

**REMOVAL OF HEAVY METALS FROM WASTEWATER BY ADSORPTION
USING CHITOSAN**

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A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Engineering in Environmental Engineering

Suranaree University of Technology

Academic Year 2002

ISBN 974-533-186-4

การกำจัดโลหะหนักออกจากน้ำเสียโดยการดูดซับด้วยไคโตซาน

นางสาวจินตนา ศรีสะอาด

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สำนักวิชาวิศวกรรมศาสตร์ สาขาวิชาวิศวกรรมสิ่งแวดล้อม

มหาวิทยาลัยเทคโนโลยีสุรนารี

ปีการศึกษา 2545

ISBN 974-533-186-4

Thesis Title

REMOVAL OF HEAVY METALS FROM WASTEWATER BY
ADSORPTION USING CHITOSAN

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

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การกำจัดโลหะหนักออกจากน้ำเสียเป็นหัวข้อที่มีความสำคัญมากในการศึกษาวิจัย โดยในแต่ละปีจะมีการค้นคว้าวิจัยเทคโนโลยีต่างๆ ขึ้นมาจำนวนมากเพื่อกำจัดโลหะหนักที่เป็นอันตรายออกจากน้ำเสียและหนึ่งในเทคโนโลยีที่ได้มีการค้นคว้าวิจัย คือการดูดซับ วัตถุประสงค์ของการวิจัยครั้งนี้ คือ 1) เพื่อวิเคราะห์ประสิทธิภาพของไคโตซานในการดูดซับและการคายโลหะประเภท ตะกั่ว และ สังกะสี ออกจากน้ำเสีย 2) เพื่อศึกษาผลของ pH คลอไรด์ไอออน และผลของโลหะชนิดอื่น ต่อการดูดซับตะกั่ว และสังกะสี 3) เพื่อศึกษา ไอโซเทอร์ม และจลนศาสตร์ ของการดูดซับและการคายโลหะ ของไคโตซาน โดยการนำน้ำเสียจากบ่อบำบัดทางชีวภาพ มหาวิทยาลัยเทคโนโลยีสุรนารี ผสมกับสารละลายมาตรฐานที่ทราบค่าความเข้มข้น ผลจากการศึกษาจลนศาสตร์ และไอโซเทอร์ม พบว่าไคโตซานมีประสิทธิภาพในการกำจัด ตะกั่ว และสังกะสี โดยในช่วงเริ่มต้นการดูดซับจะเกิดขึ้นอย่างรวดเร็ว ไคโตซาน 1 กรัม สามารถดูดซับตะกั่ว 2.7 มิลลิกรัม และสังกะสี 6.5 มิลลิกรัม ที่ความเข้มข้นสมดุลของโลหะทั้งสองชนิดเท่ากับ 1 มิลลิกรัมต่อลิตร ประสิทธิภาพในการกำจัดตะกั่วและสังกะสี โดยไคโตซาน คือ 73.3 เปอร์เซ็นต์ และ 84.6 เปอร์เซ็นต์ ตามลำดับ ในขณะที่ประสิทธิภาพในการคายตะกั่ว และสังกะสีออกจากไคโตซาน คือ 68.1 เปอร์เซ็นต์ และ 66.2 เปอร์เซ็นต์ ตามลำดับ และจากการทดลองจลนศาสตร์ พบว่าการดูดซับและการคายโลหะ โดยไคโตซานสามารถเกิดขึ้นได้ภายใน 24 ชั่วโมง ผลของการศึกษาปัจจัยของน้ำเสีย เช่น pH คลอไรด์ไอออน และสารอื่น เช่น โลหะหนักชนิดอื่น พบว่า ค่า pH ที่เหมาะสมในการดูดซับตะกั่ว และสังกะสี ออกจากน้ำเสียคือ 3.3 และ 7.3 ตามลำดับ และค่า pH ที่เหมาะสมในการคายตะกั่ว และสังกะสี ออกจากไคโตซาน คือ 2.8 และ 2.5 ตามลำดับ ในการศึกษาผลของคลอไรด์ ไอออนต่อการดูดซับโลหะหนัก พบว่า การมีอยู่ของคลอไรด์ ไอออน มีผลทำให้ลดประสิทธิภาพในการดูดซับตะกั่ว โดยไคโตซาน แต่สำหรับสังกะสีพบว่าประสิทธิภาพในการดูดซับด้วยไคโตซานจะเพิ่มขึ้นเล็กน้อยเมื่อมีความเข้มข้นของคลอไรด์ ไอออนในน้ำเสียมากขึ้น ส่วนการมีอยู่ของตะกั่วในน้ำเสียลดประสิทธิภาพในการดูดซับสังกะสี และการมีอยู่ของสังกะสีในน้ำเสียจะทำให้ประสิทธิภาพในการดูดซับตะกั่วของไคโตซานลดลงเช่นกัน

สาขาวิชาวิศวกรรมสิ่งแวดล้อม
ปีการศึกษา 2545

ลายมือชื่อนักศึกษา.....
ลายมือชื่ออาจารย์ที่ปรึกษา.....

**CHINTANA SRISA-ARD : REMOVAL OF HEAVY METALS FROM
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THESIS ADVISOR : Asst. Prof. Dr. Ranjna Jindal, Ph.D., 82 PP.

ISBN 974-533-186-4

CHITOSAN/ADSORPTION/DESORPTION/ISOTHERM/KINETICS

A number of technologies have been developed over the years to remove toxic metals from wastewater. One of the techniques utilized is adsorption. The objectives of this study were: 1) to investigate the effectiveness of chitosan for the adsorption of lead and zinc from wastewater in batch experiments through adsorption/ desorption kinetics, adsorption and desorption isotherm studies; 2) to evaluate the effect of pH, chloride ion concentration, and co-ions on the removal of lead and zinc by adsorption on chitosan. A synthetic wastewater was prepared by mixing wastewater from the biological pond of Suranaree University of Technology with known concentrations of lead and zinc compounds. Kinetics and isotherm studies indicated that lead and zinc can be effectively removed from wastewater by adsorption on chitosan. The rate of sorption was very rapid initially. About 2.7 mg of lead and 6.5 mg of zinc could be adsorbed per gram of chitosan at an equilibrium concentration of 1 mg/L of each of the two heavy metals. Adsorption efficiencies of chitosan for removal of lead and zinc were found to be 73.3% and 84.6%, respectively. Desorption efficiencies were 68.1% and 66.2% for lead and zinc, respectively. Kinetics studies verified that desorption occurred within 24 hours. Effects of influencing parameters such as pH, chloride ion concentration, and complexing agent like co-ions were investigated. The optimum pH for adsorption on chitosan were 3.3 and 7.3, and the optimum pH for desorption were 2.8 and 2.5 for lead and zinc, respectively. Presence of chloride ion under the same operating conditions as for optimum pH determination, reduced the adsorption of lead, but slightly improved adsorption of zinc by chitosan. Presence of lead significantly suppresses zinc adsorption capacity and presence of zinc also suppresses lead adsorption capacity.

สาขาวิชาวิศวกรรมสิ่งแวดล้อม

ปีการศึกษา 2545

ลายมือชื่อนักศึกษา.....

ลายมือชื่ออาจารย์ที่ปรึกษา.....

Acknowledgements

The author would like to express her heartfelt thanks to her thesis advisor, Asst. Prof. Dr. Ranjna Jindal for her valuable guidance throughout this research work. Her support, enthusiasm, and understanding made this study a rewarding experience to the author.

Sincere thanks are also due to Asst. Prof. Dr. Chongchin Polprasert and Dr. Sudjit Karuchit for providing suggestions which were of considerable help in this study.

Finally, the author wishes to acknowledge all the support extended by her parents and friends throughout the course of this study.

Chintana Srisa-ard

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List of Abbreviations and Symbols

a	=	Empirical constant for Langmiur isotherm
b	=	Empirical constant for Langmiur isotherm
BOD	=	Biochemical oxygen demand
C_0	=	Concentration of adsorbate at the beginning, mg/L
C_e	=	Equilibrium concentration, mg/L
Co	=	Cobalt
COD	=	Chemical oxygen demand
C_t	=	Concentration of adsorbate at time t, mg/L
h	=	Hour
k	=	Reaction rate constant
K_f	=	Empirical constant for Freundlich isotherm
m	=	Mass
n	=	Empirical constant for Freundlich isotherm
NOM	=	Natural organic matter
rpm	=	Revolutions per minute
t	=	Time
x	=	Amount of metal adsorbed, mg
x/m	=	Amount of adsorbate adsorbed per unit weight of adsorbent, mg/g

Chapter I

Introduction

1.1 Statement of the problem

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in aquatic environment. Mine drainage, industrial and domestic effluents, agricultural run-off, acid rain etc. have all contributed to some extent to the metal loads in the water bodies. Metals are of special concern because they are non-degradable and therefore persistent. The effects of metals in water and wastewater range from beneficial through troublesome to dangerously toxic. Some metals may be either beneficial or toxic, depending on concentration.

Lead (Pb) is a serious cumulative body poison. Natural waters seldom contains more than 5 µg/L. Lead is generated in the effluents from the production of television picture tube, storage batteries, pigments, petroleum, fuel, photographic materials, mining, smelting, painting, etc. Tap waters that are soft, acidic, and not suitably treated may contain lead resulting from an attack on lead service pipes or solder pipe joints (Clesceri et al., 1990).

Zinc (Zn) is a bluish white metal with an atomic weight of 65.37. characteristics are as follows: density, 7.13 g/cm³ at 25 °C; melting point, 419.6 °C; and boiling point, 907 °C. Zinc is chemically active and alloys readily with other metals. These properties are utilized in industrially in preparing a large number of zinc-containing alloys and compounds. The relatively high position of zinc in the electromotive series largely accounts for its extensive use to protect iron and steel products against corrosion (Nriagu, 1980).

The efficient removal of toxic metals from wastewater is an important matter and it is a widely-studied area. A number of technologies have been developed over the years to remove toxic metals from wastewater. Physical treatment can also be used to remove small concentrations of hazardous substances dissolved in water that would never settle out. One of the most commonly used techniques involves the

process of adsorption, which is the physical adhesion of chemicals onto the surface of a solid. The effectiveness of the adsorbent is directly related to the amount of surface area available to attract the molecules or particles of contaminant (Master, 1991).

Chitosan is a biopolymer, which is extracted from crustacean shells or from fungal biomass. The high porosity of this natural polymer results in novel binding properties for metal ions such as cadmium, copper, lead, uranyl, mercury, and chromium (Guibal et al., 1998). Chitosan has been used for about three decades in water purification processes. When chitosan is spread over oil spills it holds the oil mass together making it easier to clean up the spill. Water purification plants throughout the world use chitosan to remove oils, grease, heavy metals, and the fine particulate matter that cause turbidity in wastewater streams (Hennen, 1996). Various industrial, health and nutrition uses of chitosan are shown in Tables 1.1 - 1.2. Chitosan have the potential to reduce and to solve some environmental pollution problems for creating “ Greener” environment and chitosan is renewable polymers. Some of the properties which are commercially attractive are polymeric, including natural decomposition, non-toxic to both the environment and humanbeing, with no side-effects or allergenic effects if implanted in the body. Chitosan occur naturally in the environment in large quantities and run second in abundance to cellulose (Seafresh Chitosan (Lab), 2002).

Table 1.1 Industrial uses of chitosan.

* Wastewater purification	* Stabilizing oil spills
* Stabilizing fats in food preparation	* Antibacterial protection for seeds
* Flavor stabilizer	* Stabilizes perishable fruit/ vegetable
* Ion exchange media	* Bacterial immobilizer
* Cosmetic and shampoo additive	* Tableting excipient
* Absorbent for heavy metal removal	

Table 1.2 Health and nutrition uses of chitosan.

* Absorbs and bind fat	* Promotes weight loss
* Reduces LDL cholesterol	* Boosts HDL cholesterol
* Promotes wound helting	* Antibacterial/ Anticandida/ Antiviral
* Acts as antacid	* Inhibits the formation of plaque/ Tooth decay
* Helps control blood pressure	* Helps dental restoration/ recovery
* Helps to speed bone repair	* Improves calcium absorbtion
* Reduces levels of uric acid	

1.2 Research objectives

The overall objective of this study was to investigate the heavy metals removal from wastewater by adsorption using chitosan. The specific objectives included:

- 1.2.1 To investigate the effectiveness of chitosan for the adsorption of Pb and Zn from wastewater through
 - adsorption isotherms studies
 - desorption isotherms studies
 - adsorption kinetics studies
 - desorption kinetics studies
- 1.2.2 To evaluate effect of the following factors on the removal of Pb and Zn by adsorption on chitosan :
 - pH
 - Chloride ion concentration
 - Co-ions

1.3 Scope and limitations of the study

The scope of this study included the following:

- 1.3.1 All experiments were batch experiments.
- 1.3.2 Chitosan powders were used as an adsorbent in all experiments.
- 1.3.3 Three set of observations were carried out in all experiments.
- 1.3.4 A synthetic wastewater was prepared by mixing effluent from the biological pond of SUT with commercially available standard solutions

of lead and zinc.

- 1.3.5 The adsorption studies were used to evaluate the influence of some operating parameters such as pH, chloride - ion concentration, and co-ions on adsorption.
- 1.3.6 The desorption studies were used to evaluate the effect of pH on desorption process.
- 1.3.7 Adsorption isotherms studies were used to evaluate the quantity of Pb and Zn that could be taken up by chitosan as a function of the concentration of Pb and Zn at 25 °C.
- 1.3.8 Desorption isotherms studies were used to evaluate the quantity of Pb and Zn that could be desorbed from chitosan as a function of the concentration of Pb and Zn at 25 °C.
- 1.3.9 Adsorption kinetics studies were used to evaluate the equilibrium contact times for adsorption of Pb and Zn on chitosan.
- 1.3.10 Desorption kinetics studies were used to evaluate the equilibrium contact time for desorption of Pb and Zn from chitosan.
- 1.3.11 The results from this research could only used to design the wastewater treatment plant for removal of Pb and Zn from wastewater.

Chapter II

Background Information and Literature Review

2.1 Treatment technologies for metals and hazardous waste.

Chemical, biological, and physical wastewater treatment processes are currently the most commonly used methods of treating aqueous hazardous waste. Chemical treatment transforms waste into less hazardous substances using such techniques as pH neutralization, oxidation or reduction, and precipitation. Biological treatment uses microorganisms to degrade organic compounds in the waste stream. Physical treatment processes include gravity separation, phase change systems, such as air and steam stripping of volatiles from liquid wastes, and various filtration operations, including adsorption (Grey et al., 1994).

2.2 Adsorption

In general, adsorption is the process of collecting soluble substances (adsorbate) that are in a solution, on a suitable interface (with adsorbent). The interface can be between the liquid and a gas, a solid, or another liquid. One example of adsorption using the air-liquid interface is in flotation process. Adsorption at the liquid-solid interface was used in this study.

The adsorption process can be divided into three steps: 1) transfer of the adsorbate molecules through the film that surrounds the adsorbent; 2) diffusion through the pores if the adsorbent is porous; and 3) uptake of the adsorbate molecules by the active surface, including formation of the bond between the adsorbate and the adsorbent. The rate of adsorption depends on the rate at which the molecules move by diffusion in solution or the rate at which the molecules can reach available surface by diffusing through the film and the pores.

Adsorption may be classified as

- (1) physical adsorption and
- (2) chemical adsorption

Physical adsorption is primarily due to van der Waals forces and is a reversible

occurrence. When the molecular forces of attraction between the solute (adsorbate) and the adsorbent are greater than the forces of attraction between the solute and the solvent, the solute will be adsorbed onto the adsorbent surface. In chemical adsorption, a chemical reaction occurs between the solids and the adsorbed solute, and the reaction is usually irreversible. Chemical adsorption is rarely used in environmental engineering; however, physical adsorption is widely used (Metcalf & Eddy, 1991).

2.3 Adsorption isotherms

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics and concentration of adsorbate and the temperature. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called an *adsorption isotherm*. Two equations that are often used to describe the experimental isotherm data was developed by two scientists Freundlich and Langmuir (Metcalf & Eddy, 1991). The empirically derived Freundlich isotherm is defined as follows.

$$\frac{x}{m} = K_f C_e^{1/n} \quad (2.1)$$

where, $\frac{x}{m}$ = amount of adsorbate adsorbed per unit weight of adsorbent

(mg_{adsorbate}/mg_{adsorbent})

C_e = equilibrium concentration of adsorbate in solution after adsorption

(mg/L)

K_f, n = empirical constants

The constants in the Freundlich isotherm can be determined by plotting (x/m) versus C_e (as shown in Figure 2.1) and using the following equation.

$$\text{Log} \left(\frac{x}{m} \right) = \log K_f + \frac{1}{n} \log C_e \quad (2.2)$$

The Langmuir adsorption isotherm is defined as:

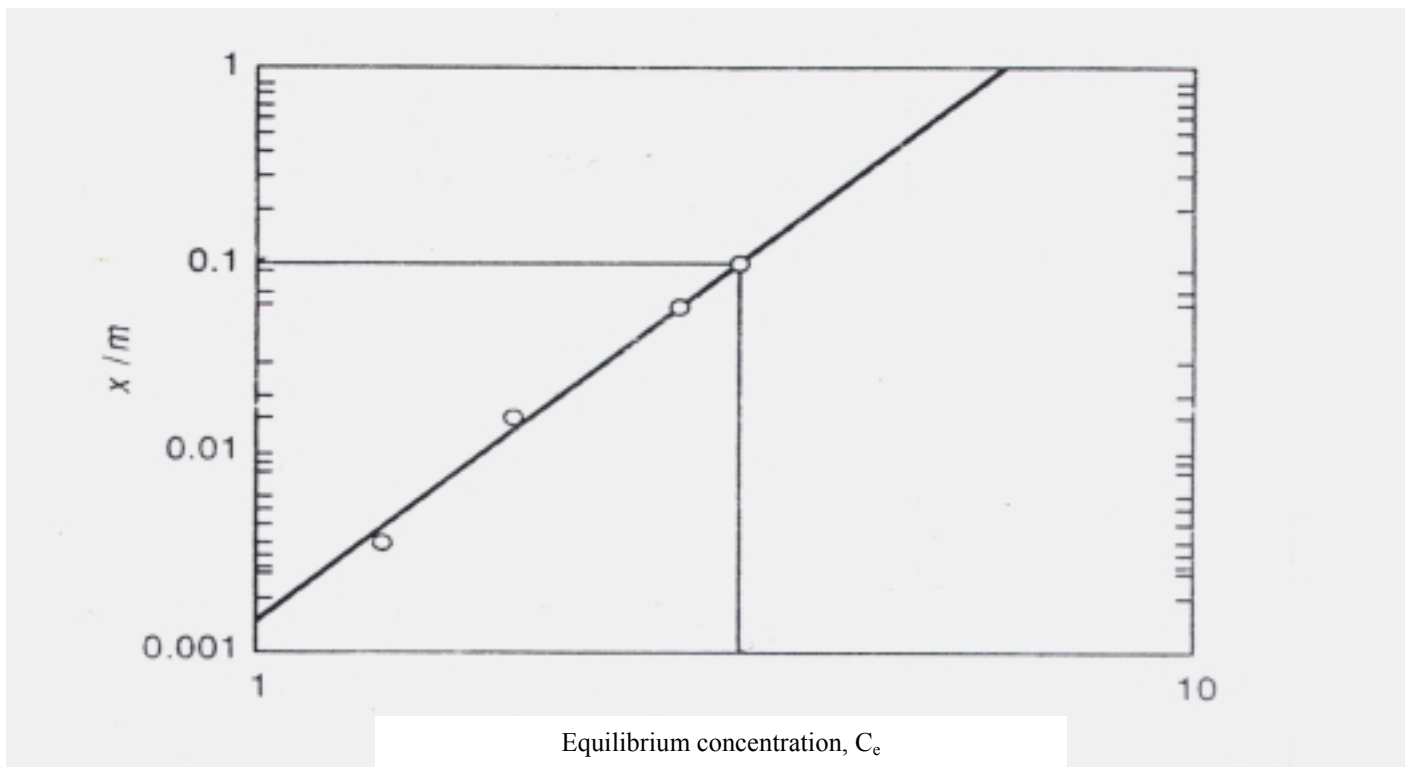


Figure 2.1 Freundlich isotherms. (Source: Metcalf & Eddy, 1991)

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e} \quad (2.3)$$

where, $\frac{x}{m}$ = amount of adsorbate adsorbed per unit weight of adsorbent
(mg_{adsorbate}/mg_{adsorbent})

a, b = empirical constants

C_e = equilibrium concentration of adsorbate in solution after adsorption
(mg/L)

