiled duck and hen egg shell.

Mg , Al , K and Sr in natural and boiled duck egg shell were higher than natural and boiled hen egg shell but S in natural and boiled hen egg shell were higher than natural and boiled duck egg shell.

Table 4-2 Chemical compositions in 4 types 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	95.13	96.76	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

Egg shells were mainly composed of $CaCO_3$ that occur displacement reaction (26,27). Lead ion displaced calcium ion in $CaCO_3$ because K_{sp} (Solubility Product constant) of $CaCO_3$ was higher than K_{sp} of $PbCO_3$ (K_{sp} of $CaCO_3$ = 4.8×10^{-9}, K_{sp} of $PbCO_3$ = 1.5×10^{-13}). Formation of $PbCO_3$ (s) and calcium ion in solution was shown in this equation.

$$\text{Egg shell } (CaCO_3) + Pb^{2+} + 2\ H_2O \longrightarrow \text{egg shell} - (PbCO_3 \cdot 2H_2O) + Ca^{2+} \quad (27)$$

From figure 3-1, the characteristics of egg shells used in this study were white powder (natural and boiled duck egg shells) and brown powder (natural and boiled hen egg shells). The surface structure of 4 types of egg shells were observed by Scanning Electron Microscope (SEM) as shown in Figure 4-1 to 4-4. It shows that egg shells surface were irregular shape. Pore size of natural and boiled hen egg shells were between 0.3-0.6 µm while natural and boiled duck egg shells were between 0.2-0.4 µm.

Numerous studies have reported that the pore structure of adsorbent has been particulary affected to the adsorption capacity (3,27) ; pictures from SEM are shown that natural and boiled duck egg shells had pore per square-centimeter more than natural and boiled hen egg shells. This results were consistent with Kasetsuwan S. (16). Moreover, amount and distribution of protein fiber in natural hen and duck egg shells were higher than boiled hen and duck egg shells as shown in Figure 4-1 to 4-4.

