# BIOSORPTION OF ZINC(II) FROM AQUEOUS SOLUTION BY USING DRIED WATER HYACINTH *(Eichhornia Crassipes)*

SITI AMINAH BINTI SHARIF BABU

A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

APRIL 2009

I declare that this dissertation entitled "*Biosorption of Zinc (II) from Aqueous Solution by Using Dried Water Hyacinth (Eichhornia Crassipes)* "is the result of my own research except as cited in the references. The Dissertation has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....................................................
Name : Siti Aminah Binti Sharif Babu
Date : .30th April 2009

Special Dedication of This Grateful Feeling to My…

***Beloved parent;***

***Mr. Sharif Babu Bin Saat & Mrs. Rahamah Bt Ismail***

***Loving brothers and sisters;***

***Rosmarina, Mohd Roslan, Mohd Rosli & Mohamad Rosnaidi***

***Understanding and helpful friends;***

For Their Love, Support and Best Wishes.

## ACKNOWLEDGEMENT

Praise is to Allah S.W.T for the help and guidance that I finally able to complete this BKC 4944, Undergraduate Research Project.

First and foremost, I wish to express my sincere appreciation to my Undergraduate Research Project supervisor, Madam Jun Haslinda Bt Hj Shariffuddin for constantly guiding and encouraging us throughout this study. Thanks a lot for giving us a professional training, advice and suggestion to bring this project to its final form. Without her support and interest, this project would not have been the same as presented here.

In preparing this dissertation, I was in contact with many people, academicians, and practitioners. They have contributed towards my understanding and thoughts. In particular, I wish to express my sincere appreciation to the staff of FKKSA Chemical Laboratory especially Mr. Razak, Mr. Zulhabri, Mr. Zaki, Mr. Annuar Ms Hafiza and Mrs Nora for encouragement, guidance, critics and friendship.

My sincere appreciation also extends to all my colleagues Awang Omar Firdaus, Siti Aishah, Nur Suhada, Nurul Shareena Aqmar, Mohd Zamri, and others who have provided assistance at various occasions. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space. And last, but not least I would like to thank my parents and other family members for their continuous support while completing this project.

# ABSTRACT

This paper shows a detailed study to investigate the potential of water hyacinth as biosorbent, to remove Zinc (II) from aqueous solution and to identify the optimum condition for the parameter involved. Before the biosorption experiment was done, the water hyacinth was first collected at Lake in Pekan, Pahang. Then the water hyacinth was washed to remove dirt and was chopped to separate the aerial and root part. Finally, the water hyacinth was dried before it was blended into a smaller particles size. There were four parameter that have been studied in this paper, they were effect of biosorbent dosage, effect of initial concentration, effect of pH and effect of time contact. It was found that the optimum dosage for the biosorbent at initial metal concentration of 10 mg/L was 0.2 g; the optimum pH was at 5.4 and the optimum time contact was at 90 minutes for initial concentration 5 mg/L and 210 minutes for initial concentration 10 mg/L. At the optimum condition the removal of zinc was increased as the initial concentration was increased. The biosorption of zinc was occurred at pH acidic because the pH dependence of metal uptake could be related to functional group of the biomass and also to solution chemistry. The result proved that the water hyacinth was a good biosorbent to remove zinc from waste water and biosorption can be used to replace the conventional treatment methods because it was low cost, high efficiency of metal removal from dilute solutions and also applicable for industrial.

# Abstrak

Kajian ini dilakukan untuk mengkaji keupayaan keladi bunting sebagai penjerap untuk menyingkirkan zink (II) dari larutan akuas dan untuk mengenalpasti keadaan optimum bagi faktor penghad terlibat. Sebelum kajian ini dijalankan, keladi bunting terlebih dahulu diambil dari tasik di Pakan, Pahang. Kemudian, keladi bunting tersebut dicuci untuk menghilangkan kotoran dan dipotong untuk mengasingkan bahagian atas dan akar pokok. Akhir sekali, keladi Bunting dikeringkan sebelum dikisar menjadi zarah yang lebih kecil. Terdapat empat faktor penghad yang telah dikaji iaitu kesan dos penjerap, kesan kepekatan awal, kesan pH dan kesan masa bersentuhan. Telah didapati bahawa dos yang optimum bagi penjerap pada kepekatan awal 10 mg/L ialah 0.2g, keadaan yang optimum bagi pH ialah pada pH 5.4 dan masa yang optimum ialah pada 90 minit untuk kepekatan awal 5 mg/L dan 210 minit untuk kepekatan awal 10 mg/L. pada keadaan yang optimum penyingkiran zink meningkat apabila kepekatan awal meningkat. Penjerapan untuk zink berlaku pada pH berasid kerana kebergantungan pH untuk menyingkirkan logam boleh dikatakan berkait dengan kumpulan berfungsi jisim bio dan juga dengan larutan kimia. Hasil kajian membuktikan bahawa keladi bunting adalah penjerap yang baik untuk menyingkirkan zink dari air buangan dan penjerapan boleh digunakan untuk menggantikan kaedah rawatan traditional kerana kosnya rendah, kecekapan penyingkiran logam yang tinggi, dari larutan cair dan juga boleh digunakan untuk industri.