The Langmuir adsorption isotherm was developed by assuming that

- (1) a fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy and that
- (2) adsorption is reversible

Equilibrium is reached when the rate of adsorption of molecules onto the surface is the same as the rate of desorption of molecules from the surface. The rate at which adsorption proceeds is proportional to the driving force, which is the difference

between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. At the equilibrium concentration, this difference is zero. The constants in the Langmuir isotherm can be determined by plotting $C_e/(x/m)$ versus C_e (as shown in Figure 2.2) and making use of the following equation (Metcalf & Eddy, 1991).

$$\frac{C_e}{(x/m)} = \frac{1}{ab} + \frac{1}{a} (C_e) \quad (2.4)$$

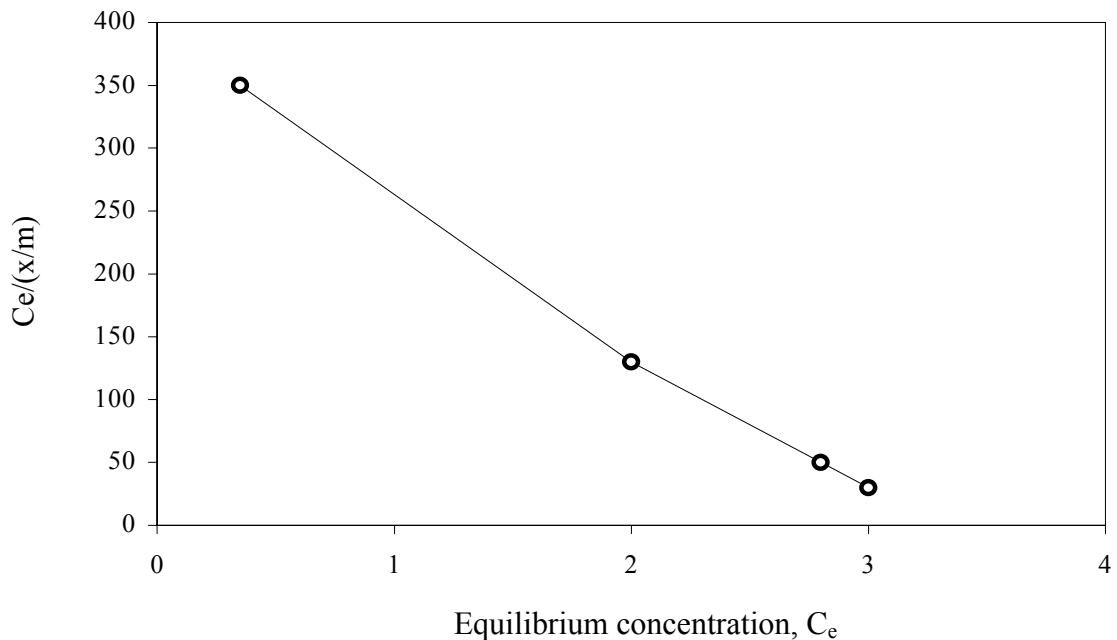


Figure 2.2 Langmuir isotherms. (Source: Metcalf & Eddy, 1991)

Isothermal data can be used to calculate the ultimate sorption capacity of the adsorbent by substituting the required equilibrium concentration in the Freundlich and/ or Langmuir equations.

2.4 Adsorption kinetics

Two important physicochemical aspects for evaluation of the sorption process as a unit operation are the kinetics and the equilibria of sorption. Adsorption kinetics are studied to estimate the time required for obtaining equilibrium concentration of

adsorbate for the adsorption of heavy metals on an adsorbent.

The adsorption kinetics of an adsorbent can be determined by plotting sorbed heavy metal concentration (C_t) versus time (t) as shown in Figures 2.3 – 2.4 for zero –order and first – order reactions rates, respectively.

- A zero-order reaction

differential form

$$\frac{dC}{dt} = k \quad (2.5)$$

solution

$$C_t = C_0 + kt \quad (2.6)$$

A plot of $\ln(C/C_0)$ versus t will yield a straight line for a first - order reaction. The rate constant can be determined directly from the slope of this line (Sawyer et al., 1994).

- A first-order reaction

differential form

$$\frac{-dC}{dt} = kC \quad (2.7)$$

solution

$$C = C_0 e^{-kt} \quad (2.8)$$

$$\ln(C/C_0) = -kt \quad (2.9)$$

Where, C_t = concentration of adsorbate at time t (mg/L)

C_0 = concentration of adsorbate at the beginning (mg/L)

k = the rate constant(concentration/time)

t = time (minute)

2.5 Desorption

Adsorption of many compounds is reversible, which means that they can be separated from adsorbent by desorption. Desorption may be caused by displacement by other compounds or by a decrease in influent concentration (Snoeyink,1990).

Desorption is equally important to adsorption for two reasons; they are

- (1) recovery of adsorbed metal and
- (2) reuse of adsorbent

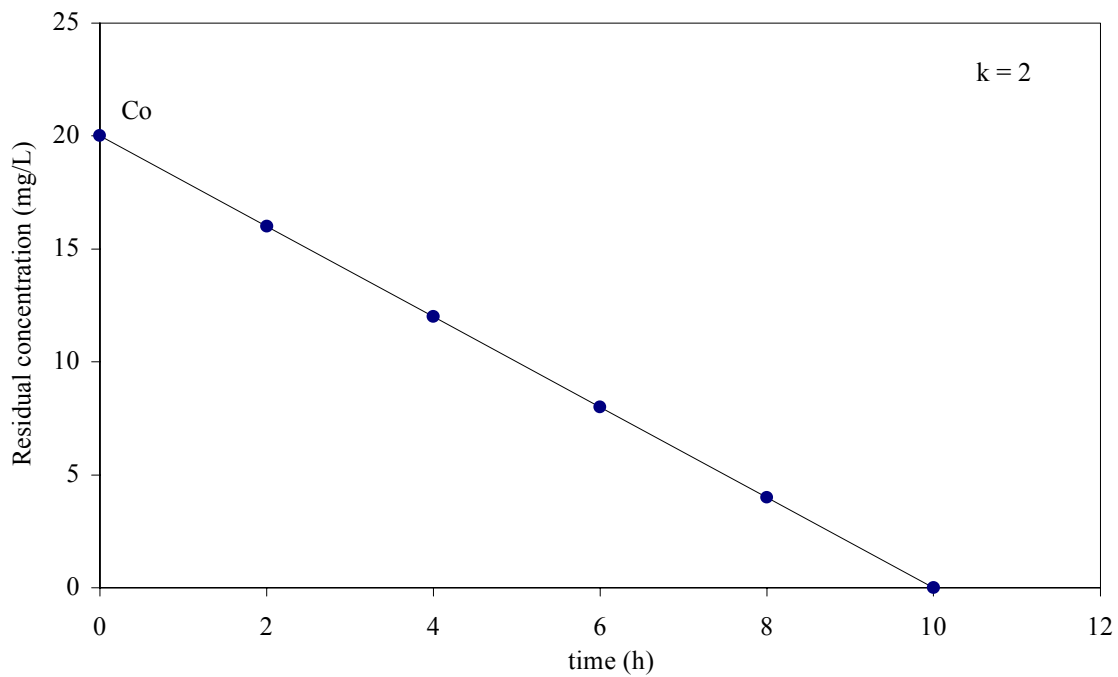


Figure 2.3 Zero-order reaction rate for adsorption (Source: Sawyer et al., 1994).

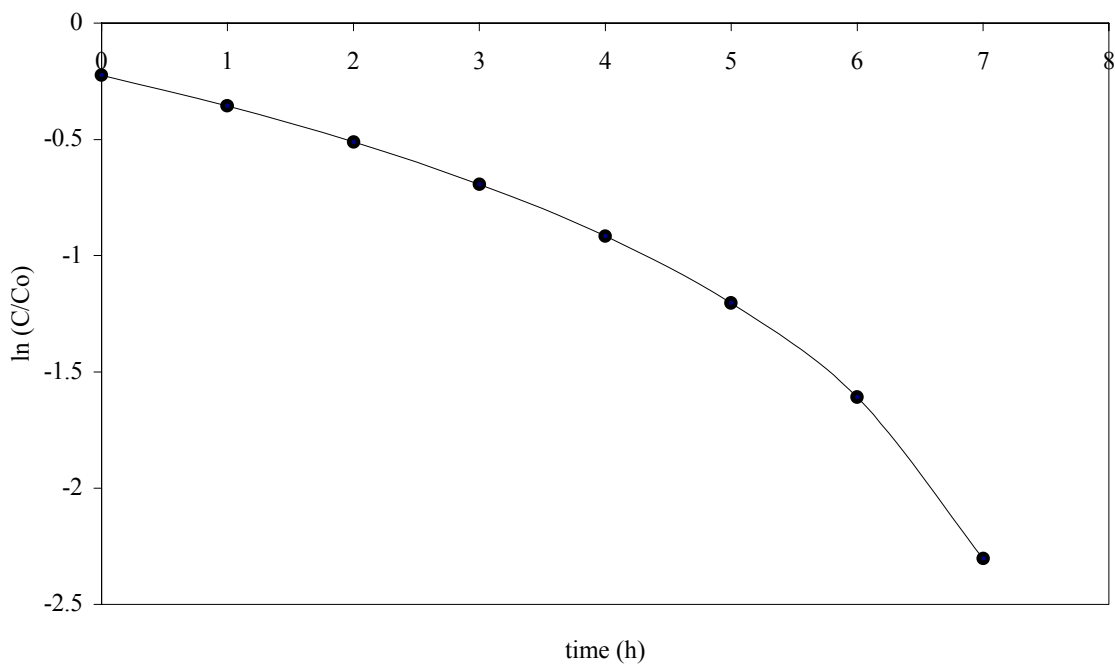


Figure 2.4 First-order reaction rate for adsorption (Source: Sawyer et al., 1994).

2.6 Desorption isotherms

A desorption isotherm describes the equilibrium surface concentration of adsorbate on the adsorbent as a function of bulk concentration of adsorbate in the solution. The amount of heavy metal remaining was obtained from mass balance concept. Freundlich and Langmuir equations were used to describe equilibrium between surface and solution as a reversible chemical equilibrium between species.

Mass balance at a steady-state in a system:

$$\begin{aligned} \text{Amount of heavy metal desorbed} &= \text{Amount of heavy metal sorbed} & (2.10) \\ (\text{mg}_{\text{adsorbate}} / \text{mg}_{\text{adsorbent}}) & \text{ on adsorbent } (\text{mg}_{\text{adsorbate}} / \text{mg}_{\text{adsorbent}}) \\ & - \text{Amount of residual heavy metal on} \\ & \text{adsorbent } (\text{mg}_{\text{adsorbate}} / \text{mg}_{\text{adsorbent}}) \end{aligned}$$

2.7 Desorption kinetics

Desorption kinetics and the equilibria of desorption are physicochemical aspects of importance for evaluating the desorption process. Desorption of adsorbate on adsorbent takes place because there are competing substances that sufficiently interfere the adsorption of the material from the surface of the adsorbent. Such an interaction may include dipole-dipole interactions, as well as hydrogen bonding.

Mass balance at a steady-state in a system:

$$\begin{aligned} \text{Conc. of desorbed heavy metal} &= \text{Initial conc. of heavy metal} & (2.11) \\ \text{during each time interval (mg/L)} & \text{ sorbed on the adsorbent (mg/L)} \\ & - \text{Conc. of heavy metal remaining sorbed} \\ & \text{on the adsorbent (mg/L)} \end{aligned}$$

The desorption kinetics of chitosan can be determined by plotting desorbed heavy metal concentration versus time for a zero-order reaction.

2.8 Chitosan

Chitin, the precursor of chitosan, was first discovered in mushrooms by the French professor Henri Braconnot in 1811. In 1820's chitin was also isolated from

insects. Chitin is an extremely long chain of N-acetyl-D-glucosamine units. Chitin is the most abundant natural fiber next to cellulose and is similar to cellulose in many respects. The most abundant source of chitin is in shell of shellfish such as crab and shrimp. Chitosan is an adsorbent used in this study. Chitosan was discovered in 1859 by Professor C. Rouget. It is made by cooking chitin in alkali, much like the process for making natural soap. After it is cooked the link of the chitosan chain are made up of glucosamine units. Each glucosamine unit contains a free amino group. These groups can take on a positive charge which gives chitosan its amazing properties. The structure of chitosan is presented schematically in Figure 2.5 and characteristics of chitosan used in this study are shown in Table 2.1.

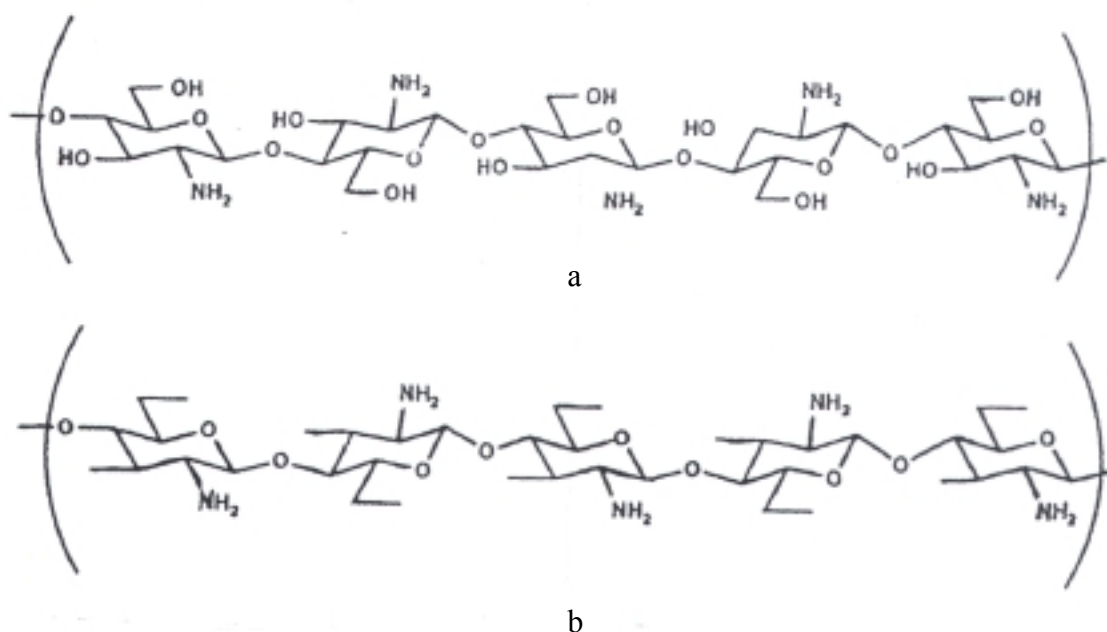


Figure 2.5 Chitosan structure. (Source: Hennen, 1996)

a) chitosan full structure.

b) abbreviated chitosan structure.

The powerful adsorption capabilities of chitosan towards most of persistent toxic found in aquatic environment, makes it one of the most suitable polymers to be used for elimination of non biodegradable toxic. Chitin, chitosan and other biopolymer are industrially attractive for a number of reasons. They are capable of

lowering transitional metal ions concentration to part per billion concentrations, widely available and environmentally safe. Another attractive feature is that they possess a number of different functional groups to which other chemical moieties can be reacted and can increase the efficiency of metal ion uptake and/or the chemical loading possible. Moreover, it is possible for *in situ* regeneration by simply exposing the metal laden materials to aqueous acid solutions, when desired (Deans and Dixon, 1992).

Table 2.1 Characteristics of chitosan.

Item	Characteristic
1. Appearance	Yellowish
2. Particle size	Mesh No. 60
3. Ash content	0.83%
4. Moisture content	8.5%
5. Deacetylation degree (%DAC)	86%
6. Solution (1% in 1% acetic acid	
Insoluble (%)	0.59%
Viscosity	152 cps
7. Heavy metal	0 ppm
8. Moisture content	
Total Plate Count	50
Yeast & Mold	20
E. Coli	Nil
Salmonelia	Nil

Source: Seafresh Chitosan (Lab), (2000).

2.9 Previous studies

Tsezos and Volesky, (1982) investigated the mechanism of thorium

biosorption by *Rhizopus arrhizus*. The results indicated that inactive cells of *Rhizopus arrhizus* exhibit a high thorium biosorptive uptake (170 mg/g) from aqueous solutions. The mechanism of thorium sequestering by this biomass type was investigated following the same method as for the uranium biosorption mechanism. The thorium sequestering mechanism appeared somewhat different from that of uranium. Experimental evidence presented indicated that, at optimum biosorption pH (4), thorium coordinates with the nitrogen of the chitin cell wall network and, in addition, more thorium is adsorbed by the external section of the fungal cell wall. At pH 3 the overall thorium uptake was reduced. The kinetic study of thorium biosorption revealed a very rapid rate of uptake. Unlike uranium at optimum solution pH, Fe^{2+} and Zn^{2+} did not interfere significantly with the thorium biosorptive uptake capacity of *R. arrhizus*.

Payne et al. (1992) investigated on tyrosinase reduction/ chitosan adsorption for selectively removing phenols from aqueous mixtures. The results indicated that chitosan was unstable to adsorb either nonphenol or unreacted cresol. However, chitosan effectively adsorbed UV-absorbing reaction products of the tyrosinase-catalyzed reaction of phenols. When mixtures of cresol and either anisole or benzyl alcohol were studied, the two-step approach was effective for completely removing the phenolic without loss of either the ether or alcohol (i.e., phenols were removed with high separation factors).

Saucedo et al. (1992) conducted a study of sorption of uranyl ions by a modified chitosan. The results obtained showed that uranium sorption capacity can be very high even at low initial and equilibrium metal concentration, higher than for pure chitosan. The modification of chitosan leads to an increase of uranium sorption of up to 3 or 4 times chitosan sorption capacity. Sorption performance (sorption rate and uptake capacity) are strongly dependent on pH, mainly as a result of metal chemistry. In an acidic medium, high uranium solubility and competition between H_3O^+ and UO_2^{2+} decrease removal performance.

Domard (1996) investigated some physicochemical and structural basis for applicability of chitin and chitosan in wastewater treatment. In the solid state, four parameters seemed to play an important role both on the kinetics of sorption and the capacity of metal uptake. The first parameter concerns the accessible surface to metal

ions. It depends both on the particle size and the porosity. The second parameter corresponds to the molecular mobility. In case of chitosan, it is essentially related to the crystallinity which limits the metal uptake and renders the amorphous domains. The third parameter is represented by the role of chemical modifications on the interactions with metals. These modifications allow essentially to decrease the crystallinity and, as a consequence, to increase the kinetics and the capacity of sorption. Last parameter concerns the role of added salts. In a general manner, the kinetics of sorption are lesser in the presence of high ionic strengths but the capacity of metal uptake is not modified. The mechanism of sorption of metals with chitosan in suspension is not well defined. Nevertheless, most of the authors agree to consider the formation of a complex between the amino groups of chitosan and the metal ions.

Naing Naing Win (1996) conducted a study on copper and chromium removal capacities of chitosan using batch and continuous column experiments. Kinetics and isotherm studies indicated that heavy metals such as chromium and copper can be effectively removed by chitosan. The rate of sorption were very rapid initially. At low equilibrium concentration, maximum adsorption were obtained within 4 and 1 hour for copper and chromium, respectively. 13 mg copper and 16.5 mg chromium could be adsorbed per gram of chitosan at an equilibrium heavy metal concentration of 1 mg/L.

Karimi-Jashni and Narbaitz (1997) investigated impact of pH on the adsorption and desorption. The adsorption and desorption kinetics of 2- Nitrophenol (2NP) from aqueous solutions using F-400 and WV-B granular activated carbons (GAC) was studied at pH 1, 4.6 and 13, in batch tests. Adsorption and desorption kinetics of 2NP on to both carbons were adequately described by the homogeneous solid surface diffusion model (HSSD). The Adsorption and desorption kinetics could be predicted at different pH by using adsorption kinetics parameters of the pH 4.6 and the isotherm parameters for the corresponding pH. Thus, the differences in the rates of adsorption were primarily attributable to the differences in the equilibrium loadings at the various pH. Adsorption reached equilibrium quickly; approximately 80-90% of the uptake occurred in less than 5 hours. The speed at which the equilibrium was reached was probably attributable to the large carbon dose.