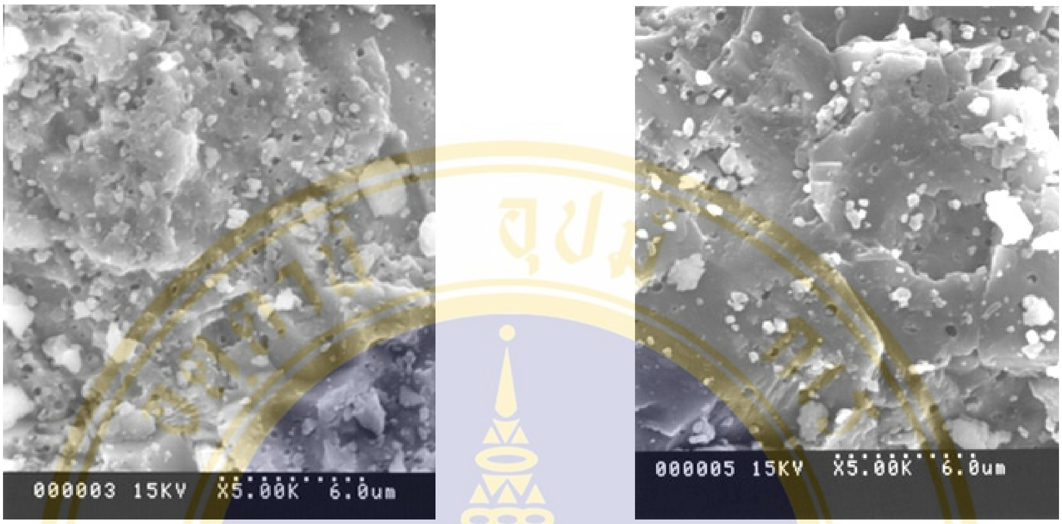


Figure 4-1 Morphology of natural hen egg shell with magnification of x 5,000

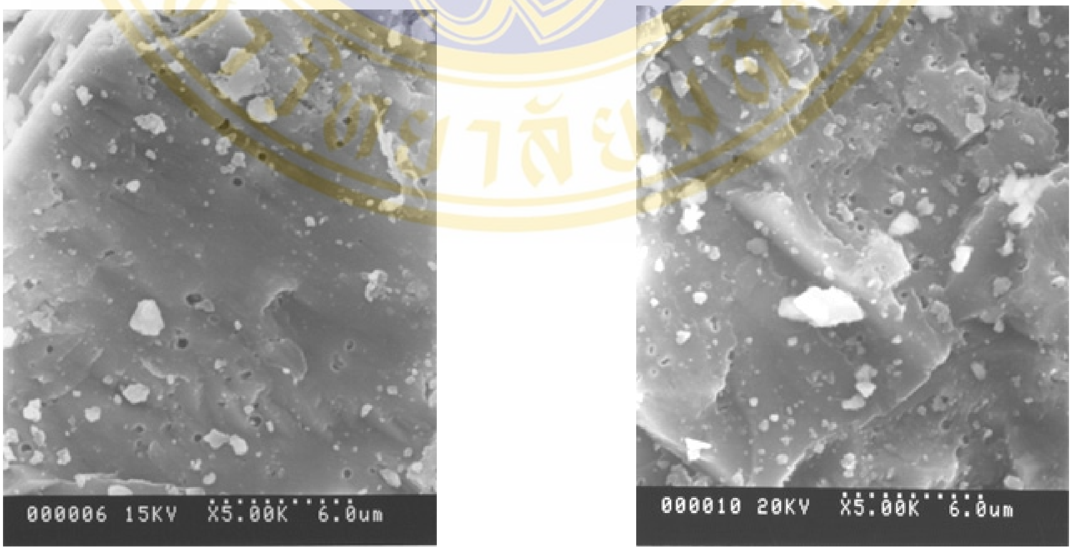


Figure 4-2 Morphology of boiled hen egg shell with magnification of x 5,000

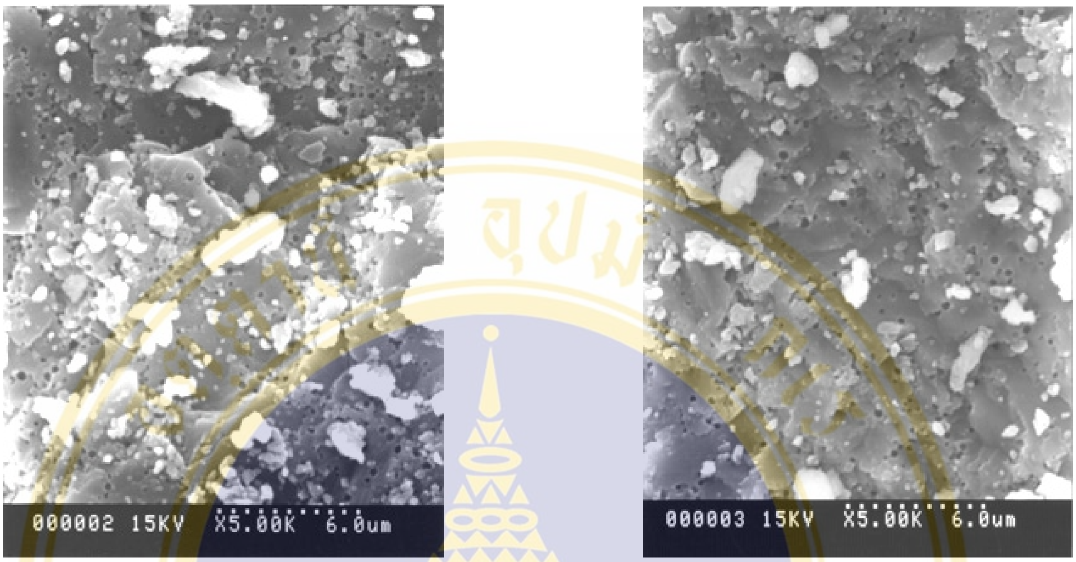


Figure 4-3 Morphology of natural duck egg shell with magnification of x 5,000

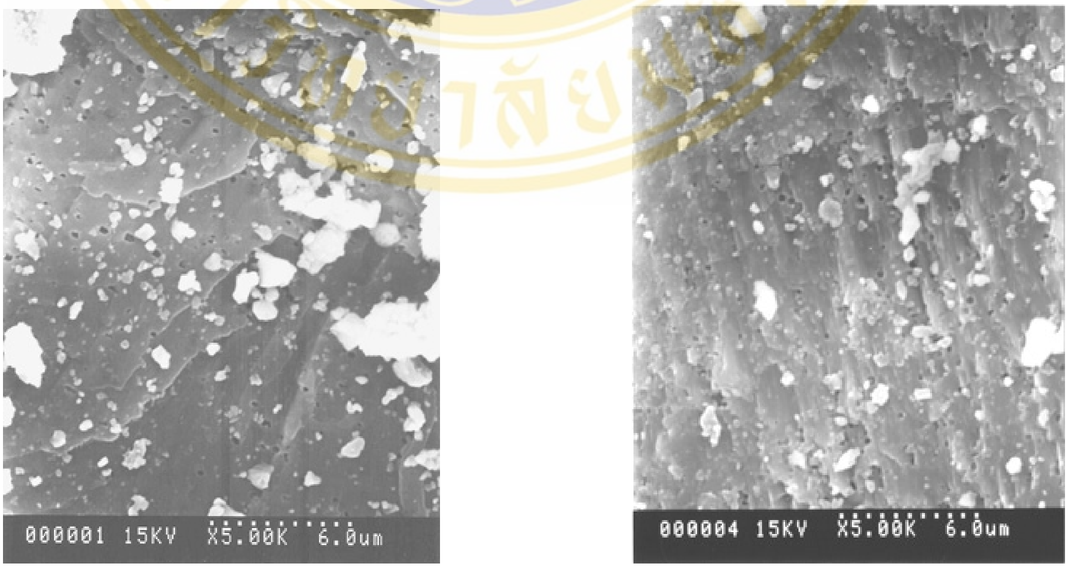


Figure 4-4 Morphology of boiled duck egg shell with magnification of x 5,000

4.3 Optimum conditions for lead removal by egg shells

To achieve optimum condition, the factor that affected to lead removal using egg shells were considered. These included pH, contact time and dose of egg shell. The results were obtained as follows.

4.3.1 Effect of pH

The experiment on the effect of pH to lead removal using egg shells has been performed in 250 mL Erlenmeyer flask. The 100 mL of wastewater were added separately with 0.05 g. of different egg shell. The pH were adjusted to 5, 6 and 7. All flasks were agitated on rotary shaker at 200 rpm for 90 mins. The results are shown in Table 4-3 and Figure 4-5.

The results indicated that the natural and boiled hen egg shell removal efficiency at pH 5, 6 and 7 were 44.78 % ,78.03 % ,100 % and 38.82 % , 72.97 % , 100% , respectively. By statistical analysis, efficiency of lead removal at all pH were significantly different ($p<0.05$) (see appendix D).

The natural and boiled duck egg shell removal efficiency at pH 5, 6 and 7 were 48.67 %, 79.18 %, 100 % and 40.70 % ,75.36 %, 100 %, respectively. By statistical analysis, efficiency of lead removal at all pH were significantly different ($p<0.05$) (see appendix D).

According to the results of this study, optimum removal efficiency of all types of egg shells were at pH 6 because this pH had high removal efficiency and final concentration of lead was lower than wastewater quality standard. At pH 6 has low final concentration of lead because dispersed hydroxyl group (OH^-) from NaOH combined with lead ion in the solution which caused lead precipitation.

Optimum pH was at pH 6 but unadjusted pH wastewater was used in the next step of the experiment because 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 reduce 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 be precipitate that confirmed with Figure 2-1. Solubility of lead continuously decreased from pH 4 until it was in stable form at pH 7 as well as the results from this study, lead concentration were non-detectable at pH 7 because lead were completely precipitated in form of $Pb(OH)_2$.

This results were consistent with Naksawas S.(39) who studied on removal of lead from battery industry wastewater by ground fish scale. Experimental group was conducted at pH 8, 9 and 10. From this results, lead removal in experimental group was mainly occurred by chemical precipitation process.

4.3.2 Effect of contact time

Effect of contact time on the equilibrium removal of lead using egg shells were investigated. The behavior of contact time on lead removal were measured by varying the equilibrium contact time between the adsorbate and adsorbent in the range of 30 , 60 , 90 , 120 and 150 mins. They were conducted by addition of 0.05 g. adsorbent to 100 mL of unadjusted pH wastewater (pH 1.35-1.45 , initial lead concentration 2.365 mg/L) , then place on a rotary shaker with 200 rpm agitation until reach the assigned contact time. The results are shown in Table 4-4 and Figure 4-6.

The natural hen egg shell removal efficiency at contact time of 30, 60 , 90, 120 and 150 mins were 14.70 %, 22.58 %, 30.79 %,30.92 % and 31.03 %, respectively. The highest removal efficiency was appeared at 150 mins and reduced orderly at the contact time of 120, 90, 60 and 30 mins.

The results of boiled hen egg shell removal efficiency at contact time of 30,60, 90, 120 and 150 mins were 7.86 %, 15.29 %, 23.10 %, 22.99 % and 22.99 % ,respectively. The highest removal efficiency was appeared at 90 mins and reduced orderly at the contact time of 120, 150 , 60 and 30 mins.

The natural duck egg shell removal efficiency at contact time of 30 ,60 , 90, 120 and 150 mins were 17.28 %, 29.76 %, 34.73 %, 35.07 % and 35.09 % , respectively. The highest removal efficiency was appeared at 150 mins and reduced orderly at the contact time of 120, 90, 60 and 30 mins.

The result of boiled duck egg shell removal efficiency at contact time of 30, 60, 90, 120 and 150 mins were 10.48 %, 18.15 %, 26.13 %, 26.70 % and 26.74 %, respectively. The highest result is appeared at 150 mins and reduced orderly at the contact time of 120, 90, 60 and 30 mins.

Removal efficiency for all types of egg shells at the contact time of 90, 120 and 150 mins were not significant different ($p<0.05$) where as the results obtained at contact time 30, 60 and 90 mins were significant different ($p<0.05$). Therefore, the optimum contact time for all types of egg shell should be at 90 mins (see appendix D).

The equilibrium time for all types of egg shells were reached at 90 mins. This indicated that the contact time is related to the removal efficiency. Initial adsorption rate was dramatically increased and then equilibrium condition were reached at a period of 90-150 mins. This is due to the active site of surface area of egg shell is decreased during the process. The mechanism can be explained that heavy metal ion bind to active site when time passing, active site for adsorbing ion is reduced affecting the decreasing of adsorption rate (33). This results were supported by Pawebang P. and Sukcharoen O. (44). who reported that the equilibrium time to remove lead in synthetic wastewater by egg shell could be reached at about 80 min. As well as the study of Lee, *et al*. (42). who studied on the equilibrium time of lead removal by crab shell particle, and the results showed that the necessary contact time to be reached equilibrium was about 90-120 min.

4.2.3 Effect of dose of egg shell

Effect of dose of egg shell to remove lead were studied. Unadjusted pH wastewater and 90 mins of contact time were conducted. Various dose of 0.05, 0.2, 0.5, 1.0, and 1.5 g. of egg shell was added then subsequently agitated at 200 rpm. The results of these reaction are shown in Table 4-5 and Figure 4-7 which indicated that removal efficiency of all egg shells were similar.

In term of natural hen egg shell removal efficiency, the results of using dose of egg shell 0.05, 0.2, 0.5, 1.0, and 1.5 g. were 30.80 %, 70.50 %, 84.85 %, 96.53 % and 96.42 %, respectively. The highest removal capacity was appeared at using dose of egg shell 1.0 g.

As boiled hen egg shell namely removal efficiency of using dose of egg shell 0.05, 0.2, 0.5, 1.0 and 1.5 g were 23.04 %, 59.83 %, 76.83 %, 94.84 % and 94.94 %, respectively. The highest removal capacity was appeared at using dose of egg shell 1.5 g.

In case of natural duck egg shell removal efficiency, the removal efficiency of using dose of egg shell 0.05, 0.2, 0.5, 1.0, and 1.5 g were 34.74 % , 78.31 % , 88.53 % , 97.51 % and 97.56 % respectively, with highest capacity at 1.5 g. of egg shell.

In case of boiled duck egg shell removal efficiency, the removal capacity of using dose of egg shell 0.05, 0.2, 0.5, 1.0 and 1.5 g. were 26.15%, 62.62%, 81.37%, 95.81% and 95.76% , respectively, with highest capacity at 1.0 g. of egg shell.

Removal efficiency for using dose of all types of egg shell 0.05, 0.2, 0.5, and 1.0 g. were significant different ($p<0.05$) where as the results obtained from using 1.0 and 1.5 g. were not significant difference. Therefore, an appropriate dose for all types of egg shell should be 1.0 g. (see appendix D).

As aboved mention, the percentage of removal increase with increasing the dose of egg shell. However, dose of egg shell 1.0 g. were found to be maximum appropriate dose for all types of egg shell. And the results in section 4.3.3 showed that dose of egg shell affected the removal of lead, because the removal efficiency of solutes increases with increasing dose of adsorbent (49). The removal efficiency increases its level according to the dose of egg shell increased at an appropriate level.