Nyein Nyein Aung (1997) carried out batch experiments for heavy metal

removal by adsorption using chitosan and desorption of adsorbed metal from adsorbent. It was concluded that the optimum pH values for adsorption on chitosan were 5.5, 6 and 4, likewise, the optimum pH values for desorption were 2.41, 2.5 and 2.5 for Cu, Cr and Pb, respectively. The amount of Cu sorbed on 710 μm chitosan particles and 425 μm chitosan particles were 2 mg/g and 7 mg/g, respectively for the equilibrium concentration of 1 mg/L. The amount of Cu sorbed at 37.5 °C and 50 °C were 6.5 mg/g and 11mg/g, respectively for the equilibrium concentration of 0.5 mg/L. The amount of Cu sorbed at the agitation speed of 50 rpm and 250 rpm were 16 mg/g and 17 mg/g, respectively for the equilibrium concentration of 5 mg/L. In case of desorption, when the initial Cu sorbed was 2.5 mg/g, Cu desorbed from 710 μm chitosan particles and 425 μm chitosan particles were 1.05 mg/g and 1.19 mg/g, respectively. When the initial amount sorbed was 5 mg/g, Cu desorbed at 37.5 °C and 50 °C were 3.5 mg/g and 4.5 mg/g, respectively. When the Cu sorbed was 17 mg/g, the amount of Cu desorbed at agitation speed of 50 rpm and 250 rpm were 1.9 mg/g and 10 mg/g, respectively. Similar trend was observed for Cr and Pb. Lower particle size, higher temperature and higher agitation speed enhanced both adsorption and desorption.

Bose and Reckhow (1998) conducted a study on adsorption of natural organic matter on preformed aluminum hydroxide flocs. Natural organic matter (NOM) was extracted from a raw water source and fractionated into eight groups: fulvic acid, humic acid, hydrophilic acid, weak hydrophobic acids, hydrophilic neutrals, hydrophobic neutrals, hydrophilic bases, and hydrophobic bases. The extent of adsorption of these fractions on preformed aluminum hydroxide flocs was determined. Also, the adsorption affinities of various fractions were correlated to selected NOM properties, i.e., organic charge, molecular weight, and specific ultraviolet absorbance. The nature of the reactions leading to adsorption was discussed, along with the induced dissolution of aluminum from the floc surface and its resulting association with NOM in particulate or colloidal forms.

Chang et al. (1998) investigated some physical and chemical properties of chitosan membrane. Chitosan membranes were prepared by casting from acetic acid solution. The tensile strength of the chitosan membrane was 1.425 kg/ 25 mm, its elongation was 3.65 % and its water vapor permeation rate was 1.25 g/ 10 cm^2 7 h at

25 °C and 90% RH. The water uptake of chitosan membrane was 242.80% in water, 782% in a phosphate buffer (pH= 6), and complete dissolution took place in a buffer with pH = 1 after soaking the membrane for 1 h. When chitosan membranes were placed in phosphate buffer (pH= 6) with 50 μ M or 100 μ M lysozyme, the amounts of chitosan membrane dissolved after 7 days were 23.7% and 49.3%, respectively.

Guibal et al. (1998) conducted a study on platinum removal from dilute effluents using chitosan-derived sorbents. This study indicated that glutaraldehyde-crosslinked chitosan is effective in removing hexachloroplatinate ions in dilute effluents. The optimum pH for platinum sorption was around pH 2. The maximum capacity exceeded 280 mg/g. Sorption isotherms could be modeled using the Langmuir equation and the sorption capacity was not influenced by particle size nor crosslinking ratio. The sorption behavior for platinum was significantly different to that observed with other metals, probably due to the speciation of metal ions: platinum forms only mononuclear species in contrast with molybdate or vanadate polynuclear hydrolysed anions.

Guibal et al. (1998) also investigated the equilibrium and kinetics of metal-anion sorption by chitosan beads. They reported that the adsorption performance of chitosan in both equilibrium and kinetic terms is controlled by diffusion processes. While for beads, particle size does not influence equilibrium, for flakes, increasing sorbent radius significantly decrease uptake capacities to 1.5 mmol/g. Sorption kinetics are mainly controlled by intraparticle diffusion for beads, while for flakes the controlling mechanisms are both external and intraparticle diffusions.

Huang et al. (1998) reported the results of a study on the electrosorption of metal ions by chitosan fabric. Chitosan fabric were woven by mixing chitosan fibers with PET fibers. The adsorption of metal ions, including Cu²⁺, Pb²⁺, Co²⁺ and Ni²⁺ onto chitosan fabrics was investigated. The adsorption capacity of different metal ions on to chitosan fabrics was Cu²⁺ > Pb²⁺ > Co²⁺ > Ni²⁺. However, the adsorption rate was Pb²⁺ > Cu²⁺ > Co²⁺ > Ni²⁺.

Kim et al. (1998) conducted a study on production of pure (fresh) water through chitinous purification systems from the used water. The results from the study indicated that chitosan outstandingly enhanced removal of COD, BOD and other contaminants from wastewater. Process mechanism involved the

graftcopolymerization of alkenoic acids and alkenedioic acids onto it to function both as polycationic and polyanionic flocculants in accordance with rapidly changing pH value of wastewater. The graftcopolymers are far more effective metal uptakers compared with pure chitosan sweeping whole pH range. In filtering columns, metal uptaking efficiency was increased remarkably with decrease of bead size and flow rate of water samples. Thus, an effective and economical way of chitosan used for purification of water was developed.

Lee et al. (1998) carried out a study on the copper (II) ion uptake by chitosan-tripolyphosphate chelating resin and related kinetics. They reported that for the lower crosslinked chitosan-TTP chelating beads, the swelling analysis results suggested the lowest working pH values for the beads in acid media to be 3, and that a hydrolysis effect may cause dissolution of the beads when pH values is below 3. Like other forms of chitosan, the adsorption capacity of Cu^{2+} ions on chitosan-TTP chelating beads was also influenced by the hydrogen ions concentration. The optimum pH range observed was 5.1-5.2. The adsorption isotherm fitted well with the Langmuir adsorption model when the initial concentration was below 1000 mg Cu^{2+} /L. The kinetics data revealed that the intraparticle diffusion was the rate-limiting step for the adsorption of Cu^{2+} ion at pH 4 and pH 5 onto chitosan-TTP chelating beads, and the intraparticle diffusion fitted well with the Fickian diffusion model when the initial concentration was below 1000 mg Cu^{2+} ion/L. Additionally, the adsorption of Cu^{2+} ions on the chitosan-TTP chelating beads was proved to proceed by chelation rather than ion-exchange mechanism.

Telisman et al. (2001) conducted a study of blood pressure in relation to biomarkers of lead, cadmium, copper, zinc and selenium in men without occupational exposure to metals. The study results indicate a significant Pb-related increase in systolic and diastolic blood pressure, particularly within the low- level Pb exposure range (BPb of 25-75 $\mu\text{g}/\text{L}$, and /or EP of 0.4-1.0 $\mu\text{mol}/\text{L}$ erythrocytes). A decrease in Se status, even within the apparently normal SSe range in the study population, can synergistically contribute to the effect of Pb in increasing systolic and diastolic blood pressure.

Peuphaibool (2002) investigated the adsorption of chromium (III) by chitosan prepared from Black Tiger shrimp shell (*Penaeus monodon*). Batch adsorption test was

used to evaluate the removal efficiency of chromium adsorption. Chromium adsorption capacity of chitosan was affected by pH, quantity, contact time and presence of co-ion. Increase in pH, quantity, and contact time resulted in the increase of chromium adsorption capacity. The adsorption capacity constants (K) for chromium (III), calculated according to Freundlich equation, were 0.45, 1.24, 2.01, 10.93, 12.36, and 21.50 mg Cr/g chitosan at pH 4, 5, 6, 7, 8 and 9, respectively. Effect of coion on chromium adsorption capacity of chitosan at initial chromium concentration of 4 mg/L was investigated. Chitosan could remove chromium about $76.31 \pm 0.07\%$ in the absent of coion. Chitosan could remove chromium about $86.87 \pm 0.47\%$ when initial copper, nickle and zinc concentration was 0.80, 0.80 and 0.06 mg/L, respectively while maintaining initial chromium concentration at 4 mg/L.

In a study, Rae and Gibb (2002) assessed the ability of commercial cryogenically milled carapace (CCMC), mechanically milled carapace (MMC), chitin and chitosan for removal of a range of alkalis, alkaline earth, and transition heavy metals from aqueous media in flow-through column trials. Materials showed a poor affinity for the alkali metals and alkaline earth metals but significantly greater affinity for transition and heavy metals. In general, chitin was the least efficient material for removal of transition and heavy metals (~35%) while chitosan was most effective (> 99%). CCMC and MMC both removed >90% of transition and heavy metals tested from solution. Equilibrium batch studies conducted using copper as a reference metal demonstrated that removal was dependant on a number of variables including pH, contact time, particle size, metal concentration, metal type and the physio-chemical characteristics of the materials. Detailed analysis of the results from these studies indicated that removal is a complex process and metals can be sequestered from solution by a number of mechanisms including; ion exchange, complexation, adsorption, absorption, micro-precipitation and bulk precipitation.

Chapter III

Research Methodology

3.1 Synthetic wastewater preparation

A synthetic wastewater was prepared by mixing the effluent from the biological pond of Suranaree University of Technology with the commercially available standard solutions of lead and zinc having 1 mg/ mL concentrations.

3.2 Source of chitosan

Commercially produced chitosan powders (as shown in Figure 3.1) were obtained from Seafresh Chitosan (Lab) Co., Ltd, Thailand to conduct adsorption and desorption experiments.

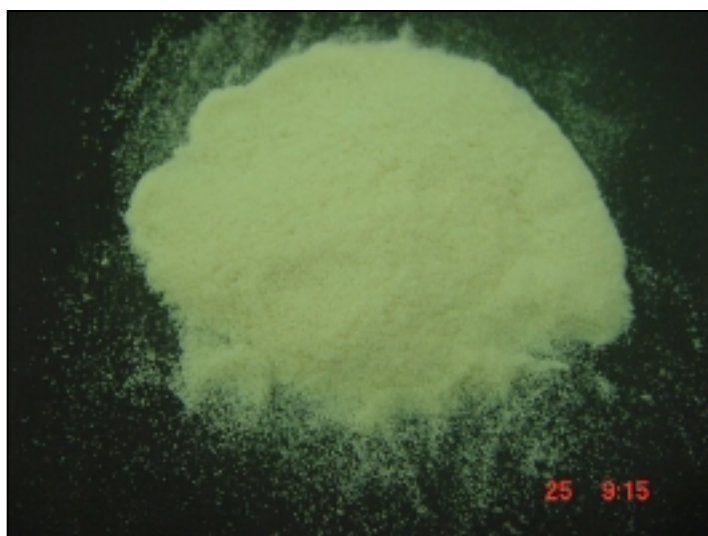


Figure 3.1 Chitosan

3.3 Adsorption experiments

In order to evaluate the adsorption performance of chitosan for the removal of lead and zinc from the synthetic wastewater, following steps were involved.

3.3.1 Determination of optimum pH for adsorption

The optimum pH for adsorption of lead and zinc by chitosan were determined experimentally. Lead and zinc solutions with the concentration of 3 mg/L were prepared from the standard solutions. Samples of 50 mL from these solutions were poured into 7 conical flasks. The initial pH of the samples were adjusted to various values in the range of 3.3 to 9 (7 values). Subsequently, 50 mg of chitosan particles were added to each flask. Equilibrium condition for heavy metal adsorption was obtained after 24 hours of agitation using a shaker water bath maintained at 25 °C and 100 rpm. Samples were withdrawn from supernatant after equilibrium was achieved and heavy metal concentrations were analyzed by using atomic adsorption spectrophotometer. A step by step methodology of this study is shown in Figure 3.2. The optimum pH for lead and zinc adsorption were ascertained from maximum metal adsorption by chitosan.

The adsorption capacity of chitosan was estimated by following equation:

$$\frac{x}{m} = \frac{V(C_0 - C_{eq})}{m} \quad (3.1)$$

Where, V = volume of solution (mL)

m = mass of adsorbent (g)

C₀ = initial metal concentration (mg/L)

C_{eq} = metal concentration at equilibrium (mg/L)

$\frac{x}{m}$ = the adsorbate concentration or sorption capacity of chitosan (mg/g)

3.3.2 Determination of adsorption kinetics

Batch experiments were conducted to estimate time required for obtaining equilibrium conditions for adsorption of heavy metals on chitosan. Solutions with an initial heavy metal concentration of 3 mg/L were prepared from the standard solutions and then adjusted to optimum adsorption pH for each metal. Samples of 50 mL from these solutions were poured into 24 conical flasks and then 50 mg of chitosan particles were added to each flask. All flasks were agitated using shaker water bath maintained at the temperature of 25 °C and the rotation speed of 100 rpm. Each flask were removed from shaker water bath at predetermined

time interval (1 hour). Flask contents were filtered using GF/C filter paper to remove chitosan particles and the amount of heavy metal contents in the filtrate were analyzed using atomic adsorption spectrophotometer. A step by step methodology of this study is shown in Figure 3.3.

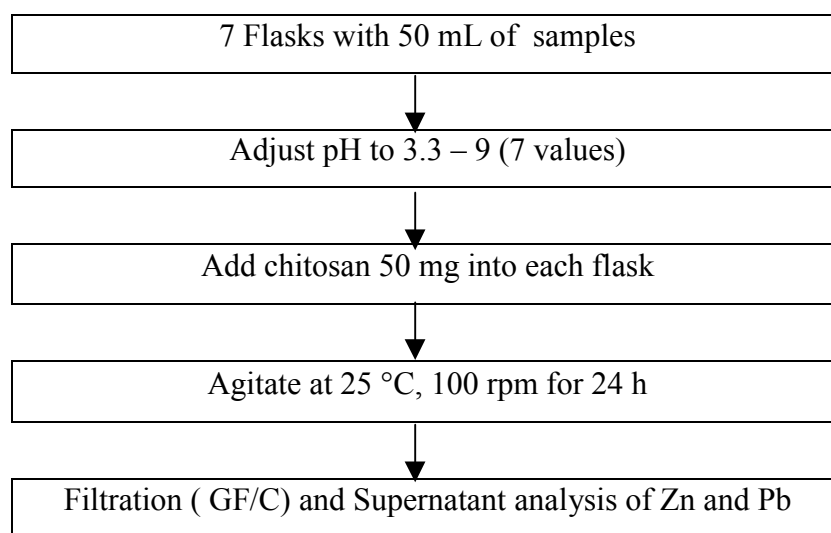


Figure 3.2 Experimental steps for determination of optimum pH for adsorption.

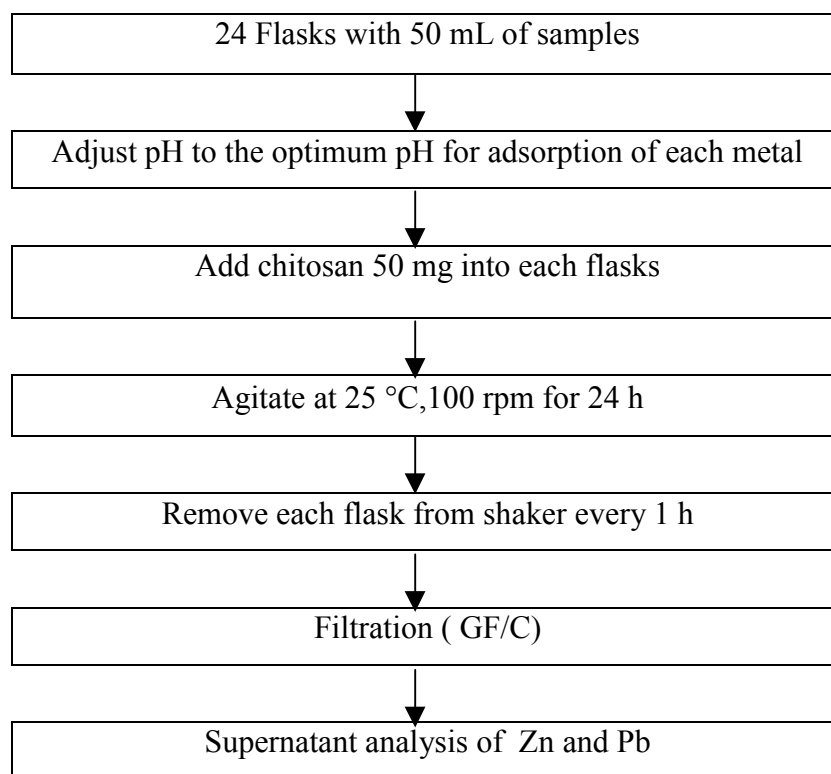


Figure 3.3 Experimental steps for adsorption kinetics studies.

3.3.3 Effect of chloride ions on the adsorption

Experiments were carried out to ascertain the effect of chloride ions on the adsorption of lead and zinc. Solutions with an initial heavy metal concentration of 3 mg/L were prepared from the standard solutions and then adjusted to optimum adsorption pH for each metal. Samples of 50 mL from these solutions were put into 5 conical flasks. Various concentrations of NaCl (0, 100, 500, 1000 and 2000 mg/L), and 50 mg of chitosan particles were added to each flask. Equilibrium condition of heavy metal adsorption was obtained after 24 hours of agitation using a shaker water bath maintained at 25 °C and 100 rpm. Samples were withdrawn from supernatant after equilibrium was achieved and heavy metal concentrations were analyzed by using atomic adsorption spectrophotometer. A step by step methodology of this study is shown in Figure 3.4.

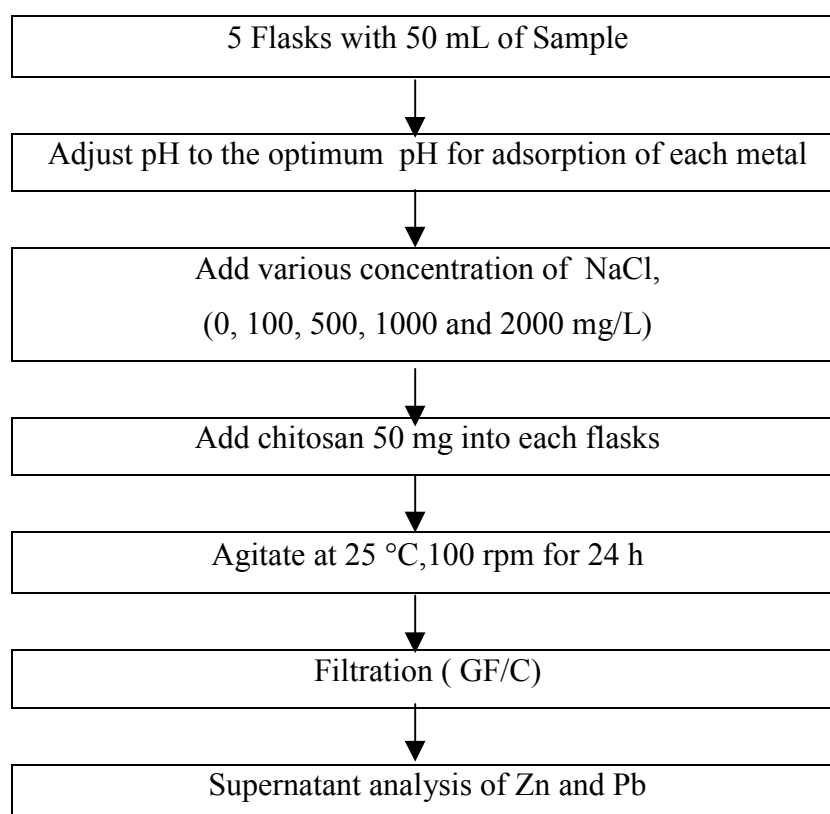


Figure 3.4 Experimental steps for evaluation of effect of chloride concentration on adsorption.

3.3.4 Effect of co-ions on the adsorption

Lead and zinc may exist together in varieties of wastewater including electroplating wastewater. Experiments were carried out to ascertain the effect of presence of other heavy metals on metal adsorption capacity of chitosan. For experiments the effect of zinc on lead adsorption, solutions with lead concentrations of 2, 5, 7 and 10 mg/L (5 flasks of each concentration) and zinc concentrations of 0, 10, 20, 30 and 50 mg/L in each concentration of lead were prepared from standard solutions. The pH of these solutions were adjusted to value of 4. Samples of 50 mL from these solutions were poured into 20 conical flasks and 50 mg of chitosan were added to each flask. Equilibrium heavy metal adsorption was obtained after 24 hours of agitation using shaker water bath maintained at 25 °C and 100 rpm. Samples were withdrawn from supernatant after equilibrium was achieved and heavy metal concentrations were analyzed by using atomic adsorption spectrophotometer. A step by step methodology of this study is shown in Figure 3.5.

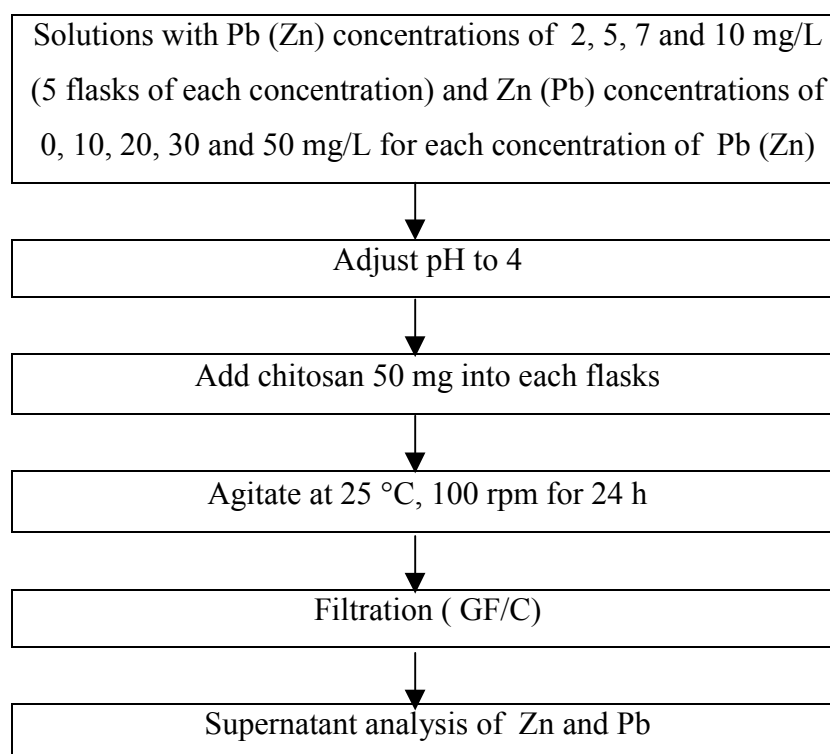


Figure 3.5 Experimental steps for evaluation of effect of co-ions on adsorption.

3.3.5 Determination of adsorption isotherms

Isotherm studies were conducted to estimate the adsorption capacity of chitosan for heavy metals removal from synthetic wastewater. Lead and zinc solutions with various concentrations were prepared from standard solutions. Samples of 50 mL from these solutions were poured into 14 conical flasks and the initial pH were adjusted to the optimum adsorption pH for each metal. Subsequently, 50 mg of chitosan were added to each flask. The content of the flasks were agitated using shaker water bath controlled at the temperature of 25 °C and the rotation speed of 100 rpm. After 24 hours, content of each flask were filtered using GF/C filter paper to remove chitosan particles and the amount of heavy metal content in the filtrate were analyzed by using atomic adsorption spectrophotometer. A step by step methodology of this study is shown in Figure 3.6.

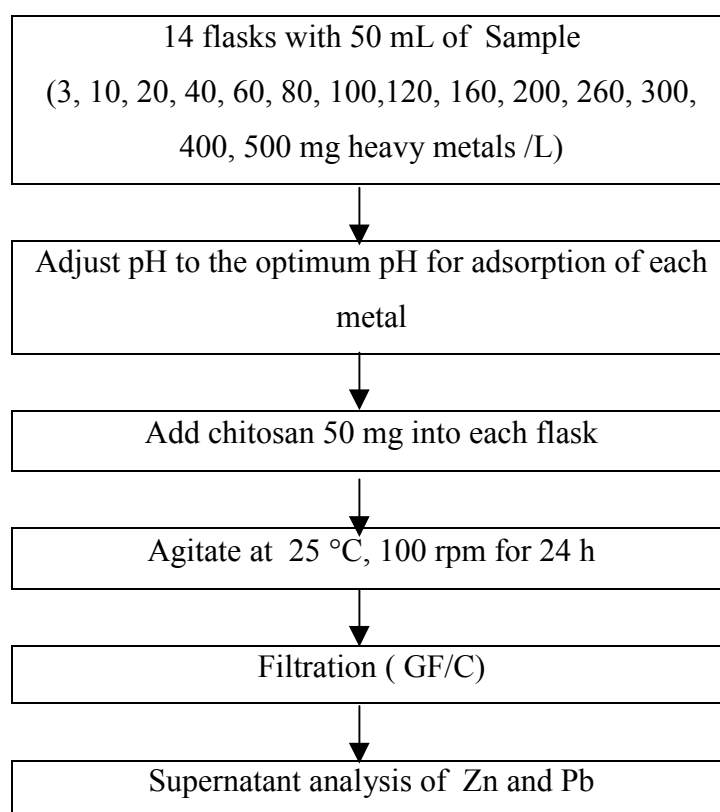


Figure 3.6 Experimental steps for adsorption isotherm studies.

3.4 Desorption experiments

In order to investigate the desorption of lead and zinc from chitosan,

following steps were involved.

3.4.1 Determination of optimum pH for desorption

In order to investigate the effect of pH on desorption of lead and zinc from chitosan, the adsorption experiments were carried out first. Lead and zinc solutions with 3 mg/L concentration were prepared from standard solutions and 50 mL from these solutions were poured into 7 conical flasks. The optimum adsorption pH for each metal were adjusted. Subsequently, 50 mg of chitosan were added into each conical flasks. The content of conical flasks were agitated for 24 hours in shaker water bath maintained at the temperature of 25 °C and the rotation speed of 100 rpm. After the adsorption took place, the chitosan particles adsorbed with heavy metal were filtered and let a few minutes to get dry. These dried chitosan particles were put into the conical flasks filled with 50 mL distilled water. The pH of these solutions were adjusted to various values in the range of 2.5 to 10 (7 values) by NaOH and HNO₃. Then the flasks were put into shaker water bath with the same operating conditions as in the adsorption experiments. Samples were withdrawn from supernatant after 24 hours, and heavy metal concentrations were analyzed by using atomic adsorption spectrophotometer. The optimum pH for lead and zinc desorption were ascertained from maximum metal concentration in solution. A step by step methodology of this study is shown in Figure 3.7.

3.4.2 Determination of desorption kinetics

Lead and zinc solutions with 3 mg/L concentration were prepared from standard solutions. Samples of 50 mL from these solutions were poured into 24 conical flasks. The optimum pH for adsorption were adjusted. 50 mL volume of the heavy metal solutions of known concentrations were taken in each conical flasks. The optimum pH for adsorption were adjusted. Subsequently, 50 mg of chitosan particles were added into each conical flask. The content of the flasks were agitated for 24 hours in shaker water bath maintained at a speed of 100 rpm and 25 °C. After the adsorption took place, the chitosan particles adsorbed with heavy metal were filtered and put into the 125 mL conical flasks filled with 50 mL distilled water which pH was adjusted to the optimum value of each metal. Then the flasks were put into Shaker Water Bath and agitation was carried out with the same condition as the adsorption experiments were conducted. Every hour, one flask was removed from

shaker water bath and the filtrate was analyzed by using atomic adsorption spectrophotometer. A step by step methodology of this study is shown in Figure 3.8. The amount of metal remaining on chitosan were estimated from material balance.

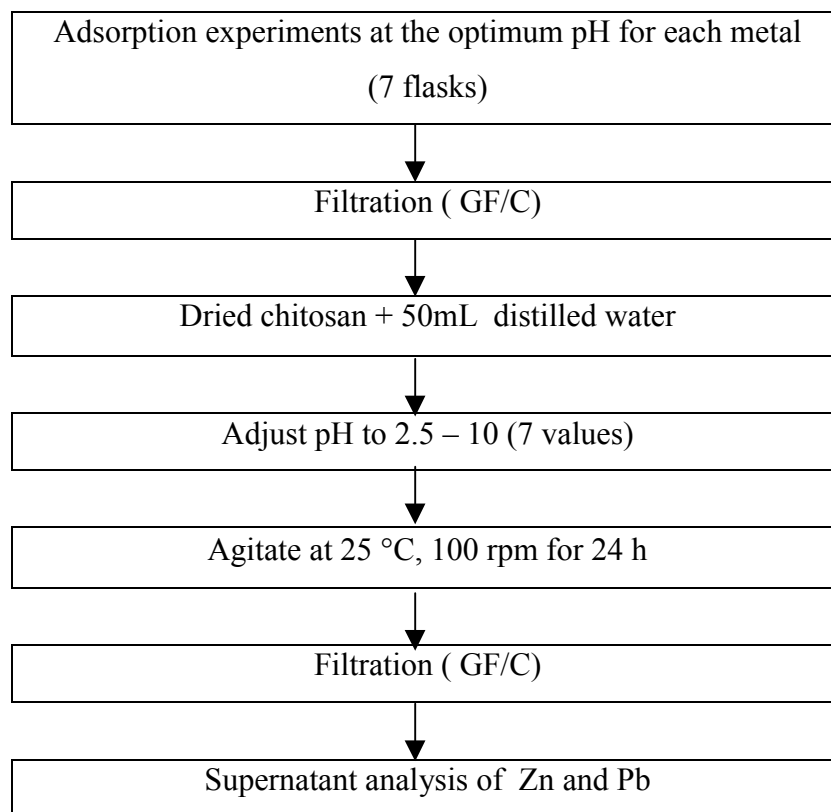


Figure 3.7 Experimental steps for determination of optimum pH for desorption.

3.4.3 Determination of desorption isotherms

Isotherm studies were conducted to ascertain heavy metal desorption from chitosan. Lead and zinc solutions with 3 mg/L concentration were prepared from standard solutions. Samples of 50 mL from these solutions were poured into 14 conical flasks. The optimum pH for adsorption was adjusted. Subsequently, 50 mg of chitosan particles were added into each conical flask. The content of the conical flasks were agitated for 24 hours in shaker water bath maintained at a speed of 100 rpm and 25 °C. After the adsorption took place, the chitosan particles adsorbed with heavy metal were filtered and put into the 125 mL conical flasks filled with 50 mL distilled water. The pH were adjusted to the optimum desorption value for each metal. Then the flasks were put into shaker water bath and agitation were carried

out with the same condition as the adsorption experiments were conducted. Sample from the supernatant was withdrawn from each flask after 24 hours and heavy metal concentration was analyzed by using atomic adsorption spectrophotometer. A step by step methodology of this study is shown in Figure 3.9. The amount of metal remaining on chitosan was estimated from material balance.

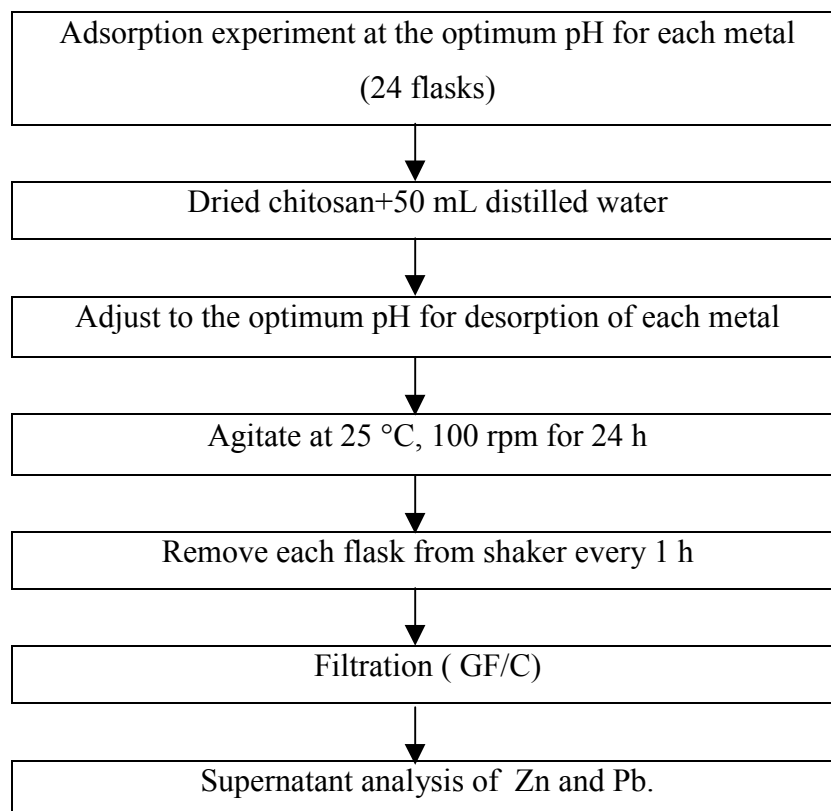


Figure 3.8 Experimental steps for desorption kinetics studies.

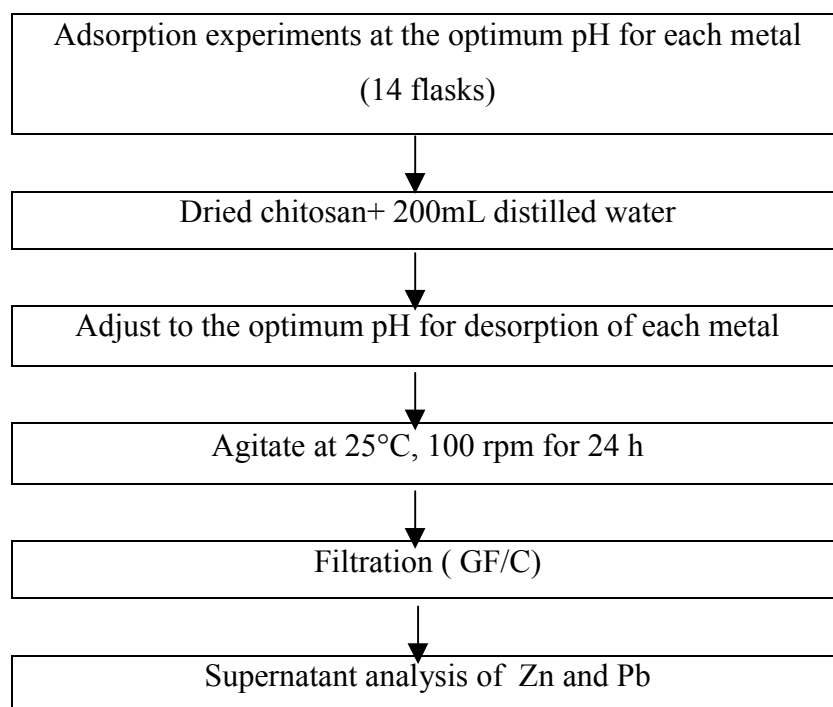


Figure 3.9 Experimental steps for desorption isotherm studies.

Chapter IV

Results and Discussion

4.1 Batch adsorption experiments

4.1.1 Effect of pH

The effect of pH on adsorption of lead (Pb) and zinc (Zn) by chitosan over a pH range of 3.3 – 9 at temperature 25 °C with agitation of 100 rpm, is illustrated in Figure 4.1. The results indicate that the adsorption capacity of chitosan for lead reached the maximum value of 2.8 mg/g with 73.3% removal at pH 3.30. At pH 3.75, the removal was 2.75 mg/g (72% removal). The adsorption showed the lowest value of 1.43 mg/g (37.4% removal) at pH 6.06.

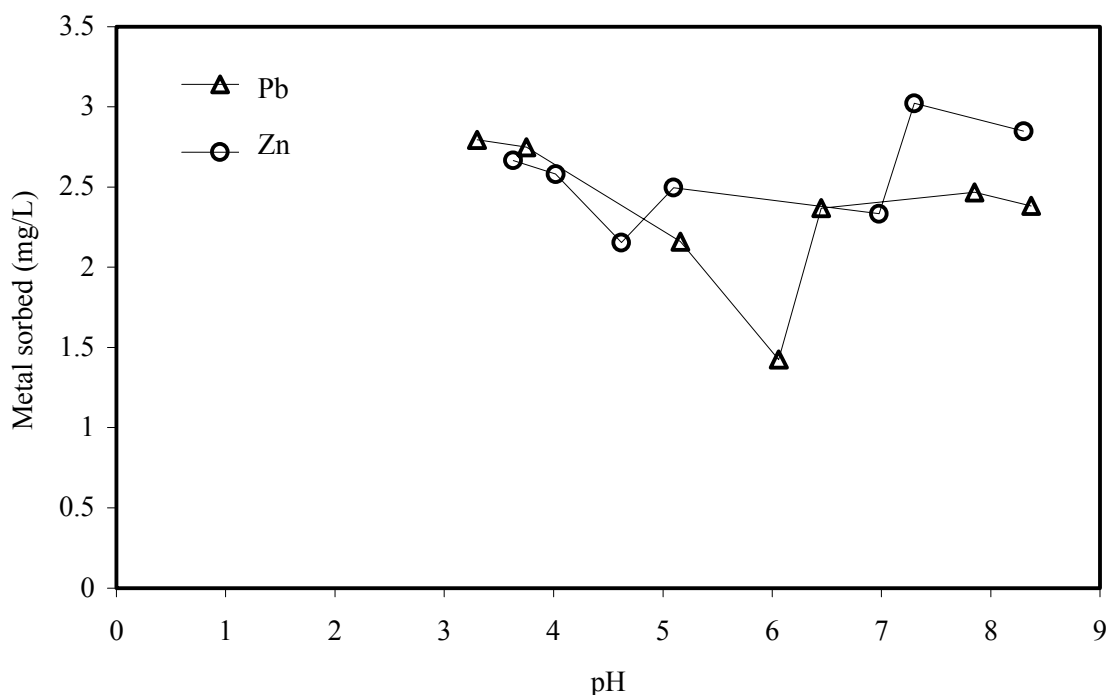


Figure 4.1 Effect of pH on lead and zinc adsorption at 25 °C and agitation of 100 rpm.

The adsorption capacity of chitosan for zinc reached the maximum value of 3.02 mg/g with 84.6% removal at pH 7.3. At pH 3.63, the removal was 2.67 mg/g

(74.8% removal). The adsorption showed the lowest value of 2.15 mg/g (60.2% removal) at pH 4.62.

Effect of pH on adsorption of lead (Pb) was also investigated at 30 °C with agitation at 150 rpm as shown in Figure 4.2. The results indicate that the adsorption capacity of chitosan for lead reached its highest value of 1.73 mg/g (86.5% removal) at pH 8.07. The adsorption showed the lowest value of 0.98 mg/g (49% removal) at pH 3.07. Hence, it can be seen that the optimum pH for maximum adsorption of lead is very much dependent on temperature and agitation.

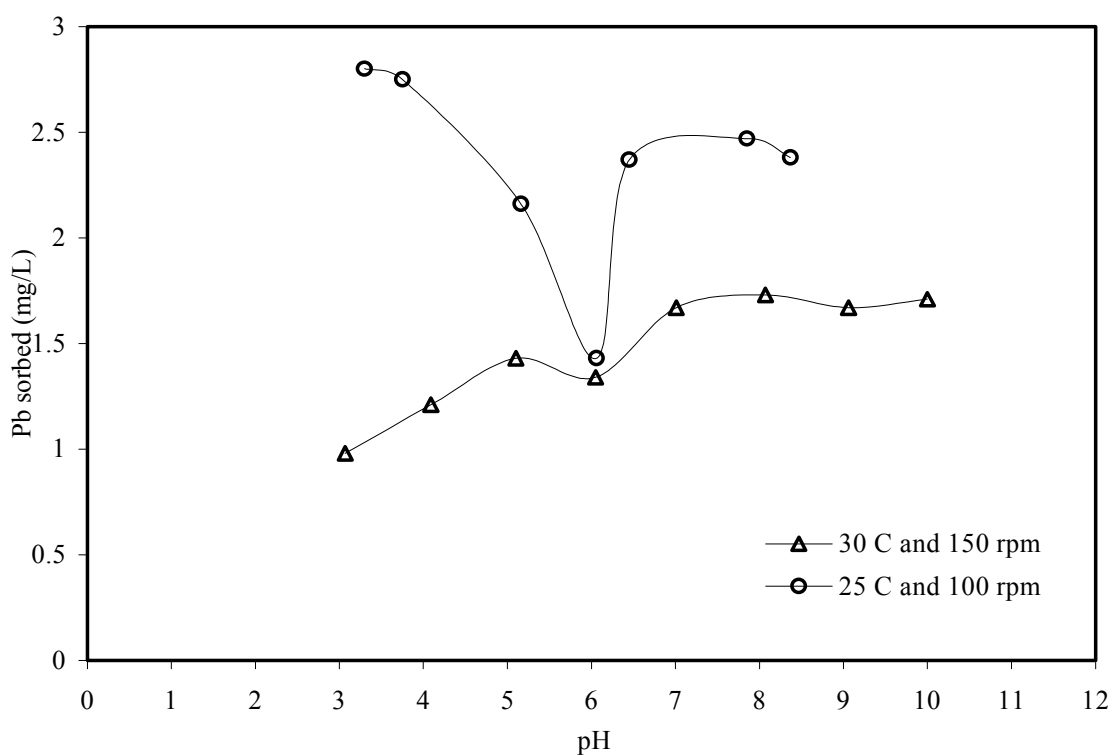


Figure 4.2 Effect of pH on lead adsorption at two different temperatures and agitation speeds.