Table 4-3 Effect of pH to lead removal by 4 types of egg shells (0.05 g of egg shell, 90 mins of contact time)

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

N.D. : non-detectable (<0.001 mg/L)

Remark : The difference of alphabets in each column statistically show the significant difference with the confidential of 95% by LSD

Table 4-4 Effect of contact time to lead removal by 4 types of egg shells (Unadjusted pH wastewater, 0.05 g of egg shell)

Contact time (min)	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 : The difference of alphabets in each column statistically show the significant difference with the confidential of 95% by LSD

Table 4-5 Effect of dose of egg shell to lead removal by 4 types of egg shells (Unadjusted pH wastewater , 90 mins of contact time)

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 : The difference of alphabets in each column statistically show the significant difference with the confidential of 95% by LSD

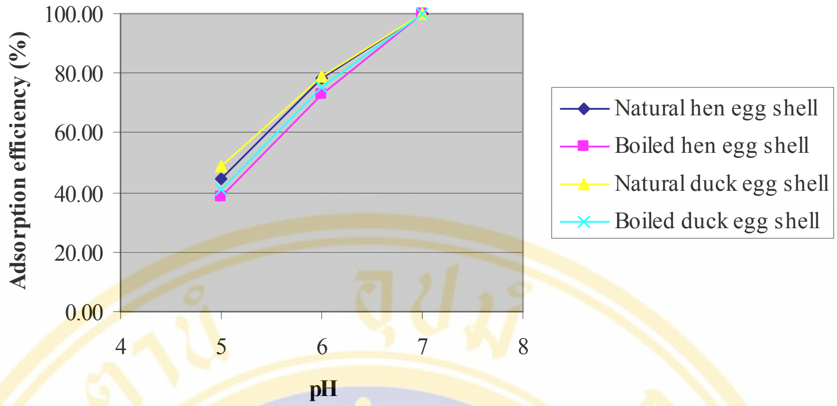


Figure 4-5 Effect of pH to lead removal by 4 types of egg shells

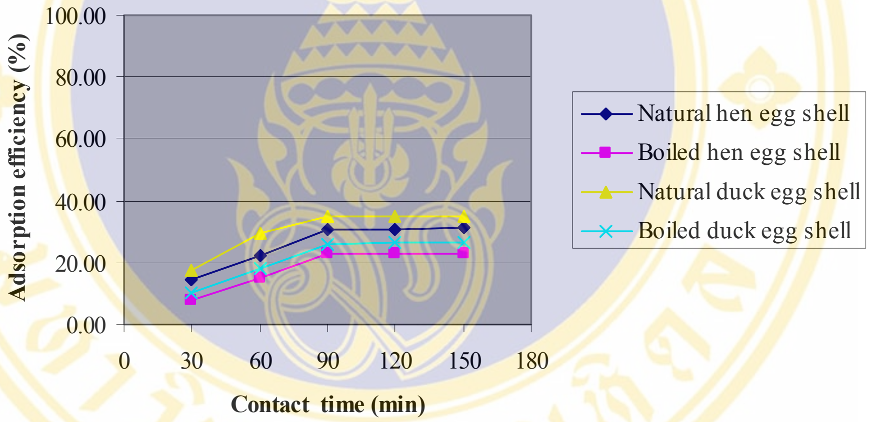


Figure 4-6 Effect of contact time to lead removal by 4 types of egg shells

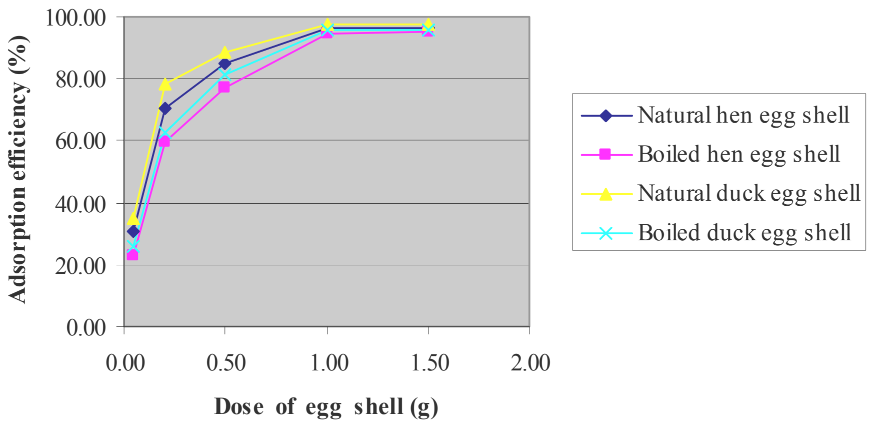


Figure 4-7 Effect of dose of egg shell to lead removal by 4 types of egg shells

According to the chemical composition analysis in Table 4-2, egg shell mainly composed of $CaCO_3$. Major alkaline contributors in egg shell is $CaCO_3$ so it was expected that any aqueous solution equilibrated with egg shell become more basic that confirmed with following mechanism (4).

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

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

Hydrolysis reaction of $CaCO_3$ occurred basic solution because Ca^{2+} and OH^- increased pH of solution as well as this experiment, adding various dose of egg shells into wastewater increased pH of solution that are shown in Table 4-6

Table 4-6 Final pH at various dose of egg shell

Dose of Egg shell (g)	Final pH at various dose 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
0.2	1.75 ± 0.02	1.74 ± 0.01	1.76 ± 0.02	1.73 ± 0.02
0.5	4.48 ± 0.03	4.44 ± 0.03	4.52 ± 0.01	4.44 ± 0.02
1.0	5.85 ± 0.01	5.80 ± 0.02	5.89 ± 0.03	5.82 ± 0.02
1.5	5.88 ± 0.02	5.85 ± 0.02	5.92 ± 0.02	5.84 ± 0.01

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

4.4 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. Unadjusted pH wastewater was used because lead tended to be precipitated at pH 6 so final concentration of lead was too low for study of adsorption isotherm.

The experimental data were calculated to determine the adsorption isotherm using the Langmuir and Freundlich model. In this study both models were applied to describe the relationship between the amount of lead adsorbed and dose of egg shell in wastewater. The Langmuir model has assumption that the equilibrium is attained when a monolayer of the adsorbate molecules saturates the adsorbent. While Freundlich model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage (52).

As the results from Table 4-6, all final concentration (C_e) of lead after sorbed by 4 types of egg shells were plot of C_e versus C_e/Q_e for Langmuir model as shown in Figure 4-8 to 4-11 , whereas the Freundlich model was plot log C_e versus log Q_e as shown in Figure 4-12 to 4-15 ,and values of the constants for each type of egg shells were determined after linearizing the equations through linear regression analysis.

Table 4-7 The final concentration of lead at various dose of egg shell and adsorption capacity for adsorption isotherm

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	0.142	0.708	1.343	-0.022	-0.150
	0.50	0.548	0.182	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

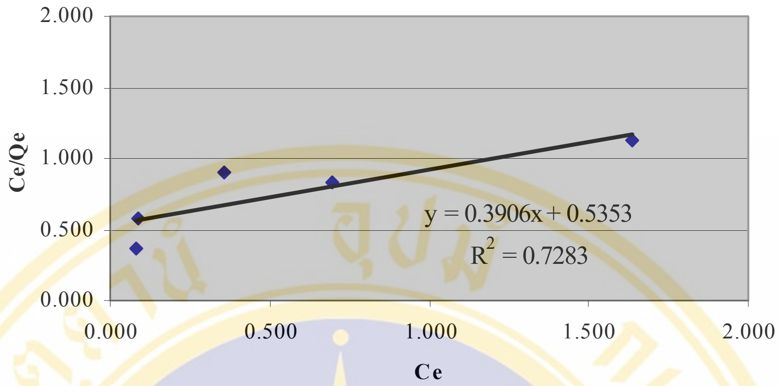


Figure 4-8 Langmuir adsorption isotherm for lead removal using natural hen egg shell

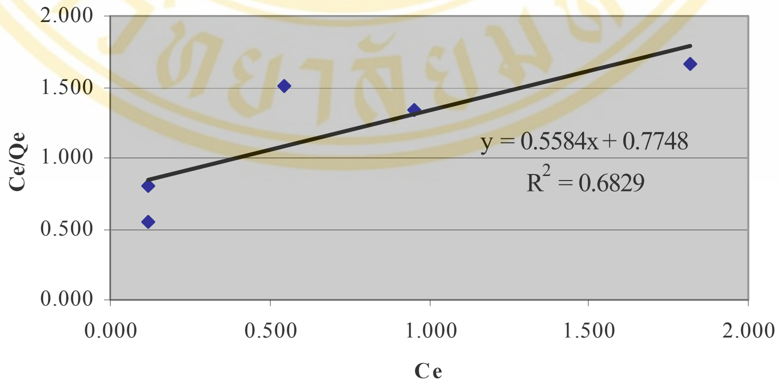


Figure 4-9 Langmuir adsorption isotherm for lead removal using boiled hen egg shell