The solubility of the metal ions plays an important role in adsorption because the distribution of species is a function of pH. Zn is present as monovalent cation $ZnOH^+$ at low pH, and as divalent ions Zn^{2+} at pH above 5 up to 10. Pb usually forms hydroxocomplexes. Below pH 6, Pb^{2+} is the major lead-containing species; at higher pH values, the polymeric hydroxocomplexes $Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$, and

$\text{Pb}(\text{OH})_4^{2+}$ predominate (Vernon et al., 1976).

4.1.2 Adsorption kinetics

The rates of uptake of lead and zinc by chitosan with time are shown in Figures 4.3 - 4.4. As can be seen from Figure 4.3, the rates of lead sorption were very rapid initially. Within first 1 hour, 46.7% of lead was sorbed while 60.7% was adsorbed in 12 hours. A total of up to 73.3 % of lead was removed in 24 hours.

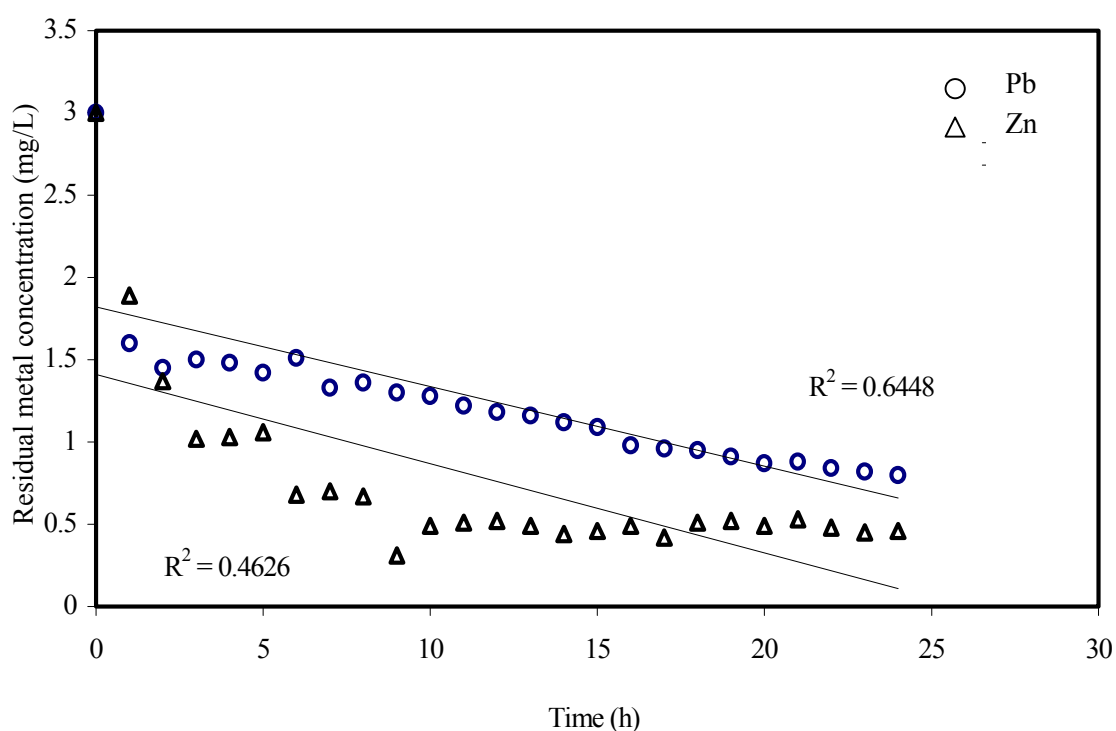


Figure 4.3 Adsorption kinetics of lead and zinc by using chitosan as adsorbent (zero-order reaction rate).

Rate of zinc adsorption was slower (37% removal) than lead (46.7% removal) during the initial one hour. However, within 12 hours period, zinc adsorption was much more rapid (more than 82.7% of zinc removal) in comparison to lead (60.7% removal). Up to 84.7% of zinc was removed in 24 hours.

Amino groups of chitosan act initially as metal coordination sites. Thus, the slower removal rate of metal after an initial rapid uptake can be due to the binding of metal by complexed metal ions. In a study on uranium removal by adsorption,

Trezis and Volesky (1981) also suggested that the mechanism of uranium removal by *T-arrhizus* initially involves the coordination of metal with the amino group of the cell wall of chitin network. The coordinated uranium functions subsequently as sites for additional uranium binding, primarily in the form of hydrated uranyl hydroxide.

Based on the results shown in Figures 4.3-4.4, reaction rate for adsorption of lead and zinc by chitosan is first-order reaction and equilibrium contact times of 24 hours were used for all further experiments.

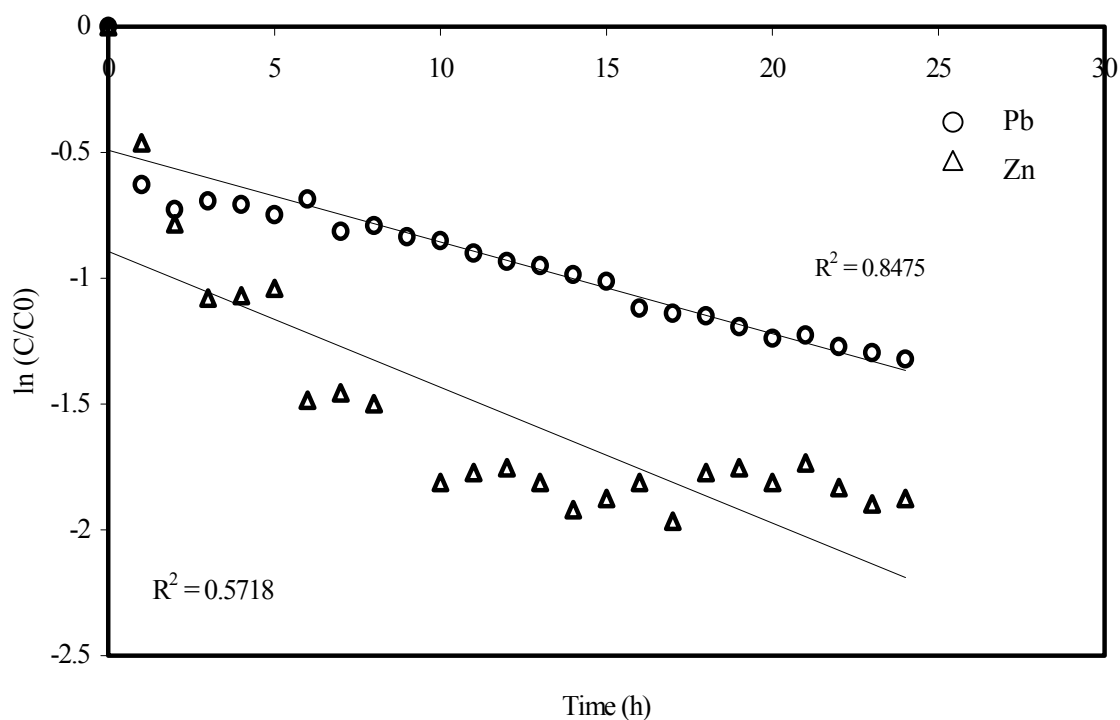


Figure 4.4 Adsorption kinetics of lead and zinc by using chitosan as adsorbent (first-order reaction rate).

4.1.3 Effect of chloride ion on adsorption

Effect of chloride ion concentration on lead (Pb) and zinc (Zn) adsorption by chitosan from synthetic wastewater at the optimum pH determined previously, is shown in Figure 4.5. As seen in Figure 4.5, presence of chloride ion in the synthetic wastewater slightly increased the zinc adsorption (19.4% improvement

at 500 mg/L of chloride ion concentration). However, there was a significant reduction(30 % reduction at 500 mg/L of chloride ion concentration) in lead uptake with increase in chloride ion concentration. There was an 23.3 % and 22.9 % increase in Zn adsorption with the chloride ion concentrations of 1,000 mg/L and 2,000 mg/L, respectively. While for Pb, there was 39.2 % and 56 % reduction in adsorption for the above two chloride ions concentrations, respectively.

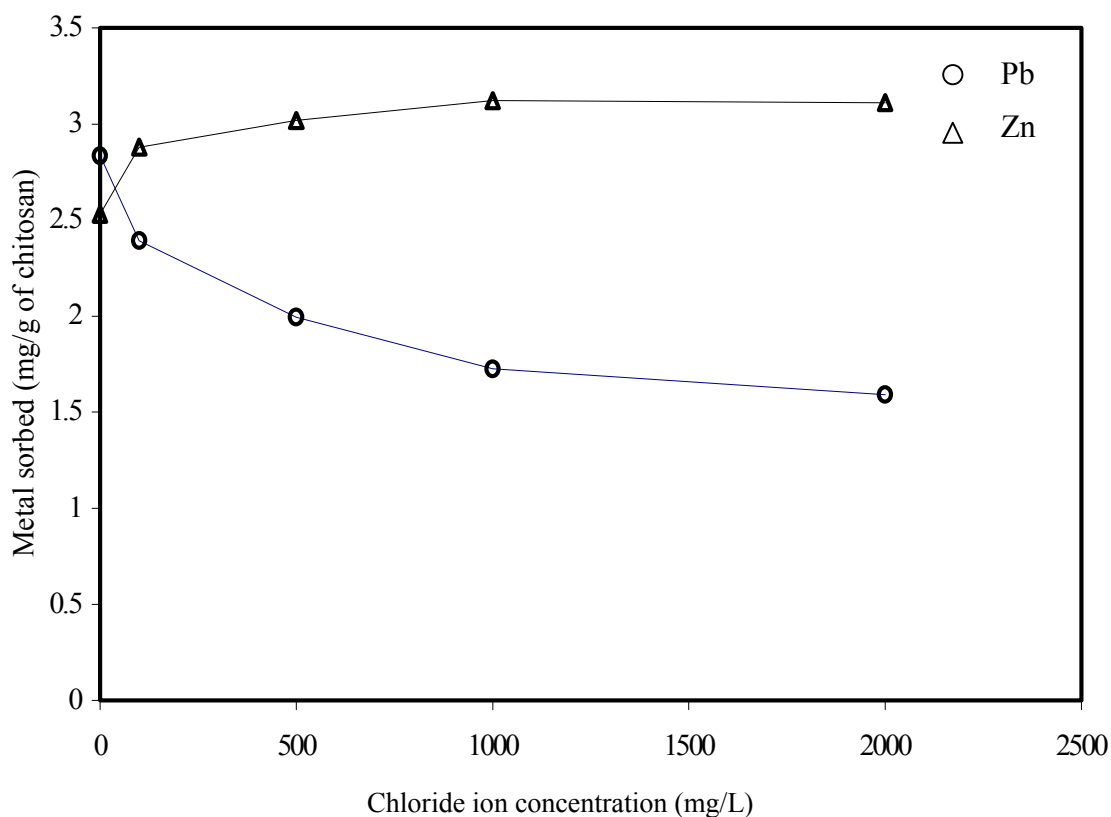


Figure 4.5 Effect of chloride ion concentration on lead and zinc adsorption.

The outmost shells of lead and zinc have the electronic configuration of $6s^2 4f^{14} 5d^{10} 6p^2$ and $4s^2 3d^{10}$, respectively (Hanpongpun, 1993). The d level orbitals of zinc are all filled and as there are no unpaired d electrons, it seems reasonable to assume that there will be a pronounced weakening of the metallic bonding. And that, the physical properties of zinc should be similar to those of copper which also has unpaired d electrons.

Lead forms various chloro complexes depending on pH and chloride

concentration. Chloride ion (Cl^-) can also actively compete with particulate binding sites for trace metals. Dissolved Na^+ , through univalent, may be able to compete for particulate binding sites, as it is present in solution at much higher concentration than trace metals. This study can not distinguish whether Cl^- competition with binding sites or Na^+ competition with trace metals, or both are occurring. However, the formation of soluble Cl^- complexes seems more possible than effective competition by Na^+ , a univalent ion, with divalent metal ions for exchange sites.

4.1.4 Effect of co-ions

Effect of co-ions on adsorption of lead and zinc by chitosan is illustrated in Figures 4.6-4.7, respectively. As can be seen from Figure 4.6, at lower equilibrium concentration of lead to be less than 2 mg/L, presence of zinc does not have any significant effect on lead adsorption capacity of chitosan. However, at equilibrium concentration of lead to be more than 2 mg/L, presence of zinc significantly suppresses lead adsorption capacity.

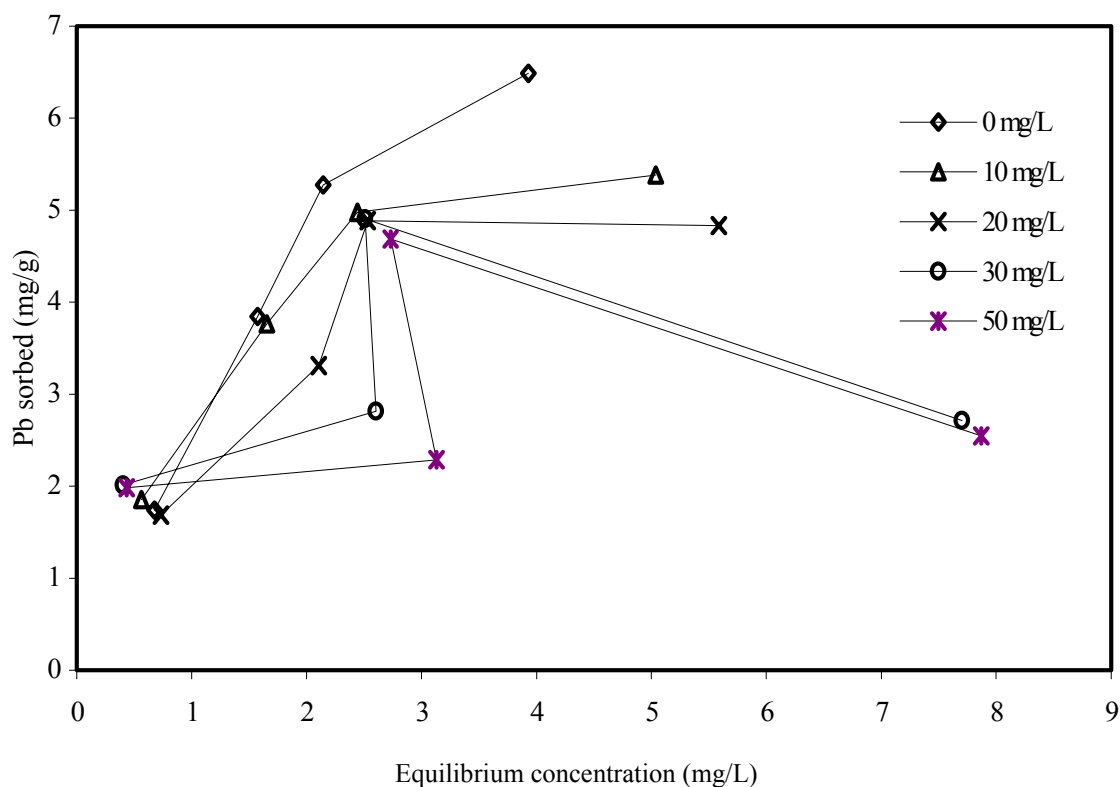


Figure 4.6 Effect of zinc concentration on adsorption of lead.

Zinc adsorption capacity of chitosan is interestingly very high in the absence of lead, as can be seen from Figure 4.7. Presence of lead significantly suppresses zinc adsorption capacity.

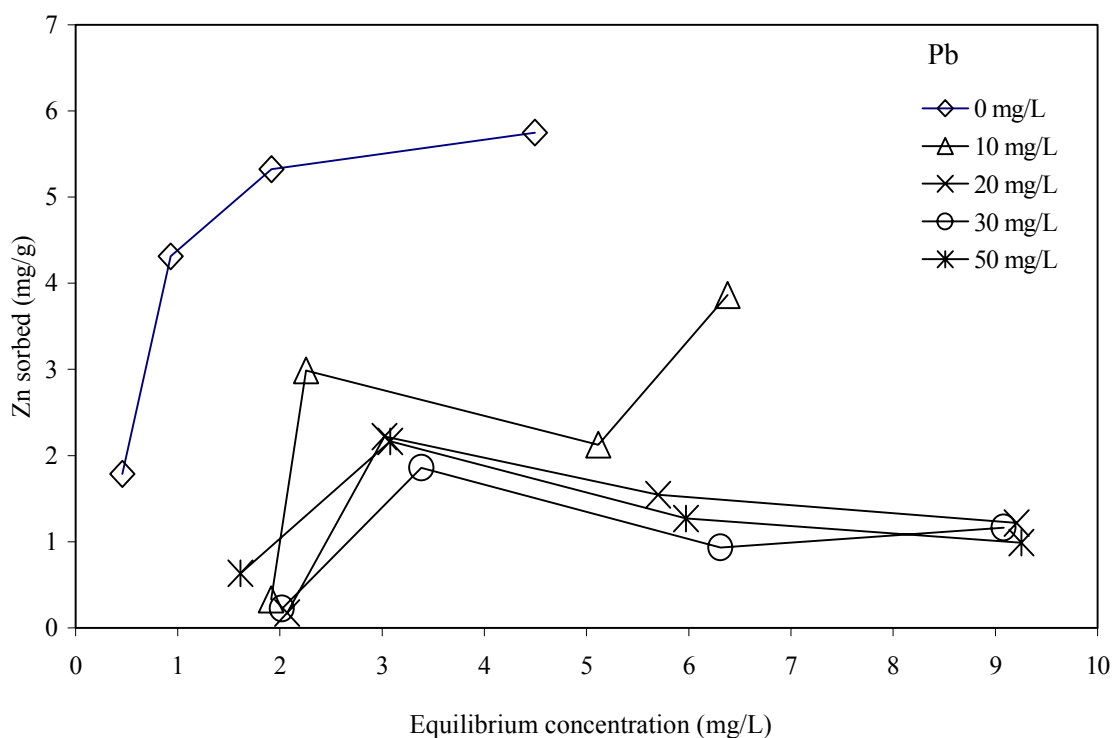


Figure 4.7 Effect of lead concentration on adsorption of zinc.

4.1.5 Adsorption isotherms

Based on the data from adsorption experiments, Langmuir and Freundlich isotherms were obtained for Pb and Zn as shown in Figures 4.8 - 4.10. The estimated Langmuir and Freundlich parameters are presented in Table 4.1. It can be seen in Figure 4.8 that 100.5 mg of lead and 165.7 mg of zinc could be adsorbed per g of chitosan at an equilibrium concentration of 300 mg/L. This Figure also suggests that zinc adsorption capacity of chitosan is higher than lead at any equilibrium concentration. Figure 4.10 illustrates that lead adsorption capacity sharply increase from 2.48 mg/g at equilibrium concentration of 0.92 mg/L to 59.08 mg/g at equilibrium concentration of 21.32 mg/L, remain steady up to equilibrium concentration of 227.73 mg/L. Beyond this adsorption capacity increase slightly to

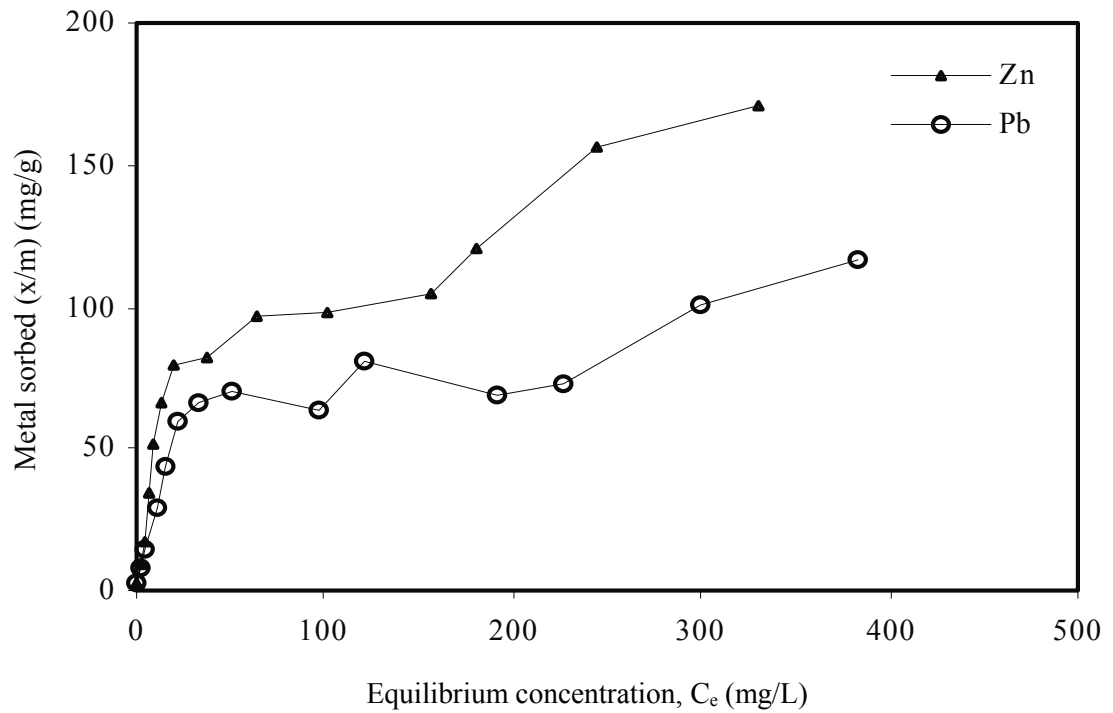


Figure 4.8 Langmuir adsorption isotherms for lead and zinc.

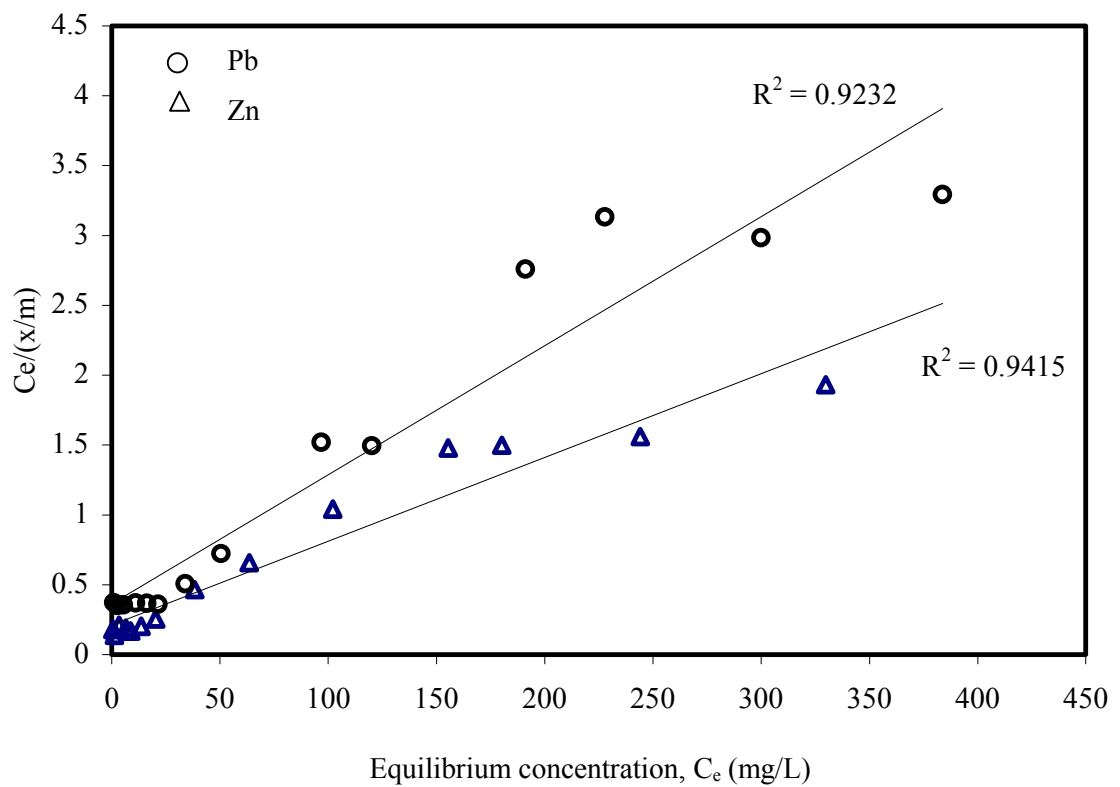


Figure 4.9 Linearized Langmuir adsorption isotherms for lead and zinc.

116.56 mg/g at equilibrium concentration of 383.84 mg/L. In the case of zinc, adsorption capacity increase sharply from 2.92 mg/g at equilibrium concentration of 0.523 mg/L to 36.121 mg/g at equilibrium of 4.319 mg/L. Beyond this, adsorption capacity increase slightly to 80.12 mg/g at equilibrium concentration of 20.32 mg/L, remain steady up to equilibrium concentration of 102.22 mg/L. Beyond this, sharp increase in adsorption capacity up to 156.35 mg/g at the equilibrium concentration of 244.09 mg/L.

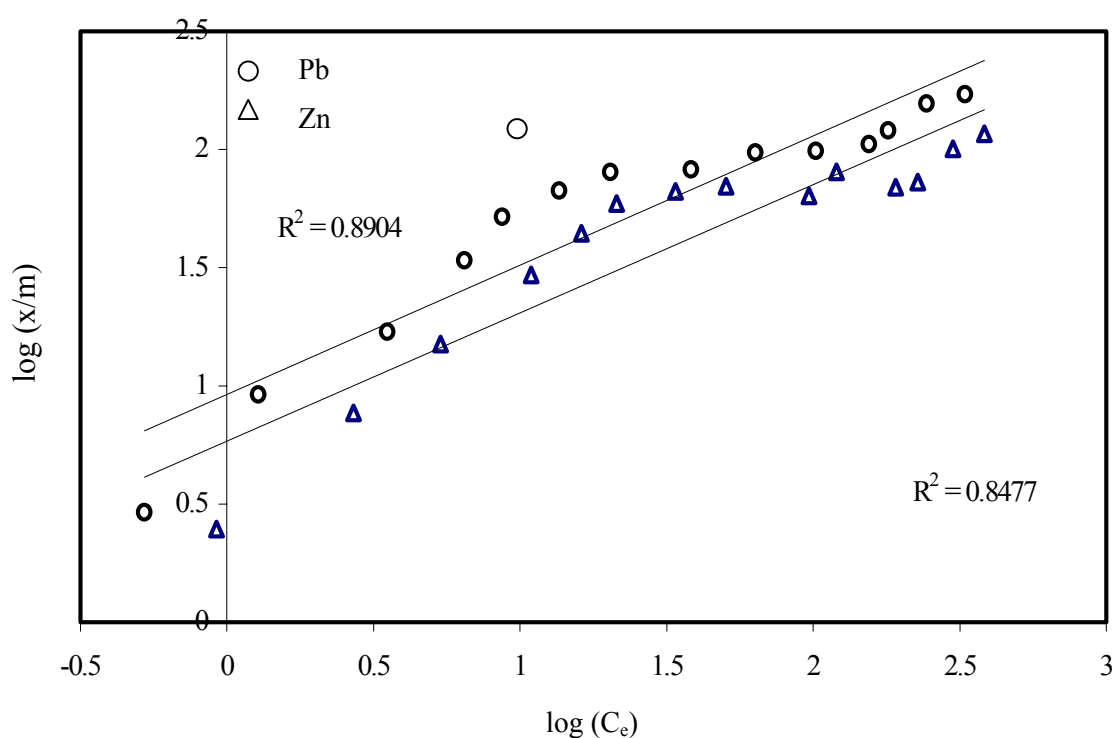


Figure 4.10 Linearized Langmuir adsorption isotherm of lead and zinc.

Table 4.1 Estimated Langmuir and Freundlich parameters for adsorption.

Metals	Freundlich Parameters		Langmuir Parameters	
	Intercept	Slope	a	b
	log k (mg/g)	1/n		
Lead	0.59	0.63	2.00	60.36
Zinc	0.54	0.90	3.81	49.27

Langmuir Isotherms for adsorption of lead and zinc were

$$\frac{x}{m} = \frac{2(60.36)C_e}{1 + 60.36C_e} \quad \text{and} \quad \frac{x}{m} = \frac{3.81(49.27)C_e}{1 + 49.27C_e}, \text{ respectively.}$$

Freundlich Isotherms for adsorption of lead and zinc were

$$\frac{x}{m} = (3.9)C_e^{1/1.58} \quad \text{and} \quad \frac{x}{m} = (3.48)C_e^{1/1.11}, \text{ respectively.}$$

4.2 Batch desorption experiments

4.2.1 Effect of pH

The effect of pH on desorption of lead and zinc by chitosan over a pH range of 2.5-10, at temperature 25 °C with agitation speed 100 rpm is illustrated in Figure 4.11. The results indicate that the desorption capacity for lead was maximum, 1.90 mg/g of chitosan, with 68.1% removal at about pH 2.8. At pH 6, the desorption was 1.13 mg/g (40.4% removal). The desorption showed the lowest value of 0.77 mg/g (27.4% removal) at pH 9.7. Similar trend was observable for desorption of zinc.

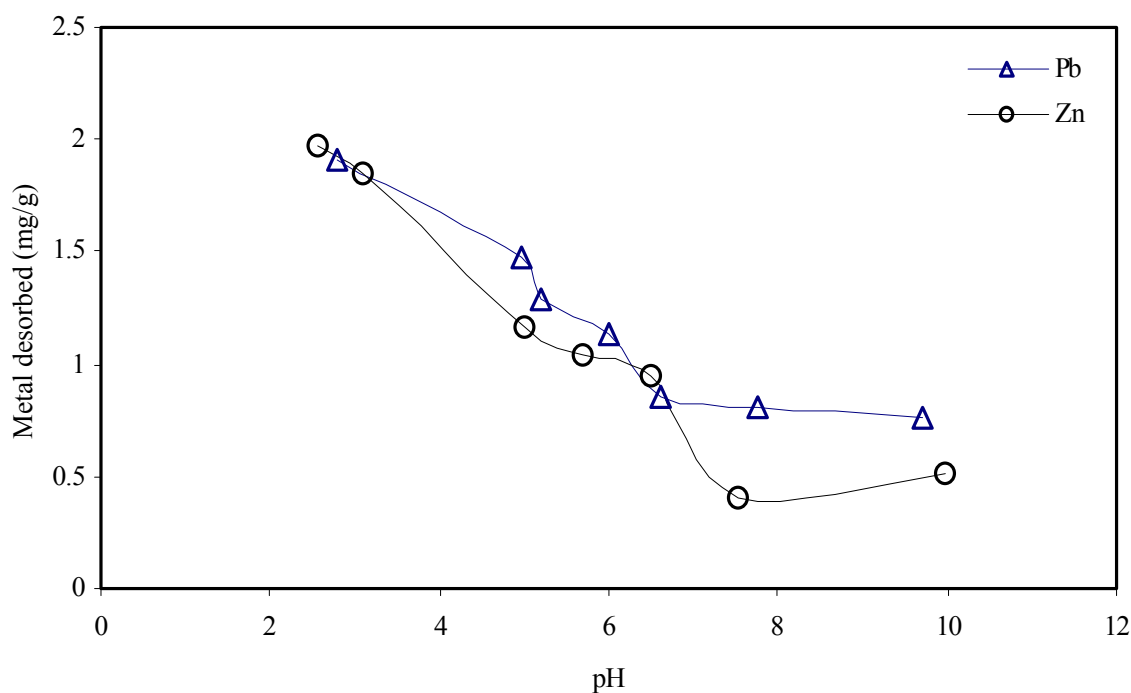


Figure 4.11 Effect of pH on lead and zinc desorption.

The desorption capacity for zinc was maximum, 1.97 mg/g of chitosan, with 66.2% removal at low pH of about 2.5. At pH 5.7, the desorption was 1.03 mg/g (34.7% removal). The desorption showed the lowest value of 0.51 mg/g (16.9% removal) at pH around 10. Muzzarelli and Tubertini (1969) indicated a qualitative decline in the metal uptake capacity of chitin and chitosan for an extended series of metals, when the solution pH was reduced from 7 to 2.5. A similar observation was reported by Trezos (1983), who studied uranium uptake by chitosan. At low pH, abundant proton compete for the adsorption site with metal, thus release the metal ions adsorbed on chitosan particles to the suspending medium causing desorption. Hence, higher amount of metals desorbed from chitosan at lower pH values.

4.2.2 Desorption kinetics

The results of desorption kinetics study of lead and zinc are presented in Figures 4.12-4.13. Lead desorption kinetics presented in Figure 4.12 suggests that 31.9 % of lead was desorbed in first 1 hour, while 60% was desorbed within next 12 hours. Desorption of lead from chitosan was almost completed within 19 hours. After

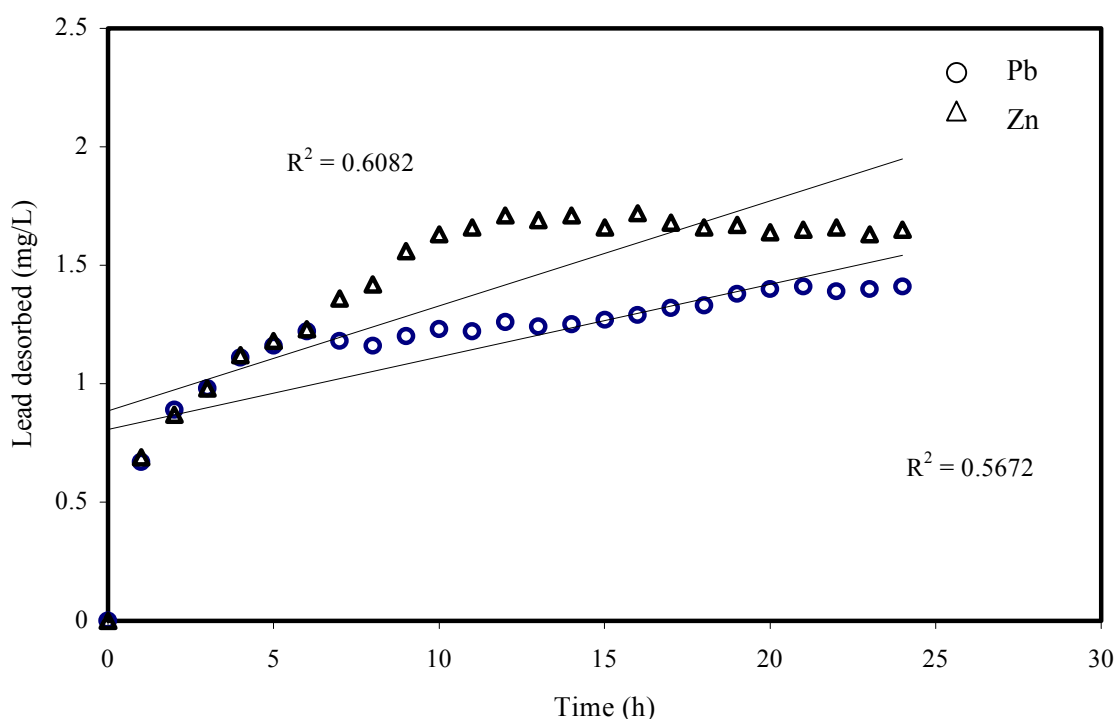


Figure 4.12 Desorption kinetics of lead and zinc from chitosan.
(zero-order reaction rate)

(66.7% removal). Zinc desorption kinetics also showed the similar trend with 27.6% removal in first 1 hour and 68.4% being desorbed within 12 hours. Zinc desorption from chitosan was almost complete within 11 hours, beyond which the amount of zinc desorbed came to a steady value of 1.7 mg/g (68.4% removal). Based on the results shown in Figure 4.12 – 4.13, reaction rate for desorption of Pb and Zn from chitosan is zero- order reaction.

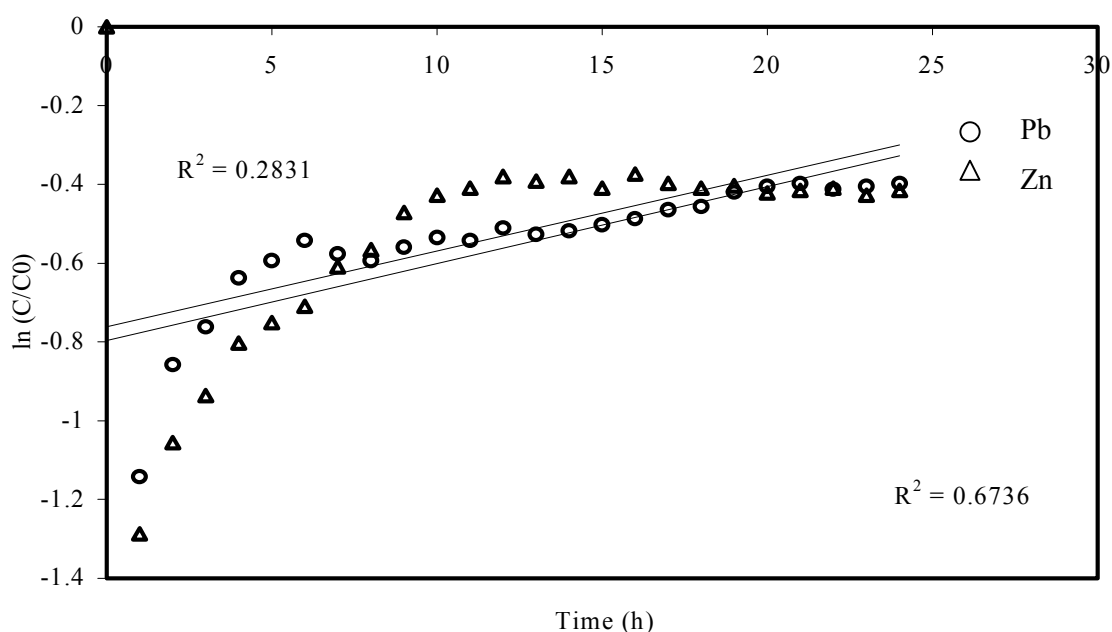


Figure 4.13 Desorption kinetics of lead and zinc from chitosan (first-order reaction rate).

4.2.3 Desorption isotherms

The data obtained from the desorption experiments, conducted at optimum pH for each metal, were analysed for both Langmuir and Freundlich isotherms as shown in Figure 4.14. Linearized plot of these data are presented in Figure 4.15. Freundlich isotherms are as illustrated in Figure 4.16. The estimated Langmuir and Freundlich parameters are presented in Table 4.2. As shown in Figure 4.14, 33.8 mg of lead was remaining per g of chitosan at an equilibrium concentration of 20 mg/L. And 48.6 mg of zinc was remaining per g of chitosan at an equilibrium concentration of 20 mg/L. At these equilibrium concentrations, 36.5 % of lead and 35.7 % of zinc were desorbed from chitosan. Desorption capacity of chitosan for lead

was higher than for zinc at any equilibrium concentration.

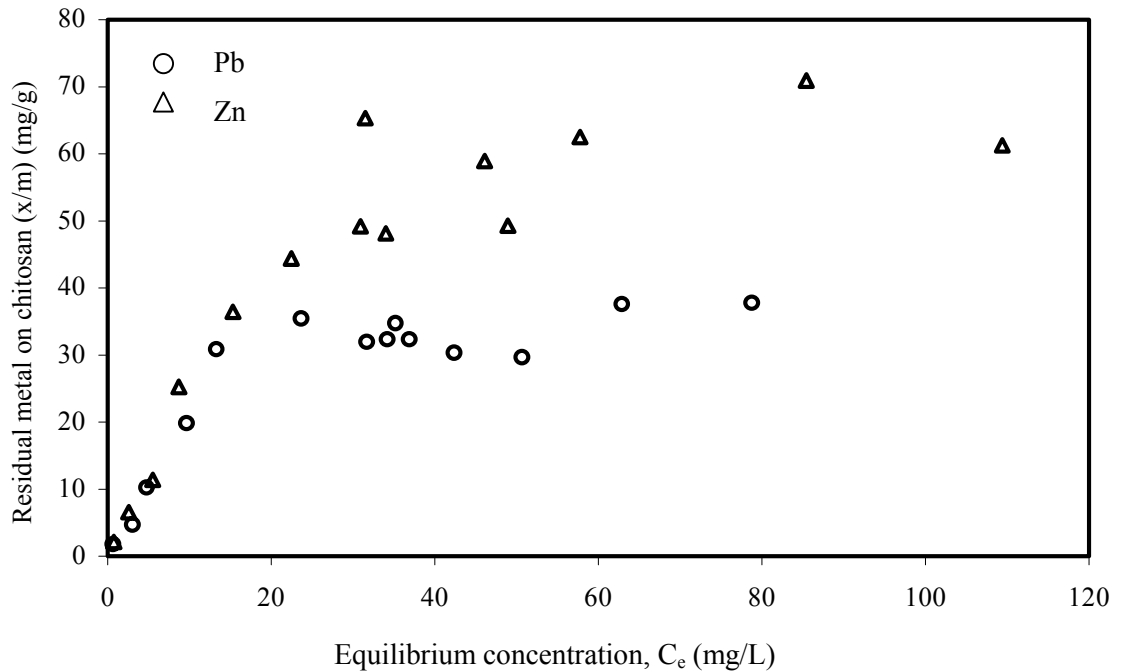


Figure 4.14 Langmuir desorption isotherms for lead and zinc.