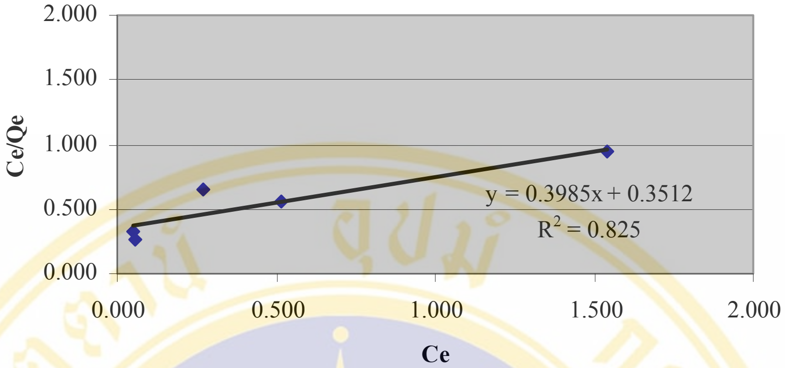


Figure 4-10 Langmuir adsorption isotherm for lead removal using natural duck egg shell

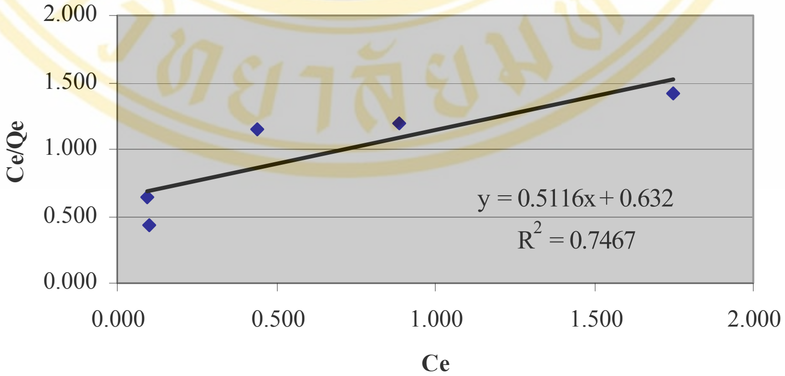


Figure 4-11 Langmuir adsorption isotherm for lead removal using boiled duck egg shell

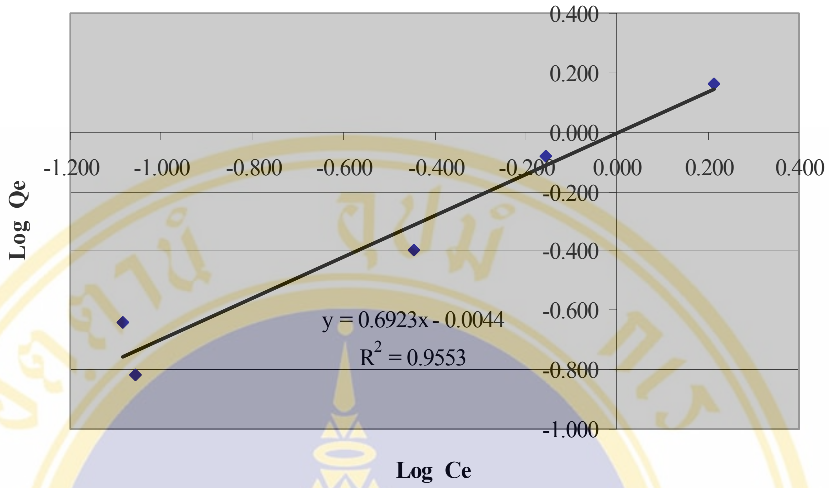


Figure 4-12 Freundlich adsorption isotherm for lead removal using natural hen egg shell

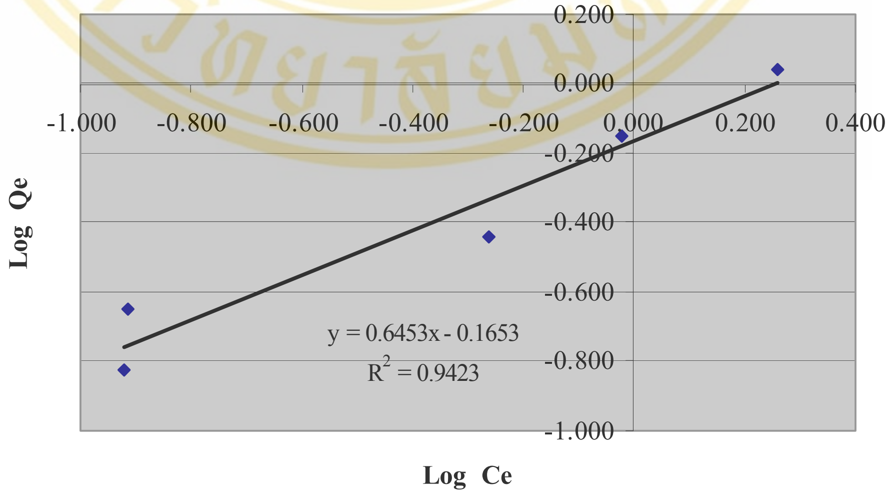


Figure 4-13 Freundlich adsorption isotherm for lead removal using boiled hen egg shell

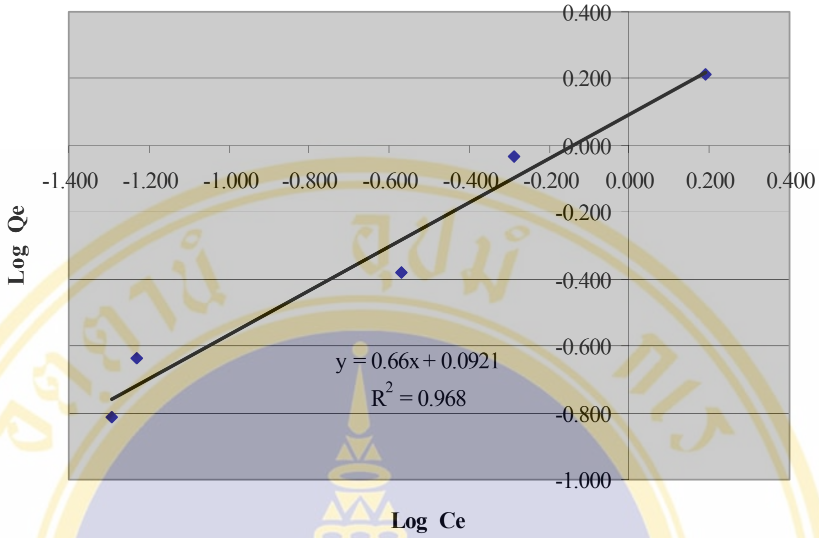


Figure 4-14 Freundlich adsorption isotherm for lead removal using natural duck egg shell

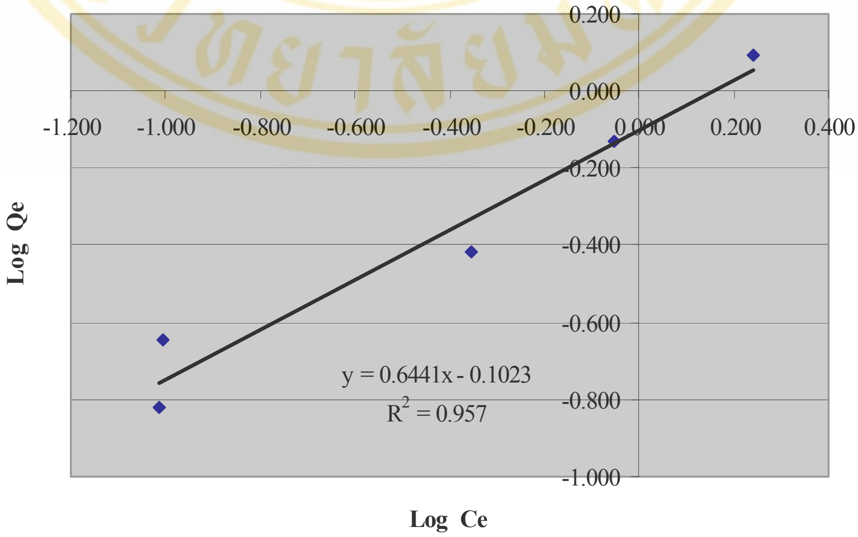


Figure 4-15 Freundlich adsorption isotherm for lead removal using boiled duck egg shell

Table 4-8 Constants and correlation coefficients for lead removal with 4 types of egg shells

Type of egg shell	Langmuir model			Freundlich model		
	X_m	b	R^2	K	1/n	R^2
Natural hen 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

The results are shown in Table 4-8 which indicated that the Langmuir equation were fitted to the data with the least square fit (R^2) of natural and boiled hen egg shell , natural and boiled duck egg shell were 0.7283 and 0.6829 , 0.8250 and 0.7467 , respectively. For the Freundlich equation, the value of R^2 of natural and boiled hen egg shell , natural and boiled duck egg shell were 0.9553 and 0.9423 , 0.9680 and 0.9570 respectively. The all constant values in Langmuir (X_m,b) and Freundlich (K,1/n) equations are also presented in Table 4-8.