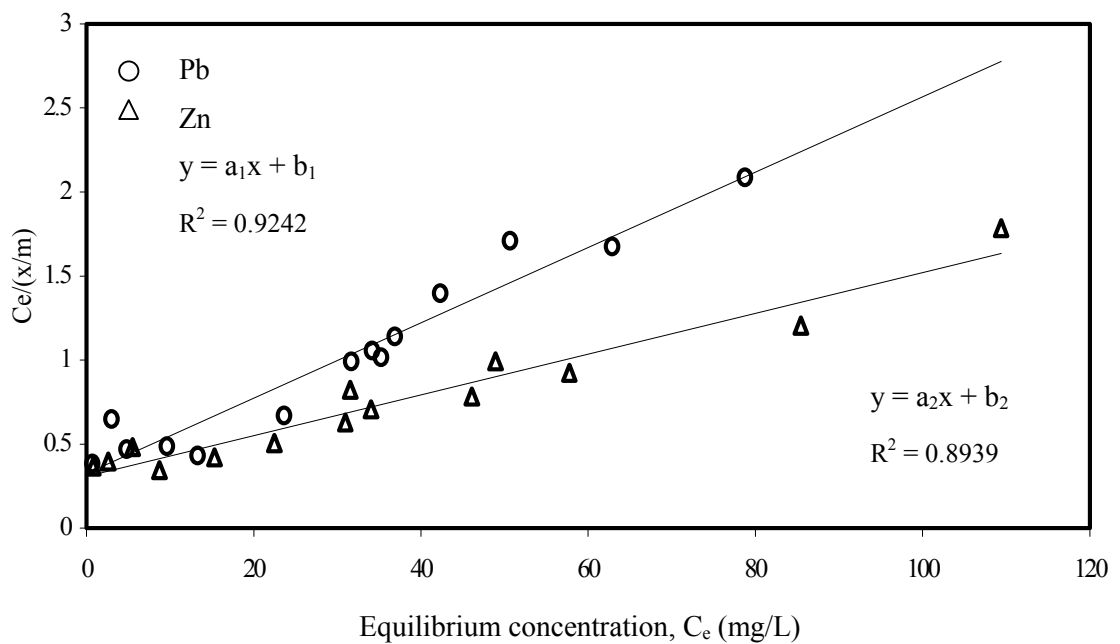


Figure 4.15 Linearized Langmuir desorption isotherms for lead and zinc.

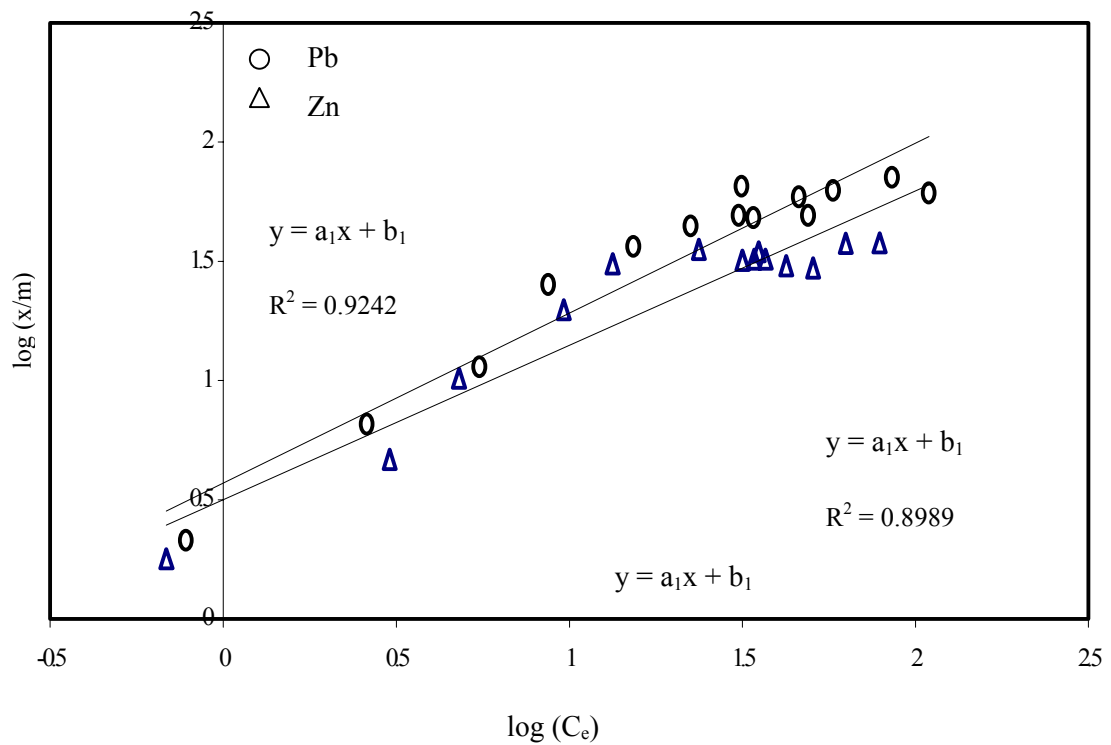


Figure 4.16 Freundlich isotherms for desorption of lead and zinc.

Table 4.2 Langmuir and Freundlich parameters for desorption.

Metals	Freundlich Parameters		Langmuir Parameters	
	Intercept	Slope	a	b
	log k (mg/g)	1/n		
Lead	1.52	-0.54	0.26	0.25
Zinc	1.23	-0.51	-43.23	-89.26

Langmuir Isotherms for desorption of lead and zinc were

$$\frac{x}{m} = \frac{0.26 (0.25)C_e}{1 + 0.25C_e} \text{ and } \frac{x}{m} = \frac{-43.23 (-89.26)C_e}{1 + (-89.26)C_e}, \text{ respectively.}$$

Freundlich Isotherms for desorption of lead and zinc were

$$\frac{x}{m} = (33.5)C_e^{1/(-1.85)} \text{ and } \frac{x}{m} = (16.94)C_e^{1/(-1.95)}, \text{ respectively.}$$

Chapter V

Conclusions and Recommendations

5.1 Conclusions

Based on the results of this study, following conclusions could be drawn:

- 5.1.1 The optimum pH values for adsorption on chitosan at 25 °C and agitation speed of 100 rpm were 3.3 and 7.3 for lead and zinc, respectively.
- 5.1.2 The optimum pH values for lead and zinc desorption from chitosan were 2.5 and 2.8 , respectively.
- 5.1.3 Presence of chloride ions did not significantly affect the zinc removal. However, it could greatly affect the lead uptake by chitosan.
- 5.1.4 The amount of lead and zinc adsorbed decreased in the presence of co-ions.
- 5.1.5 Equilibrium contact times for both adsorption and desorption of lead and zinc were 24 hours.
- 5.1.6 Langmuir Isotherms for adsorption of lead and zinc were

$$\frac{x}{m} = \frac{2(60.36)C_e}{1 + 60.36C_e} \text{ and } \frac{x}{m} = \frac{3.81(49.27)C_e}{1 + 49.27C_e}, \text{ respectively.}$$
- 5.1.7 Freundlich Isotherms for adsorption of lead and zinc were

$$\frac{x}{m} = (3.9)C_e^{1/1.58} \text{ and } \frac{x}{m} = (3.48)C_e^{1/1.11}, \text{ respectively.}$$
- 5.1.8 Langmuir Isotherms for desorption of lead and zinc were

$$\frac{x}{m} = \frac{0.26(0.25)C_e}{1 + 0.25C_e} \text{ and } \frac{x}{m} = \frac{-43.23(-89.26)C_e}{1 + (-89.26)C_e}, \text{ respectively.}$$
- 5.1.9 Freundlich Isotherms for desorption of lead and zinc were

$$\frac{x}{m} = (33.5)C_e^{1/(-1.85)} \text{ and } \frac{x}{m} = (16.94)C_e^{1/(-1.95)}, \text{ respectively.}$$

5.2 Recommendations

Following recommendations are suggested for future research:

- 5.2.1 Adsorption capacity of regenerated chitosan should be further evaluated.
- 5.2.2 Life of regenerated chitosan should be investigated.
- 5.2.3 Some other characteristics of chitosan, useful in wastewater purification, should be investigated, such as for removal of suspended solids, dissolved solids, BOD, COD, free chlorine, and total kjedahl nitrogen (TKN).

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Appendix A
First Set of Observations

Table A.1 Effect of pH on lead adsorption (25 °C, 100 rpm)

(Initial concentration = 3.78 mg/L)

pH	Final concentration (mg/L)	Pb sorbed (mg/L)	Pb sorbed (mg/g)
3.30	1.05	2.70	2.70
3.75	1.04	2.68	2.68
5.16	1.68	2.08	2.08
6.06	2.34	1.39	1.39
6.45	1.42	2.28	2.28
7.85	1.37	2.41	2.41
8.37	1.47	2.30	2.30

Table A.2 Effect of pH on zinc adsorption (25 °C, 100 rpm)

(Initial concentration = 3.54 mg/L)

PH	Final concentration (mg/L)	Zn sorbed (mg/L)	Zinc sorbed (mg/g)
3.63	0.99	2.55	2.55
4.02	1.04	2.48	2.48
4.62	1.37	2.09	2.09
5.10	1.03	2.51	2.51
6.98	1.26	2.28	2.28
7.30	0.56	2.98	2.98
8.30	0.65	2.89	2.89

Table A.3 Effect of pH on lead adsorption (30 °C, 150 rpm)

(Initial concentration = 2.00 mg/L)

sample	pH	Pb sorbed (mg/g)
1	3.07	0.94
2	4.09	1.23
3	5.1	1.46
4	6.05	1.29
5	7.01	1.64
6	8.07	1.7
7	9.06	1.69
8	10	1.63

Table A.4 Effect of pH on lead desorption (25 °C, 100 rpm)

(Initial concentration = 2.694 mg/g)

sample	pH	Pb desorbed
1	2.8	1.882
2	4.96	1.385
3	5.2	1.285
4	6	1.124
5	6.6	0.846
6	7.75	0.782
7	9.7	0.758

Table A.5 Effect of pH on zinc desorption (25 °C, 100 rpm)

(Initial concentration = 2.862 mg/g)

sample	pH	Zn desorbed (mg/g)
1	2.55	1.981
2	3.1	1.821
3	5	1.149
4	5.7	1.022
5	6.5	0.939
6	7.52	0.406
7	9.96	0.489

Table A.6 Effect of pH on lead desorption (30 °C, 150 rpm)

(Initial concentration = 1.51 mg/g)

sample	pH	Pb desorbed (mg/g)
1	2.5	1.20
2	2.97	1.26
3	4.1	0.33
4	4.97	0.12
5	6.03	0.03
6	7.1	0
7	8	0
8	9.1	0
9	10	0

Table A.7 Kinetics study (lead)

Adsorption study: initial conc.= 3 mg/L			Desorption study: Initial conc.=2.08 mg/g		
Time (h)	Remaining concentration (mg/L)	Pb Sorbed (mg/g)	Time (h)	Remaining concentration (mg/L)	Pb Desorbed (mg/g)
0	3	0	0	2.08	0
1	1.62	1.38	1	1.45	0.63
2	1.49	1.51	2	1.22	0.86
3	1.51	1.49	3	1.18	0.9
4	1.48	1.52	4	0.98	1.1
5	1.44	1.56	5	0.96	1.12
6	1.58	1.42	6	0.88	1.2
7	1.35	1.65	7	0.92	1.16
8	1.34	1.66	8	0.93	1.15
9	1.28	1.72	9	0.88	1.2
10	1.29	1.71	10	0.89	1.19
11	1.22	1.78	11	0.87	1.21
12	1.21	1.79	12	0.82	1.26
13	1.14	1.86	13	0.88	1.2
14	1.17	1.83	14	0.85	1.23
15	1.05	1.95	15	0.82	1.26
16	0.95	2.05	16	0.84	1.24
17	1	2	17	0.79	1.29
18	0.96	2.04	18	0.77	1.31
19	0.94	2.06	19	0.74	1.34
20	0.87	2.13	20	0.69	1.39
21	0.86	2.14	21	0.67	1.41
22	0.86	2.14	22	0.72	1.36
23	0.83	2.17	23	0.7	1.38
24	0.81	2.19	24	0.7	1.38

Table A.8 Kinetics study (zinc)

Adsorption study: initial concentration = 3 mg/L			Desorption study: Initial concentration =2.45 mg/g		
Time (h)	Remaining concentration (mg/L)	Zn sorbed (mg/g)	Time (h)	Remaining concentration (mg/L)	Zn desorbed (mg/g)
0	3	0	0	2.45	0
1	2.03	0.97	1	1.81	0.64
2	1.38	1.62	2	1.6	0.85
3	0.99	2.01	3	1.49	0.96
4	1.02	1.98	4	1.36	1.09
5	1.11	1.89	5	1.26	1.19
6	0.68	2.32	6	1.22	1.23
7	0.72	2.28	7	1.07	1.38
8	0.65	2.35	8	1.06	1.39
9	0.28	2.72	9	0.92	1.53
10	0.46	2.54	10	0.83	1.62
11	0.56	2.44	11	0.86	1.59
12	0.54	2.46	12	0.77	1.68
13	0.52	2.48	13	0.75	1.7
14	0.43	2.57	14	0.75	1.7
15	0.48	2.52	15	0.81	1.64
16	0.47	2.53	16	0.72	1.73
17	0.45	2.55	17	0.79	1.66
18	0.47	2.53	18	0.79	1.66
19	0.57	2.43	19	0.81	1.64
20	0.49	2.51	20	0.77	1.68
21	0.51	2.49	21	0.82	1.63
22	0.51	2.49	22	0.8	1.65
23	0.46	2.54	23	0.82	1.63
24	0.44	2.56	24	0.81	1.64

Table A.9 Effect of chloride ions concentration on lead adsorption

Chloride ion concentration (mg/L)	Initial Pb concentration (mg/L)	Pb sorbed (mg/g)
0	4.02	2.80
100	4.02	2.44
500	4.02	2.03
1000	4.02	1.65
2000	4.02	1.52

Table A.10 Effect of chloride ions concentration on zinc adsorption

Chloride ion concentration (mg/L)	Initial Zn concentration (mg/L)	Zn sorbed (mg/g)
0	3.76	2.45
100	3.76	2.99
500	3.76	2.98
1000	3.76	3.06
2000	3.76	3.15

Table A.11 Effect of zinc concentration on adsorption of lead

Initial Pb concentration (mg/L)	Zn concentration (mg/L)	Equivalent concentration (mg/L)	Pb sorbed (mg/g)
2.287	0	0.665	1.622
5.287	0	1.446	3.841
7.287	0	2.115	5.172
10.287	0	3.764	6.523
2.287	10	0.501	1.786
5.287	10	1.578	3.709
7.287	10	2.441	4.798
10.287	10	5.036	5.203
2.287	20	0.673	1.614
5.287	20	2.009	3.278
7.287	20	2.533	4.833
10.287	20	5.587	4.843
2.287	30	0.266	2.021
5.287	30	2.492	2.795
7.287	30	2.401	4.886
10.287	30	7.581	2.706
2.287	50	0.341	1.946
5.287	50	3.02	2.267
7.287	50	2.618	4.669
10.287	50	7.76	2.527

Table A.12 Effect of lead concentration on adsorption of zinc

Initial Zn concentration (mg/L)	Pb concentration (mg/L)	Equivalent concentration (mg/L)	Zn sorbed (mg/g)
2.318	0	0.531	1.787
5.318	0	1.002	4.316
7.318	0	1.987	5.331
10.318	0	4.572	5.746
2.318	10	1.913	0.343
5.318	10	2.327	2.991
7.318	10	5.186	2.132
10.318	10	6.452	3.866
2.318	20	2.139	0.179
5.318	20	3.087	2.231
7.318	20	5.773	1.545
10.318	20	9.092	1.226
2.318	30	2.09	0.228
5.318	30	3.45	1.868
7.318	30	6.387	0.931
10.318	30	9.152	1.166
2.318	50	1.62	0.698
5.318	50	3.152	2.166
7.318	50	6.046	1.272
10.318	50	9.327	0.991

Table A.13 Isotherm study (lead)

Initial concentration (mg/L)	Final concentration (mg/L)	Pb sorbed (mg/g)	% Removal	Pb remaining on chitosan (mg/g)	Pb desorbed (mg/g)	% Desorption
3.484	0.901	2.583	74.13892078	1.756	0.827	32.01703446
10.484	2.698	7.786	74.2655475	4.598	3.188	40.94528641
20.484	5.361	15.123	73.82835384	10.251	4.872	32.21583019
40.484	10.921	29.563	73.02391068	19.866	9.697	32.80113656
60.484	16.167	44.317	73.27061702	30.74	13.577	30.63609901
80.484	21.325	59.159	73.50405049	35.389	23.77	40.17985429
100.484	33.844	66.64	66.31901596	32.396	34.244	51.38655462
120.484	50.446	70.038	58.13054015	34.841	35.197	50.25414775
160.484	96.733	63.751	39.72420927	31.756	31.995	50.18744804
200.484	120.009	80.475	40.14036033	29.642	50.833	63.16620068
260.484	191.129	69.355	26.62543573	32.326	37.029	53.390527
300.484	227.455	73.029	24.30378989	30.288	42.741	58.52606499
400.484	300.07	100.414	25.07316147	37.64	62.774	62.51518713
500.484	382.899	117.585	23.49425756	37.89	79.695	67.7765021

Table A.14 Isotherm study (zinc)

Initial concentration (mg/L)	Final concentration Ce (mg/L)	Zn sorbed (mg/g)	% Removal	Zn remaining on chitosan (mg/g)	Zn desorbed (mg/g)	% Desorption
3.514	0.534	2.98	84.80364257	2.114	0.866	29.06040268
10.514	1.282	9.232	87.80673388	6.485	2.747	29.75519931
20.514	3.527	16.987	82.80686361	11.501	5.486	32.29528463
40.514	6.449	34.065	84.08204571	25.291	8.774	25.75664171
60.514	8.712	51.802	85.60333146	36.478	15.324	29.58186943
80.514	13.614	66.9	83.09113943	44.374	22.526	33.67115097
100.514	30.324	70.19	69.83106831	49.109	21.081	30.0341929
120.514	38.281	82.233	68.23522578	48.144	34.089	41.45416074
160.514	63.601	96.913	60.37666496	65.341	31.572	32.57767276
200.514	102.229	98.285	49.01652752	49.274	49.011	49.86620542
260.514	155.547	104.967	40.29226836	58.891	46.076	43.89570055
300.514	180.191	120.323	40.0390664	62.51	57.813	48.04817034
400.514	244.096	156.418	39.0543152	71.023	85.395	54.59410042
500.514	329.774	170.74	34.11293191	59.877	110.863	64.93088907

Appendix B
Second Set of Observations

Table B.1 Effect of pH on lead adsorption (25 °C, 100 rpm)

(Initial concentration = 3.84 mg/L)

pH	Final concentration (mg/L)	Pb sorbed (mg/L)	Pb sorbed (mg/g)
3.30	1.05	2.78	2.78
3.75	1.08	2.76	2.76
5.16	1.69	2.21	2.21
6.06	2.40	1.51	1.51
6.45	1.46	2.42	2.42
7.85	1.38	2.44	2.44
8.37	1.43	2.43	2.43

Table B.2 Effect of pH on zinc adsorption (25 °C, 100 rpm)