In our experimental ranges, the results of 4 types of egg shells tended to be described by the Freundlich model, because the regression line obtained from the Freundlich curve tended to be fit better than the Langmuir curve.

The constant value (K) given by the Freundlich equation for natural and boiled hen egg shell , natural and boiled duck egg shell were 0.9889 and 0.6834, 1.2362 and 0.7901, respectively. Normally value of 1/n is between 0.2 to 0.7 (48). In this study 1/n values is about 0.64 - 0.69.

The calculated n value was qualitative related to the distribution of site bonding energies. The n values obtained from this study were higher than 1, which may indicated that the energies of adsorption were decreased with the increasing of surface area of egg shell covered the heavy metal ion (53).

From the results in adsorption isotherm experiments, the K values in Freundlich equation (Table 4-8) , the values of which express the selective uptake of lead and affinity of adsorbent, K values can be used to compare the removal efficiency of each adsorbent for different components. It demonstrated 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 results were consistent with Polamesanaporn Y.(27) who studied on the comparison of cadmium removal efficiency by natural and protein - removed hen egg shell. Removal efficiency of natural egg shell was higher than protein - removed egg shell.

From this experiment, natural hen and duck egg shells have protein fiber more 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 hen egg shell to bind lead ions better than boiled duck and hen egg shell. Moreover, acid condition of wastewater may caused protein fiber in natural hen and duck egg shell contracted and tightly captured that blocked reaction between H^+ and $CaCO_3$. This phenomenon resulted in decreasing of solubility of natural hen and duck egg shell so amount of adsorbent increased. In addition ,removal efficiency of duck egg shell was higher than hen egg shell because duck egg shells had pore per square-centimeter more than hen egg shells that was consistent with Kasetsuwan S. (16).

Chemical composition analysis from XRF in Table 4-2 indicated that $CaCO_3$ in 4 types of egg shells may slightly affected to different removal efficiency due to amount of $CaCO_3$ were slightly different.

From this study, removal of lead by 4 types of egg shells might go 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) which increased final pH more than 4 so precipitation might take part in the adsorption process that confirm with Figure 2-1, 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 but at low dose of egg shell (0.05-0.2 g.), final pH of solution was lower than 4 so adsorption was the main mechanism.

This results were consistent with other studies that 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 (54). Moreover, the results from this study were consistent with Boonpaniad C.(55) who studied the removal of lead and zinc in synthetic wastewater by fly ash. Hydroxide ion might participate in the adsorption process and increased the pH of solution so adsorption capacity will increase. Formation of $Pb(OH)_2$ on the surface of ash was presumably mechanism followed by adsorption. Precipitation of some $Pb(OH)_2$ could be deposit on fly ash particles.

Comparative with the study of Krisanasup S.(45) who studied about lead removal using column of egg shell. The results showed that egg shell had a good removal efficiency at all condition (99 % at pH 3, 5, 7 and 9) as well as the results of Surasen C.(3) that studied the efficiency and suitable condition of Cd removal in synthetic wastewater by egg shell filter. The highest removal efficiency more than 99 % at the 50 cm. height of egg shell, 5 mg/L of Cd concentration for 24 hours of filtration time. From the results of these studies showed that the highest removal efficiency were higher than the efficiency at optimum condition from this experiment (97.51 %).

Comparative with other studies that related to removal of lead from battery manufacturing wastewater with similar composition adsorbents such as the results of Poomngam C. (38) who studied the removal of 5.980 mg/L of initial lead concentration using cockle shells and mussel shells. The best adsorbent was 20-60 mesh size particle of cockle shells. The constant from Freundlich adsorption isotherm was found to be 9.46×10^5 , the best removal efficiency was 98.33 % that slightly better than efficiency at optimum condition from this study (97.51 %). Amount of $CaCO_3$ in cockle shell (96.83 %) were slightly higher than natural duck egg shell (96.73 %) that may promote increasing of removal efficiency. In addition, the results of Naksawas S.(39) who studied the removal of 5.849 mg/L of initial lead concentration using ground fish scale, the optimum conditions were at 30 g of ground fish scale (20-50 mesh size particle), pH 8 and 2 hours of the settling time. Optimum removal efficiency was 99.20 % that was higher than 97.51 % at optimum condition of this study.

Table 4-9 Constants and correlation coefficients for lead removal with other adsorbents

Type of adsorbents	**Langmuir model**			**Freundlich model**			**Reference**
	X_m	b	R^2	K	1/n	R^2	
Crab shell	-0.0957	7.2674	0.4645	1050	3.61	0.8596	Tanusa S. (28)
Fly ash	-	-	-	10.43	1.07	-	Cho H. *et al.* (56)
Crab shell	-	-	0.990	-	-	0.900	H.K. An, *et al.* (43)
Grape stalk	0.241	82.84	0.959	0.296	0.161	0.729	Martinez M.,*et al.*(48)
Cereal chaff	12.5	0.0920	0.996	1.102	5.747	0.952	Han R., *et al.*(47)
Banana stem	91.74	0.04	0.974	8.00	0.46	0.991	Nocline B.F., *et al.*(57)

The results from Table 4-9 are shown that removal of lead with basic adsorbent material (crab shell and fly ash) mostly tended to be fit with Freundlich model as well as the results from this study. K values can be used to compare the removal efficiency. Removal efficiency of crab shell and fly ash were higher than 4 types of egg shell. Moreover, other agricultural waste adsorbents tended to be fit with Langmuir model (grape stalk and cereal chaff) and Freundlich model (banana stem).

CHAPTER V
CONCLUSION AND RECOMMENDATION

5.1 Conclusion

From the experimental results , it is demonstrated that egg shells are able to be an alternative raw material for lead removal. On the basis of the results reported in the present investigation, the conclusion are as follows :

The characteristics of egg shells used in this study were white powder (duck egg shells) and brown powder (hen egg shells). Pore site of natural and boiled duck egg shells were 0.2-0.4 µm , natural and boiled hen egg shells were 0.3-0.6 µm. Natural and boiled duck egg shells had pore per square-centimeter more than natural and boiled hen egg shells. Moreover, amount and distribution of protein fiber in natural hen and duck egg shells were higher than boiled hen and duck egg shells. The chemical composition in 4 types of egg shells were mainly composed of $CaCO_3$ and a few of other elements ; i.e. S, Mg, P, Al, K, Sr.

The results from this work showed that the optimum pH for removal of lead by 4 types of egg shells were 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. And the contact time of approximately 90 minutes was require on egg shells to reach the equilibrium for lead removal from battery manufacturing wastewater. The suitable amount of egg shell were 1.0 g. for 2.365 mg/L of lead in 100 mL of wastewater. Final concentration of lead at optimum condition was lower than the wastewater quality standard.

Considering both predicting models used in this experiments, the adsorption isotherm data tended to be fit with the Freundlich model. Form this research, precipitation might take part in the adsorption process, especially at the high doses of egg shells which increased the high final pH of solution more than 4. 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. In the study of adsorption isotherm, final pH should be stable when adsorbents were filled into wastewater. From this experiment, final pH varied according to various dose of egg shell that was the limitation of real wastewater for uncontrol final pH and it was different from synthetic wastewater which filled fixed dose of adsorbents into various initial concentration of wastewater so final pH was stable.

In summary, the egg shell could remove lead from battery manufacturing wastewater due to its physical and chemical properties. Factor of egg shell that affected to removal of lead such as $CaCO_3$, pore structure and functional group i.e., carboxyl , amine and sulfate group. Moreover, egg shell is neutralizing agent, any aqueous solution equilibrated with egg shell become more basic so heavy metal can precipitate and deposit on egg shell particles. The egg shell was good for the heavy metal removal. This experiment was cheap, easy to carry out, and appropriate for the low quantity of wastewater. In addition, it could reduce chemical residues, decrease operation cost, and possible to recycle of waste or by-product.

5.2 Recommendation

5.2.2.1 Be careful about preparing of egg shells , when they were taken into hot air oven, temperature should not higher than 40 ^oC because protein fiber in egg shell could denature.

5.2.2.2 Pilot scale should be performed in further studied. Egg shell could be packed in column but clogging problem should be considered. So during the experiment, the column should be washed regularly.

5.2.2.3 Further study should be conducted using other types of wastewater containing higher concentrations of heavy metals and comparative study removal efficiency of lead with other adsorbents should be investigated.

5.2.2.4 Egg shells after treatment should be mixed with cement or other appropriate substances for protection the leachate of lead into the environment.

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APPENDIX

APPENDIX A
WASTEWATER QUALITY STANDARD

Table A-1 The wastewater quality standard control of Industrial Works Department in 1992 (continued)

Characteristic of Wastewater	Unit	Standard
1. pH	mg/L	5-9
2. Permanganate	mg/L	<60
3. Total Dissolved Solid (TDS)	mg/L	<2000 or <5000
4. Sulfide (H_2S)	mg/L	< 1.0
5. Cyanide (HCN)	mg/L	<0.2
6. Heavy Metals		
- Zinc	mg/L	< 5.0
- Chromium	mg/L	< 0.5
- Arsenic	mg/L	< 0.25
- Copper	mg/L	< 1.0
- Mercury	mg/L	< 0.005
- Cadmium	mg/L	< 0.03
- Barium	mg/L	< 1.0
- Selenium	mg/L	< 0.2
- Lead	mg/L	< 0.2
- Nickel	mg/L	< 0.2
- Manganese	mg/L	< 0.5
- Silver	mg/L	-

Source : Department of Industrial Works ,1992 (15)

Table A-1 The wastewater quality standard control of Industrial Works Department in 1992 (continued)

Characteristic of Wastewater	**Unit**	**Standard**
7. Tar	mg/L	-
8. Oil and Grease	mg/L	< 5.0
9. Formaldehyde	mg/L	< 1.0
10. Phenol	mg/L	< 1.0
11. Free Chloride	mg/L	< 1.0
12. Pesticide	mg/L	-
13. Radioactive	mg/L	-
14. Suspended Solids (SS)	mg/L	The ratio between effluent and water - 1/8 to 1/150 < 30 - 1/151 to 1/300 < 60 - 1/301 to 1/500 < 150
15. BOD	mg/L	< 20
16. Temperature	^{0}C	< 40
17. Color and Odor	-	Aesthetic
18. TKN	mg/L	< 40
19. COD	mg/L	< 120

Source : Department of Industrial Works ,1992 (15)

APPENDIX B
HEAVY METAL ANALYSIS

The Analysis of Lead Concentration Using Nitric Acid - Hydrochloric Acid Digestion Method

Add 100 ml of water sample to beaker

Add 3 ml of Conc. HNO_3

Place beaker on the hot plate

Evaporate until the final volumn reduce to less than 5 ml and cool down

Add 5 ml of Conc. HNO_3

Cover container with a watch glass

Place beaker on the hot plate
(Increase Temp. of hot plate so that a gentle reflux action occurs)

Evaporate until the final volumn reduce to less than 5 ml and cool down
(until digestate is light in color)

Add 5 ml of 6 M. HCl

Heat at 95^{O}C for 15 minutes and allow it to cool down

Wash down beaker walls and watch glass with deionized water

Filter through filter paper no.4

Adjust final volumn to 100 ml with deionized water

Stored at 4 ^{O}C

Diagram B-1 The Analysis of Lead Concentration Using Nitric Acid-Hydrochloric Acid Digestion Method (51)

APPENDIX C
EXPERIMENTAL INSTRUMENT

Figure C-1 Atomic Absorption Spectrophotometer

Figure C-2 X-ray Fluorescence Spectrometer

Figure C-3 Scanning Electron Microscope (SEM)

Figure C-4 Rotary Shaker

APPENDIX D
STATISTICAL ANALYSIS

Effect of pH_Natural hen egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
5	3	.58700	.014526	.008386	.55092	.62308	.572	.601
6	3	.07667	.005132	.002963	.06392	.08941	.071	.081
7	3	.00000	.000000	.000000	.00000	.00000	.000	.000
Total	9	.22122	.276442	.092147	.00873	.43371	.000	.601

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.611	2	.305	3860.942	.000
Within Groups	.000	6	.000		
Total	.611	8			

Multiple Comparisons

Dependent Variable: final concentration

LSD

(I) pH of wastewater	(J) pH of wastewater	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
5	6	.51033*	.007262	.000	.49256	.52810
	7	.58700*	.007262	.000	.56923	.60477
6	5	-.51033*	.007262	.000	-.52810	-.49256
	7	.07667*	.007262	.000	.05890	.09444
7	5	-.58700*	.007262	.000	-.60477	-.56923
	6	-.07667*	.007262	.000	-.09444	-.05890

*. The mean difference is significant at the .05 level.

Effect of pH_Boiled hen egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
5	3	.65033	.013868	.008007	.61588	.68478	.635	.662
6	3	.09433	.005508	.003180	.08065	.10801	.089	.100
7	3	.00000	.000000	.000000	.00000	.00000	.000	.000
Total	9	.24822	.304428	.101476	.01422	.48223	.000	.662

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.741	2	.370	4991.552	.000
Within Groups	.000	6	.000		
Total	.741	8			

Multiple Comparisons

Dependent Variable: final concentration
LSD

(I) pH of wastewater	(J) pH of wastewater	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
5	6	.55600*	.007034	.000	.53879	.57321
	7	.65033*	.007034	.000	.63312	.66755
6	5	-.55600*	.007034	.000	-.57321	-.53879
	7	.09433*	.007034	.000	.07712	.11155
7	5	-.65033*	.007034	.000	-.66755	-.63312
	6	-.09433*	.007034	.000	-.11155	-.07712

*. The mean difference is significant at the .05 level.

Effect of pH_Natural duck egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	Upper Bound	Minimum	Maximum
5	3	.54567	.013317	.007688	.51259	.57875	.531	.557
6	3	.07267	.004726	.002728	.06093	.08441	.069	.078
7	3	.00000	.000000	.000000	.00000	.00000	.000	.000
Total	9	.20611	.256700	.085567	.00879	.40343	.000	.557

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.527	2	.263	3957.307	.000
Within Groups	.000	6	.000		
Total	.527	8			

Multiple Comparisons

Dependent Variable: final concentration
LSD

(I) pH of wastewater	(J) pH of wastewater	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	Upper Bound
5	6	.47300*	.006661	.000	.45670	.48930
	7	.54567*	.006661	.000	.52937	.56197
6	5	-.47300*	.006661	.000	-.48930	-.45670
	7	.07267*	.006661	.000	.05637	.08897
7	5	-.54567*	.006661	.000	-.56197	-.52937
	6	-.07267*	.006661	.000	-.08897	-.05637

*. The mean difference is significant at the .05 level.

Effect of pH_Boiled duck egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
5	3	.63033	.013868	.008007	.59588	.66478	.615	.642
6	3	.08600	.005292	.003055	.07286	.09914	.080	.090
7	3	.00000	.000000	.000000	.00000	.00000	.000	.000
Total	9	.23878	.296111	.098704	.01117	.46639	.000	.642

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.701	2	.351	4772.416	.000
Within Groups	.000	6	.000		
Total	.701	8			

Multiple Comparisons

Dependent Variable: final concentration
LSD

(I) pH of wastewater	(J) pH of wastewater	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
5	6	.54433*	.006997	.000	.52721	.56146
	7	.63033*	.006997	.000	.61321	.64746
6	5	-.54433*	.006997	.000	-.56146	-.52721
	7	.08600*	.006997	.000	.06888	.10312
7	5	-.63033*	.006997	.000	-.64746	-.61321
	6	-.08600*	.006997	.000	-.10312	-.06888

*. The mean difference is significant at the .05 level.

Effect of Contact time _ Natural hen egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
30	3	2.01700	.005000	.002887	2.00458	2.02942	2.01	2.02
60	3	1.83133	.015503	.008950	1.79282	1.86984	1.82	1.85
90	3	1.63700	.006000	.003464	1.62210	1.65190	1.63	1.64
120	3	1.63367	.011504	.006642	1.60509	1.66224	1.62	1.65
150	3	1.63133	.011240	.006489	1.60341	1.65925	1.62	1.64
Total	15	1.75007	.159460	.041172	1.66176	1.83837	1.62	2.02

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.355	4	.089	792.109	.000
Within Groups	.001	10	.000		
Total	.356	14			

Multiple Comparisons

Dependent Variable: final concentration

LSD

(I) contact time	(J) contact time	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
30	60	.18567*	.008641	.000	.16641	.20492
	90	.38000*	.008641	.000	.36075	.39925
	120	.38333*	.008641	.000	.36408	.40259
	150	.38567*	.008641	.000	.36641	.40492
60	30	-.18567*	.008641	.000	-.20492	-.16641
	90	.19433*	.008641	.000	.17508	.21359
	120	.19767*	.008641	.000	.17841	.21692
	150	.20000*	.008641	.000	.18075	.21925
90	30	-.38000*	.008641	.000	-.39925	-.36075
	60	-.19433*	.008641	.000	-.21359	-.17508
	120	.00333	.008641	.708	-.01592	.02259
	150	.00567	.008641	.527	-.01359	.02492
120	30	-.38333*	.008641	.000	-.40259	-.36408
	60	-.19767*	.008641	.000	-.21692	-.17841
	90	-.00333	.008641	.708	-.02259	.01592
	150	.00233	.008641	.793	-.01692	.02159
150	30	-.38567*	.008641	.000	-.40492	-.36641
	60	-.20000*	.008641	.000	-.21925	-.18075
	90	-.00567	.008641	.527	-.02492	.01359
	120	-.00233	.008641	.793	-.02159	.01692

*. The mean difference is significant at the .05 level.