(Initial concentration = 3.59 mg/L)

pH	Final concentration (mg/L)	Zn sorbed (mg/L)	Zinc sorbed (mg/g)
3.63	0.92	2.67	2.71
4.02	0.95	2.64	2.64
4.62	1.46	2.13	2.22
5.10	1.05	2.54	2.57
6.98	1.28	2.31	2.31
7.30	0.55	3.04	3.11
8.30	0.72	2.87	2.87

Table B.3 Effect of pH on lead adsorption (30 °C, 150 rpm)

Initial concentration = 2.00 mg/L

sample	pH	Pb sorbed (mg/g)
1	3.07	0.99
2	4.09	1.17
3	5.1	1.41
4	6.05	1.35
5	7.01	1.65
6	8.07	1.67
7	9.06	1.62
8	10	1.66

Table B.4 Effect of pH on lead desorption (25 °C, 100 rpm)

Initial concentration = 2.7 mg/g

sample	pH	Pb desorbed
1	2.8	1.898
2	4.96	1.378
3	5.2	1.269
4	6	1.131
5	6.6	0.787
6	7.75	0.871
7	9.7	0.754

Table B.5 Effect of pH on zinc desorption (25 °C, 100 rpm)

Initial concentration = 2.992 mg/g

sample	pH	Zn desorbed (mg/g)
1	2.55	1.970
2	3.1	1.862
3	5	1.169
4	5.7	1.041
5	6.5	0.955
6	7.52	0.381
7	9.96	0.496

Table B.6 Effect of pH on lead desorption (30 °C, 150 rpm)

Initial concentration = 1.36 mg/g

sample	pH	Pb desorbed (mg/g)
1	2.5	1.11
2	2.97	1.18
3	4.1	1.24
4	4.97	0.06
5	6.03	0.01
6	7.1	0
7	8	0
8	9.1	0
9	10	0

Table B.7 Kinetics study (lead)

Adsorption study: initial concentration = 3 mg/L			Desorption study: Initial concentration = 2.14 mg/g		
Time (h)	Remaining concentration (mg/L)	Pb sorbed (mg/g)	Time (h)	Remaining concentration (mg/L)	Pb desorbed (mg/g)
0	3	0	0	2.14	0
1	1.59	1.41	1	1.48	0.66
2	1.45	1.55	2	1.23	0.91
3	1.47	1.53	3	1.16	0.98
4	1.5	1.5	4	1.05	1.09
5	1.46	1.54	5	0.96	1.18
6	1.53	1.47	6	0.89	1.25
7	1.32	1.68	7	0.96	1.18
8	1.36	1.64	8	0.96	1.18
9	1.26	1.74	9	0.93	1.21
10	1.26	1.74	10	0.94	1.2
11	1.24	1.76	11	0.9	1.24
12	1.19	1.81	12	0.89	1.25
13	1.18	1.82	13	0.9	1.24
14	1.14	1.86	14	0.88	1.26
15	1.19	1.81	15	0.85	1.29
16	0.92	2.08	16	0.86	1.28
17	0.95	2.05	17	0.81	1.33
18	0.96	2.04	18	0.84	1.3
19	0.89	2.11	19	0.78	1.36
20	0.9	2.1	20	0.72	1.42
21	0.89	2.11	21	0.74	1.4
22	0.84	2.16	22	0.73	1.41
23	0.82	2.18	23	0.73	1.41
24	0.79	2.21	24	0.72	1.42

Table B.8 Kinetics study (zinc)

Adsorption study: initial concentration = 3 mg/L			Desorption study: Initial concentration =2.52 mg/g		
Time (h)	Remaining concentration (mg/L)	Zn sorbed (mg/g)	Time (h)	Remaining concentration (mg/L)	Zn desorbed (mg/g)
0	3	0	0	2.52	0
1	2.88	0.12	1	1.84	0.68
2	1.39	1.61	2	1.63	0.89
3	1.04	1.96	3	1.46	1.06
4	1.06	1.94	4	1.34	1.18
5	1.05	1.95	5	1.36	1.16
6	0.65	2.35	6	1.28	1.24
7	0.69	2.31	7	1.17	1.35
8	0.67	2.33	8	1.07	1.45
9	0.33	2.67	9	0.93	1.59
10	0.48	2.52	10	0.91	1.61
11	0.51	2.49	11	0.85	1.67
12	0.48	2.52	12	0.75	1.77
13	0.49	2.51	13	0.8	1.72
14	0.51	2.49	14	0.81	1.71
15	0.47	2.53	15	0.83	1.69
16	0.47	2.53	16	0.79	1.73
17	0.46	2.54	17	0.84	1.68
18	0.47	2.53	18	0.83	1.69
19	0.51	2.49	19	0.82	1.7
20	0.5	2.5	20	0.84	1.68
21	0.49	2.51	21	0.89	1.63
22	0.51	2.49	22	0.87	1.65
23	0.47	2.53	23	0.87	1.65
24	0.48	2.52	24	0.89	1.63

Table B.9 Effect of chloride ions concentration on lead adsorption

Chloride ion concentration (mg/L)	Initial Pb concentration (mg/L)	Pb sorbed (mg/g)
0	4.02	2.77
100	4.02	2.34
500	4.02	1.95
1000	4.02	1.77
2000	4.02	1.55

Table B.10 Effect of chloride ions concentration on zinc adsorption

Chloride ion concentration (mg/L)	Initial Zn concentration (mg/L)	Zn sorbed (mg/g)
0	3.76	2.55
100	3.76	2.86
500	3.76	3.10
1000	3.76	3.18
2000	3.76	3.06

Table B.11 Effect of zinc concentration on adsorption of lead

Initial Pb concentration (mg/L)	Zn concentration (mg/L)	Equivalent concentration (mg/L)	Pb sorbed (mg/g)
2.494	0	0.696	1.798
5.494	0	1.638	3.856
7.494	0	2.23	5.264
10.494	0	3.99	6.504
2.494	10	0.632	1.862
5.494	10	1.773	3.721
7.494	10	2.441	5.116
10.494	10	5.036	5.462
2.494	20	0.833	1.661
5.494	20	2.182	3.312
7.494	20	2.533	4.769
10.494	20	5.587	4.786
2.494	30	0.453	2.041
5.494	30	2.58	2.914
7.494	30	2.487	5.007
10.494	30	7.77	2.724
2.494	50	1.281	1.213
5.494	50	3.215	2.279
7.494	50	2.871	4.623
10.494	50	7.881	2.613

Table B.12 Effect of lead concentration on adsorption of zinc

Initial Zn concentration (mg/L)	Pb concentration (mg/L)	Equivalent concentration (mg/L)	Zn sorbed (mg/g)
2.226	0	0.454	1.772
5.226	0	0.928	4.298
7.226	0	1.912	5.314
10.226	0	4.485	5.741
2.226	10	1.913	0.292
5.226	10	2.24	2.986
7.226	10	5.106	2.12
10.226	10	6.368	3.858
2.226	20	2.058	0.168
5.226	20	3.025	2.201
7.226	20	5.685	1.541
10.226	20	9.017	1.209
2.226	30	2.008	0.218
5.226	30	3.368	1.858
7.226	30	6.293	0.933
10.226	30	9.061	1.165
2.226	50	1.602	0.624
5.226	50	3.063	2.163
7.226	50	5.964	1.262
10.226	50	9.244	0.982

Table B.13 Isotherm study (lead)

Initial concentration (mg/L)	Final concentration (mg/L)	Pb sorbed (mg/g)	% Removal	Pb remaining on chitosan (mg/g)	Pb desorbed (mg/g)	% Desorption
3.318	0.918	2.4	72.33273056	1.766	0.634	26.41666667
10.318	2.699	7.619	73.84182981	4.61	3.009	39.49337183
20.318	5.242	15.076	74.20021656	10.233	4.843	32.12390555
40.318	9.912	30.406	75.41544719	19.833	10.573	34.77274222
60.318	16.191	44.127	73.15726649	30.94	13.187	29.88419788
80.318	21.288	59.03	73.49535596	35.485	23.545	39.88649839
100.318	33.647	66.671	66.45965829	32.312	34.359	51.53515022
120.318	50.341	69.977	58.16004255	34.601	35.376	50.55375338
160.318	96.314	64.004	39.92315273	31.567	32.437	50.67964502
200.318	120.004	80.314	40.09325173	29.66	50.654	63.06995044
260.318	190.166	70.152	26.94857828	32.331	37.821	53.91293192
300.318	227.139	73.179	24.3671708	30.214	42.965	58.71219885
400.318	298.14	102.178	25.52420825	36.78	65.398	64.00399303
500.318	381.899	118.419	23.66874668	38.788	79.631	67.24512114

Table B.14 Isotherm study (zinc)

Initial concentration (mg/L)	Final concentration Ce (mg/L)	Zn sorbed (mg/g)	% Removal	Zn remaining on chitosan (mg/g)	Zn desorbed (mg/g)	% Desorption
3.402	0.511	2.891	84.9794239	2.144	0.747	25.8388101
10.402	1.264	9.138	87.8484907	6.546	2.592	28.36506894
20.402	3.514	16.888	82.7761984	11.468	5.42	32.09379441
40.402	6.39	34.012	84.1839513	25.312	8.7	25.57920734
60.402	8.687	51.715	85.6180259	36.514	15.201	29.3937929
80.402	13.499	66.903	83.2106167	44.396	22.507	33.6412418
100.402	20.786	79.616	79.2972252	49.211	30.405	38.18955989
120.402	38.266	82.136	68.2181359	48.007	34.129	41.5518165
160.402	63.614	96.788	60.3408935	65.356	31.432	32.47510022
200.402	102.317	98.085	48.9441223	49.237	48.848	49.8017026
260.402	155.512	104.89	40.2800286	58.726	46.164	44.01182191
300.402	180.191	120.211	40.0167109	63.081	57.13	47.52476895
400.402	245.033	155.369	38.8032527	70.689	84.68	54.50250694
500.402	327.742	172.66	34.5042586	60.947	111.713	64.70114676

Appendix C
Third Set of Observations

Table C.1 Effect of pH on lead adsorption (25 °C, 100 rpm)

(Initial concentration = 3.82 mg/L)

pH	Final concentration (mg/L)	Pb sorbed (mg/L)	Pb sorbed (mg/g)
3.30	1.02	2.80	2.80
3.75	1.07	2.75	2.75
5.16	1.66	2.16	2.16
6.06	2.39	1.43	1.43
6.45	1.45	2.37	2.37
7.85	1.35	2.47	2.47
8.37	1.44	2.38	2.38

Table C.2 Effect of pH on zinc adsorption (25 °C, 100 rpm)

(Initial concentration = 3.57 mg/L)

pH	Final concentration (mg/L)	Zn sorbed (mg/L)	Zinc sorbed (mg/g)
3.63	0.90	2.67	2.67
4.02	0.98	2.58	2.58
4.62	1.41	2.15	2.15
5.10	1.07	2.50	2.50
6.98	1.23	2.33	2.33
7.30	0.54	3.02	3.02
8.30	0.71	2.85	2.85

Table C.3 Effect of pH on lead adsorption (30 °C, 150 rpm)

(Initial concentration = 2.00 mg/L)

sample	pH	Pb sorbed (mg/g)
1	3.07	0.98
2	4.09	1.21
3	5.1	1.43
4	6.05	1.34
5	7.01	1.67
6	8.07	1.73
7	9.06	1.67
8	10	1.71

Table C.4 Effect of pH on lead desorption (25 °C, 100 rpm)

(Initial concentration = 2.795 mg/g)

sample	pH	Pb desorbed
1	2.8	1.904
2	4.96	1.474
3	5.2	1.292
4	6	1.129
5	6.6	0.849
6	7.75	0.801
7	9.7	0.767

Table C.5 Effect of pH on zinc desorption (25 °C, 100 rpm)

(Initial concentration = 2.984 mg/g)

sample	pH	Zn desorbed (mg/g)
1	2.55	1.975
2	3.1	1.852
3	5	1.164
4	5.7	1.035
5	6.5	0.946
6	7.52	0.397
7	9.96	0.505

Table C.6 Effect of pH on lead desorption (30 °C, 150 rpm)

(Initial concentration = 1.47 mg/g)

sample	pH	Pb desorbed (mg/g)
1	2.5	1.21
2	2.97	1.29
3	4.1	0.31
4	4.97	0.09
5	6.03	0.02
6	7.1	0
7	8	0
8	9.1	0
9	10	0

Table C.7 Kinetics study (lead)

Adsorption study: initial concentration = 3 mg/L			Desorption study: Initial concentration = 2.10 mg/g		
Time (h)	Remaining concentration (mg/L)	Pb sorbed (mg/g)	Time (h)	Remaining concentration (mg/L)	Pb desorbed (mg/g)
0	3	0	0	2.1	0
1	1.6	1.4	1	1.43	0.67
2	1.45	1.55	2	1.21	0.89
3	1.5	1.5	3	1.12	0.98
4	1.48	1.52	4	0.99	1.11
5	1.42	1.58	5	0.94	1.16
6	1.51	1.49	6	0.88	1.22
7	1.33	1.67	7	0.92	1.18
8	1.36	1.64	8	0.94	1.16
9	1.3	1.7	9	0.9	1.2
10	1.28	1.72	10	0.87	1.23
11	1.22	1.78	11	0.88	1.22
12	1.18	1.82	12	0.84	1.26
13	1.16	1.84	13	0.86	1.24
14	1.12	1.88	14	0.85	1.25
15	1.09	1.91	15	0.83	1.27
16	0.98	2.06	16	0.81	1.29
17	0.96	2.04	17	0.78	1.32
18	0.95	2.05	18	0.77	1.33
19	0.91	2.09	19	0.72	1.38
20	0.87	2.13	20	0.7	1.4
21	0.88	2.12	21	0.69	1.41
22	0.84	2.16	22	0.71	1.39
23	0.82	2.18	23	0.7	1.4
24	0.8	2.2	24	0.69	1.41

Table C.8 Kinetics study (zinc)

Adsorption study: initial concentration = 3 mg/L			Desorption study: Initial concentration = 2.50 mg/g		
Time (h)	Remaining concentration (mg/L)	Zn sorbed (mg/g)	Time (h)	Remaining concentration (mg/L)	Zn desorbed (mg/g)
0	3	0	0	2.5	0
1	1.89	1.11	1	1.81	0.69
2	1.37	1.63	2	1.63	0.87
3	1.02	1.98	3	1.52	0.98
4	1.03	1.97	4	1.38	1.12
5	1.06	1.91	5	1.32	1.18
6	0.68	2.32	6	1.27	1.23
7	0.7	2.3	7	1.14	1.36
8	0.67	2.33	8	1.08	1.42
9	0.31	2.69	9	0.94	1.56
10	0.49	2.51	10	0.87	1.63
11	0.51	2.49	11	0.84	1.66
12	0.52	2.48	12	0.79	1.71
13	0.49	2.51	13	0.81	1.69
14	0.44	2.56	14	0.79	1.71
15	0.46	2.54	15	0.84	1.66
16	0.49	2.51	16	0.78	1.72
17	0.42	2.58	17	0.82	1.68
18	0.51	2.49	18	0.84	1.66
19	0.52	2.48	19	0.83	1.67
20	0.49	2.51	20	0.86	1.64
21	0.53	2.47	21	0.85	1.65
22	0.48	2.52	22	0.84	1.66
23	0.45	2.55	23	0.87	1.63
24	0.46	2.54	24	0.85	1.65

Table C.9 Effect of chloride ions concentration on lead adsorption

Chloride ion concentration (mg/L)	Initial Pb concentration (mg/L)	Pb sorbed (mg/g)
0	4.02	2.84
100	4.02	2.39
500	4.02	1.99
1000	4.02	1.73
2000	4.02	1.59

Table C.10 Effect of chloride ions concentration on zinc adsorption

Chloride ion concentration (mg/L)	Initial Zn concentration (mg/L)	Zn sorbed (mg/g)
0	3.76	2.53
100	3.76	2.88
500	3.76	3.02
1000	3.76	3.12
2000	3.76	3.11

Table C.11 Effect of zinc concentration on adsorption of lead

Initial Pb concentration (mg/L)	Zn concentration (mg/L)	Equivalent concentration (mg/L)	Pb sorbed (mg/g)
2.418	0	0.677	1.741
5.418	0	1.574	3.844
7.418	0	2.143	5.275
10.418	0	3.93	6.488
2.418	10	0.563	1.855
5.418	10	1.654	3.764
7.418	10	2.441	4.977
10.418	10	5.036	5.382
2.418	20	0.731	1.687
5.418	20	2.107	3.311
7.418	20	2.533	4.885
10.418	20	5.587	4.831
2.418	30	0.405	2.013
5.418	30	2.604	2.814
7.418	30	2.511	4.907
10.418	30	7.704	2.714
2.418	50	0.434	1.984
5.418	50	3.131	2.287
7.418	50	2.731	4.687
10.418	50	7.871	2.547

Table C.12 Effect of lead concentration on adsorption of zinc

Initial Zn concentration (mg/L)	Pb concentration (mg/L)	Equivalent concentration (mg/L)	Zn sorbed (mg/g)
2.243	0	0.457	1.786
5.243	0	0.931	4.312
7.243	0	1.919	5.324
10.243	0	4.495	5.748
2.243	10	1.913	0.33
5.243	10	2.255	2.988
7.243	10	5.116	2.127
10.243	10	6.379	3.864
2.243	20	2.071	0.172
5.243	20	3.023	2.22
7.243	20	5.699	1.544
10.243	20	9.027	1.216
2.243	30	2.021	0.222
5.243	30	3.384	1.859
7.243	30	6.311	0.932
10.243	30	9.081	1.162
2.243	50	1.612	0.631
5.243	50	3.079	2.164
7.243	50	5.974	1.269
10.243	50	9.255	0.988

Table C.13 Isotherm study (lead)

Initial concentration (mg/L)	Final concentration (mg/L)	Pb sorbed (mg/g)	% Removal	Pb remaining on chitosan (mg/g)	Pb desorbed (mg/g)	% Desorption
3.4	0.922	2.478	72.88235294	1.792	0.686	27.68361582
10.4	2.703	7.697	74.00961538	4.672	3.025	39.30102637
20.4	5.355	15.045	73.75	10.242	4.803	31.92422732
40.4	10.918	29.482	72.97524752	19.838	9.644	32.71148497
60.4	16.197	44.203	73.18377483	30.87	13.333	30.16311111
80.4	21.316	59.084	73.48756219	35.414	23.67	40.0616072
100.4	33.849	66.551	66.28585657	32.363	34.188	51.37112891
120.4	50.464	69.936	58.08637874	34.707	35.229	50.37319835
160.4	96.745	63.655	39.68516209	31.974	31.681	49.76985311
200.4	120.063	80.337	40.08832335	29.659	50.678	63.08176805
260.4	191.163	69.237	26.58870968	32.352	36.885	53.27353871
300.4	227.733	72.667	24.19007989	30.318	42.349	58.27817304
400.4	299.9	100.5	25.0999001	37.59	62.91	62.59701493
500.4	383.837	116.563	23.29396483	37.779	78.784	67.58920069

Table C.14 Isotherm study (zinc)

Initial concentration (mg/L)	Final concentration Ce (mg/L)	Zn sorbed (mg/g)	% Removal	Zn remaining on chitosan (mg/g)	Zn desorbed (mg/g)	% Desorption
3.44	0.523	2.917	84.79651163	2.135	0.782	26.80836476
10.44	1.279	9.161	87.74904215	6.561	2.6	28.38118109
20.44	3.524	16.916	82.7592955	11.402	5.514	32.59635848
40.44	6.47	33.97	84.00098912	25.258	8.712	25.64615838
60.44	8.698	51.742	85.6088683	36.422	15.32	29.60844188
80.44	13.594	66.846	83.10044754	44.385	22.461	33.60111301
100.44	20.318	80.122	79.77100757	49.184	30.938	38.61361424
120.44	38.279	82.161	68.21736964	48.145	34.016	41.40163825
160.44	63.599	96.841	60.359636	65.328	31.513	32.54096922
200.44	102.224	98.216	49.00019956	49.286	48.93	49.8187668
260.44	155.418	105.022	40.32483489	58.91	46.112	43.90699092
300.44	180.188	120.252	40.02529623	62.497	57.755	48.02830722
400.44	244.087	156.353	39.04530017	70.93	85.423	54.6347048
500.44	329.789	170.651	34.10019183	61.263	109.388	64.10041547

Biography

Miss Chintana Srisa-ard was born on October 29, 1976 in Prachinburi. She studied in Benchama Ratcharungsarit School, Chachoengsao. She graduated from Suranaree University of Technology (SUT), in the School of Environmental Engineering in 1998 and started Master's Degree Program since 1999.