Effect of Contact time _ Boiled hen egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	Upper Bound	Minimum	Maximum
30	3	2.17900	.007000	.004041	2.16161	2.19639	2.17	2.19
60	3	2.00333	.014012	.008090	1.96853	2.03814	1.99	2.02
90	3	1.81900	.008544	.004933	1.79778	1.84022	1.81	1.83
120	3	1.82133	.016258	.009387	1.78095	1.86172	1.80	1.83
150	3	1.82133	.013013	.007513	1.78901	1.85366	1.81	1.83
Total	15	1.92880	.149148	.038510	1.84620	2.01140	1.80	2.19

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.310	4	.077	515.174	.000
Within Groups	.002	10	.000		
Total	.311	14			

Multiple Comparisons

Dependent Variable: final concentration
LSD

(I) contact time	(J) contact time	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	Upper Bound
30	60	.17567*	.010013	.000	.15336	.19798
	90	.36000*	.010013	.000	.33769	.38231
	120	.35767*	.010013	.000	.33536	.37998
	150	.35767*	.010013	.000	.33536	.37998
60	30	-.17567*	.010013	.000	-.19798	-.15336
	90	.18433*	.010013	.000	.16202	.20664
	120	.18200*	.010013	.000	.15969	.20431
	150	.18200*	.010013	.000	.15969	.20431
90	30	-.36000*	.010013	.000	-.38231	-.33769
	60	-.18433*	.010013	.000	-.20664	-.16202
	120	-.00233	.010013	.820	-.02464	.01998
	150	-.00233	.010013	.820	-.02464	.01998
120	30	-.35767*	.010013	.000	-.37998	-.33536
	60	-.18200*	.010013	.000	-.20431	-.15969
	90	.00233	.010013	.820	-.01998	.02464
	150	.00000	.010013	1.000	-.02231	.02231
150	30	-.35767*	.010013	.000	-.37998	-.33536
	60	-.18200*	.010013	.000	-.20431	-.15969
	90	.00233	.010013	.820	-.01998	.02464
	120	.00000	.010013	1.000	-.02231	.02231

*. The mean difference is significant at the .05 level.

Effect of Contact time _ Natural duck egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
30	3	1.95633	.009018	.005207	1.93393	1.97874	1.95	1.97
60	3	1.66100	.014422	.008327	1.62517	1.69683	1.65	1.68
90	3	1.54400	.004000	.002309	1.53406	1.55394	1.54	1.55
120	3	1.53567	.006506	.003756	1.51950	1.55183	1.53	1.54
150	3	1.53500	.013229	.007638	1.50214	1.56786	1.52	1.55
Total	15	1.64640	.168042	.043388	1.55334	1.73946	1.52	1.97

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.394	4	.099	942.973	.000
Within Groups	.001	10	.000		
Total	.395	14			

Multiple Comparisons

Dependent Variable: final concentration
LSD

(I) contact time	(J) contact time	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
30	60	.29533*	.008348	.000	.27673	.31393
	90	.41233*	.008348	.000	.39373	.43093
	120	.42067*	.008348	.000	.40207	.43927
	150	.42133*	.008348	.000	.40273	.43993
60	30	-.29533*	.008348	.000	-.31393	-.27673
	90	.11700*	.008348	.000	.09840	.13560
	120	.12533*	.008348	.000	.10673	.14393
	150	.12600*	.008348	.000	.10740	.14460
90	30	-.41233*	.008348	.000	-.43093	-.39373
	60	-.11700*	.008348	.000	-.13560	-.09840
	120	.00833	.008348	.342	-.01027	.02693
	150	.00900	.008348	.306	-.00960	.02760
120	30	-.42067*	.008348	.000	-.43927	-.40207
	60	-.12533*	.008348	.000	-.14393	-.10673
	90	-.00833	.008348	.342	-.02693	.01027
	150	.00067	.008348	.938	-.01793	.01927
150	30	-.42133*	.008348	.000	-.43993	-.40273
	60	-.12600*	.008348	.000	-.14460	-.10740
	90	-.00900	.008348	.306	-.02760	.00960
	120	-.00067	.008348	.938	-.01927	.01793

*. The mean difference is significant at the .05 level.

Effect of Contact time _ Boiled duck egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
30	3	2.11700	.008000	.004619	2.09713	2.13687	2.11	2.13
60	3	1.93567	.010504	.006064	1.90957	1.96176	1.93	1.95
90	3	1.74733	.068311	.039439	1.57764	1.91703	1.70	1.83
120	3	1.73367	.014503	.008373	1.69764	1.76969	1.72	1.75
150	3	1.73267	.013317	.007688	1.69959	1.76575	1.72	1.75
Total	15	1.85327	.160291	.041387	1.76450	1.94203	1.70	2.13

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.349	4	.087	83.498	.000
Within Groups	.010	10	.001		
Total	.360	14			

Multiple Comparisons

Dependent Variable: final concentration

LSD

(I) contact time	(J) contact time	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
30	60	.18133*	.026403	.000	.12250	.24016
	90	.36967*	.026403	.000	.31084	.42850
	120	.38333*	.026403	.000	.32450	.44216
	150	.38433*	.026403	.000	.32550	.44316
60	30	-.18133*	.026403	.000	-.24016	-.12250
	90	.18833*	.026403	.000	.12950	.24716
	120	.20200*	.026403	.000	.14317	.26083
	150	.20300*	.026403	.000	.14417	.26183
90	30	-.36967*	.026403	.000	-.42850	-.31084
	60	-.18833*	.026403	.000	-.24716	-.12950
	120	.01367	.026403	.616	-.04516	.07250
	150	.01467	.026403	.591	-.04416	.07350
120	30	-.38333*	.026403	.000	-.44216	-.32450
	60	-.20200*	.026403	.000	-.26083	-.14317
	90	-.01367	.026403	.616	-.07250	.04516
	150	.00100	.026403	.971	-.05783	.05983
150	30	-.38433*	.026403	.000	-.44316	-.32550
	60	-.20300*	.026403	.000	-.26183	-.14417
	90	-.01467	.026403	.591	-.07350	.04416
	120	-.00100	.026403	.971	-.05983	.05783

*. The mean difference is significant at the .05 level.

Effect of Dose of Egg shell _ Natural hen egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
.05	3	1.63700	.006000	.003464	1.62210	1.65190	1.63	1.64
.20	3	.69767	.008505	.004910	.67654	.71879	.689	.706
.50	3	.35867	.010504	.006064	.33257	.38476	.348	.369
1.00	3	.08200	.004000	.002309	.07206	.09194	.078	.086
1.50	3	.08467	.009074	.005239	.06213	.10721	.078	.095
Total	15	.57200	.598808	.154612	.24039	.90361	.078	1.64

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5.019	4	1.255	19792.45	.000
Within Groups	.001	10	.000		
Total	5.020	14			

Multiple Comparisons

Dependent Variable: final concentration

LSD

(I) dose of eggshell	(J) dose of eggshell	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
.05	.20	.93933*	.006501	.000	.92485	.95382
	.50	1.27833*	.006501	.000	1.26385	1.29282
	1.00	1.55500*	.006501	.000	1.54051	1.56949
	1.50	1.55233*	.006501	.000	1.53785	1.56682
.20	.05	-.93933*	.006501	.000	-.95382	-.92485
	.50	.33900*	.006501	.000	.32451	.35349
	1.00	.61567*	.006501	.000	.60118	.63015
	1.50	.61300*	.006501	.000	.59851	.62749
.50	.05	-1.27833*	.006501	.000	-1.29282	-1.26385
	.20	-.33900*	.006501	.000	-.35349	-.32451
	1.00	.27667*	.006501	.000	.26218	.29115
	1.50	.27400*	.006501	.000	.25951	.28849
1.00	.05	-1.55500*	.006501	.000	-1.56949	-1.54051
	.20	-.61567*	.006501	.000	-.63015	-.60118
	.50	-.27667*	.006501	.000	-.29115	-.26218
	1.50	-.00267	.006501	.690	-.01715	.01182
1.50	.05	-1.55233*	.006501	.000	-1.56682	-1.53785
	.20	-.61300*	.006501	.000	-.62749	-.59851
	.50	-.27400*	.006501	.000	-.28849	-.25951
	1.00	.00267	.006501	.690	-.01182	.01715

*. The mean difference is significant at the .05 level.

Effect of Dose of Egg shell _ Boiled hen egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
.05	3	1.81900	.008544	.004933	1.79778	1.84022	1.81	1.83
.20	3	.95000	.008000	.004619	.93013	.96987	.942	.958
.50	3	.54800	.018000	.010392	.50329	.59271	.530	.566
1.00	3	.14200	.030414	.017559	.06645	.21755	.122	.177
1.50	3	.11967	.005508	.003180	.10599	.13335	.114	.125
Total	15	.71573	.652296	.168422	.35450	1.07696	.114	1.83

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5.954	4	1.489	5254.796	.000
Within Groups	.003	10	.000		
Total	5.957	14			

Multiple Comparisons

Dependent Variable: final concentration
LSD

(I) dose of egg shell	(J) dose of egg shell	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
.05	.20	.86900*	.013742	.000	.83838	.89962
	.50	1.27100*	.013742	.000	1.24038	1.30162
	1.00	1.67700*	.013742	.000	1.64638	1.70762
	1.50	1.69933*	.013742	.000	1.66871	1.72995
.20	.05	-.86900*	.013742	.000	-.89962	-.83838
	.50	.40200*	.013742	.000	.37138	.43262
	1.00	.80800*	.013742	.000	.77738	.83862
	1.50	.83033*	.013742	.000	.79971	.86095
.50	.05	-1.27100*	.013742	.000	-1.30162	-1.24038
	.20	-.40200*	.013742	.000	-.43262	-.37138
	1.00	.40600*	.013742	.000	.37538	.43662
	1.50	.42833*	.013742	.000	.39771	.45895
1.00	.05	-1.67700*	.013742	.000	-1.70762	-1.64638
	.20	-.80800*	.013742	.000	-.83862	-.77738
	.50	-.40600*	.013742	.000	-.43662	-.37538
	1.50	.02233	.013742	.135	-.00829	.05295
1.50	.05	-1.69933*	.013742	.000	-1.72995	-1.66871
	.20	-.83033*	.013742	.000	-.86095	-.79971
	.50	-.42833*	.013742	.000	-.45895	-.39771
	1.00	-.02233	.013742	.135	-.05295	.00829

*. The mean difference is significant at the .05 level.

Effect of Dose of Egg shell _ Natural duck egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean Lower Bound	95% Confidence Interval for Mean Upper Bound	Minimum	Maximum
.05	3	1.54400	.004000	.002309	1.53406	1.55394	1.54	1.55
.20	3	.51300	.006000	.003464	.49810	.52790	.507	.519
.50	3	.27133	.023587	.013618	.21274	.32993	.249	.296
1.00	3	.05900	.005000	.002887	.04658	.07142	.054	.064
1.50	3	.05067	.002517	.001453	.04442	.05692	.048	.053
Total	15	.48760	.574164	.148248	.16964	.80556	.048	1.55

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	4.614	4	1.154	9016.450	.000
Within Groups	.001	10	.000		
Total	4.615	14			

Multiple Comparisons

Dependent Variable: final concentration
LSD

(I) dose of eggshell	(J) dose of eggshell	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
.05	.20	1.03100*	.009235	.000	1.01042	1.05158
	.50	1.27267*	.009235	.000	1.25209	1.29324
	1.00	1.48500*	.009235	.000	1.46442	1.50558
	1.50	1.49333*	.009235	.000	1.47276	1.51391
.20	.05	-1.03100*	.009235	.000	-1.05158	-1.01042
	.50	.24167*	.009235	.000	.22109	.26224
	1.00	.45400*	.009235	.000	.43342	.47458
	1.50	.46233*	.009235	.000	.44176	.48291
.50	.05	-1.27267*	.009235	.000	-1.29324	-1.25209
	.20	-.24167*	.009235	.000	-.26224	-.22109
	1.00	.21233*	.009235	.000	.19176	.23291
	1.50	.22067*	.009235	.000	.20009	.24124
1.00	.05	-1.48500*	.009235	.000	-1.50558	-1.46442
	.20	-.45400*	.009235	.000	-.47458	-.43342
	.50	-.21233*	.009235	.000	-.23291	-.19176
	1.50	.00833	.009235	.388	-.01224	.02891
1.50	.05	-1.49333*	.009235	.000	-1.51391	-1.47276
	.20	-.46233*	.009235	.000	-.48291	-.44176
	.50	-.22067*	.009235	.000	-.24124	-.20009
	1.00	-.00833	.009235	.388	-.02891	.01224

*. The mean difference is significant at the .05 level.

Effect of Dose of Egg shell _ Boiled duck egg shell

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
.05	3	1.74733	.068311	.039439	1.57764	1.91703	1.70	1.83
.20	3	.88400	.005000	.002887	.87158	.89642	.879	.889
.50	3	.44067	.011504	.006642	.41209	.46924	.429	.452
1.00	3	.09900	.008000	.004619	.07913	.11887	.091	.107
1.50	3	.10033	.013317	.007688	.06725	.13341	.089	.115
Total	15	.65427	.640045	.165259	.29982	1.00871	.089	1.83

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	5.725	4	1.431	1412.903	.000
Within Groups	.010	10	.001		
Total	5.735	14			

Multiple Comparisons

Dependent Variable: final concentration
LSD

(I) dose of egg shell	(J) dose of egg shell	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
.05	.20	.86333*	.025987	.000	.80543	.92124
	.50	1.30667*	.025987	.000	1.24876	1.36457
	1.00	1.64833*	.025987	.000	1.59043	1.70624
	1.50	1.64700*	.025987	.000	1.58910	1.70490
.20	.05	-.86333*	.025987	.000	-.92124	-.80543
	.50	.44333*	.025987	.000	.38543	.50124
	1.00	.78500*	.025987	.000	.72710	.84290
	1.50	.78367*	.025987	.000	.72576	.84157
.50	.05	-1.30667*	.025987	.000	-1.36457	-1.24876
	.20	-.44333*	.025987	.000	-.50124	-.38543
	1.00	.34167*	.025987	.000	.28376	.39957
	1.50	.34033*	.025987	.000	.28243	.39824
1.00	.05	-1.64833*	.025987	.000	-1.70624	-1.59043
	.20	-.78500*	.025987	.000	-.84290	-.72710
	.50	-.34167*	.025987	.000	-.39957	-.28376
	1.50	-.00133	.025987	.960	-.05924	.05657
1.50	.05	-1.64700*	.025987	.000	-1.70490	-1.58910
	.20	-.78367*	.025987	.000	-.84157	-.72576
	.50	-.34033*	.025987	.000	-.39824	-.28243
	1.00	.00133	.025987	.960	-.05657	.05924

*. The mean difference is significant at the .05 level.

Removal efficiency at optimum condition (four types of egg shells)

Descriptives

final concentration

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	3	.08200	.004000	.002309	.07206	.09194	.078	.086
2	3	.12200	.005000	.002887	.10958	.13442	.117	.127
3	3	.05900	.005000	.002887	.04658	.07142	.054	.064
4	3	.09900	.008000	.004619	.07913	.11887	.091	.107
Total	12	.09050	.024582	.007096	.07488	.10612	.054	.127

ANOVA

final concentration

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.006	3	.002	65.508	.000
Within Groups	.000	8	.000		
Total	.007	11			

Multiple Comparisons

Dependent Variable: final concentration
LSD

(I) type of eggshell	(J) type of eggshell	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
1	2	-.04000*	.004655	.000	-.05073	-.02927
	3	.02300*	.004655	.001	.01227	.03373
	4	-.01700*	.004655	.006	-.02773	-.00627
2	1	.04000*	.004655	.000	.02927	.05073
	3	.06300*	.004655	.000	.05227	.07373
	4	.02300*	.004655	.001	.01227	.03373
3	1	-.02300*	.004655	.001	-.03373	-.01227
	2	-.06300*	.004655	.000	-.07373	-.05227
	4	-.04000*	.004655	.000	-.05073	-.02927
4	1	.01700*	.004655	.006	.00627	.02773
	2	-.02300*	.004655	.001	-.03373	-.01227
	3	.04000*	.004655	.000	.02927	.05073

*. The mean difference is significant at the .05 level.

Remark : **Type 1** : Natural hen egg shell
Type 2 : Boiled hen egg shell
Type 3 : Natural duck egg shell
Type 4 : Boiled duck egg shell

BIOGRAPHY

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