# TABLE OF CONTENT

# LIST OF TABLES

# LIST OF FIGURES

# LIST OF ABBREVIATION

| | |
|---|---|
| µ | Micro |
| AAS | Atomic Absorption Spectrophotometer |
| FTIR | Fourier transform infra red |
| g | Gram |
| HCL | Hydrochloric Acid |
| $HNO_3$ | Nitric Acid |
| L | Liter |
| m | Meter |
| M | Molar |
| NaOH | Sodium Hydroxide |
| $^oC$ | Degree Celcius |
| SEM | Scanning Electron Microscopy |
| rpm | Revolution per minutes |

# LIST OF APPENDIX

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of study

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc.,(Kadirvelu *et al.*,2001 and Williams *et al.*,1998). The presence of certain heavy metals in the environment specifically in various water resources is of major concern because of their toxicity, non-biodegradable nature and threat to human, animal and plant life.

Removal of toxic heavy metals from industrial wastewater is essential from the standpoint of environmental pollution control (Yuan *et al.*, 2001). Removal of these contaminants can be accomplished by use of physical or chemical methods, including the use of chemical reagents, ion exchange, activated carbon sorption and membrane technology. Most of these approaches have significant disadvantages. For example, chemical reagents are costly (Kadiverlu *et al.*, 2001), as the active agents cannot be recovered for use in successive treatment cycles. Moreover, the end product is usually a low volume, highly concentrated metalliferous sludge that may be difficult to dewater and dispose of (Sandau *et al.*, 1996).

Biosorption, which is the ability of certain biomaterials to bind and concentrate heavy metals from even the most dilute aqueous solutions, offers a technically feasible and economically attractive alternative to the conventional technologies for removal of heavy metal from the contaminated effluents (Davis *et al*.,2000;De Carvalho *et al.*,2001;Esposito *et al*.,2001;Demir and Arisoy.,2007). The usefulness of the biomass of non-living Water hyacinth roots in removing metal ions from solution was investigated recently and it was shown that the roots have the potential of being used as a cheap source of biosorbent for metal ions (Kaustubha Mohanty *et a*l., 2005). Water hyacinth is a submerged aquatic plant, found abundantly throughout the year in very large and drainage channel systems in and around the fields of irrigation, which are common in India.

## 1.2 Problem Statement

The increased attention on the harmful effects of heavy metal ions on human health and the environment over the past few decades has led to a serious focus on improved water quality. Heavy metals can be released into the aqueous environment from a variety of sources such as metal smelters, effluents from the plastic, textile, microelectronic and wood preservative-producing industry, and even fertilizer and pesticide usage (Prasad and Hagemayer, 1999). One common pollutant is Zinc; wastewater that contains Zinc is harmful for both irrigational and industrial applications. Zinc is introduced into the water from metal mining, melting, plating, pesticides, oil-based paint pigments, alloy processing and sewage sludge.

Water hyacinth is listed as one of the most productive plants on earth and is considered the world's worst aquatic plant. It forms dense mats that interfere with navigation, recreation, irrigation, and power generation. These mats competitively exclude native submersed and floating-leaved plants. Low oxygen conditions develop beneath water hyacinth mats and the dense floating mats impede water flow and create good breeding conditions for mosquitoes. Therefore, using water hyacinth as biosorbent could solve these problems.

This research was used dried water hyacinth. The water hyacinth was sun dried for 24 h and then oven dried at 60 ◦C for 24 h. The reason for using dried water hyacinth are because if we used living water hyacinth, the low oxygen conditions develop beneath water hyacinth mats and the dense floating mats impede water flow and create good breeding conditions for mosquitoes. In living condition, a huge and massive area needed for maintaining the growth of water hyacinth. The transportation also difficult since the living water hyacinth was in a large amount and heavy.

## 1.3 Objectives

The objectives of this study are:-

- To investigate the potential of water hyacinth as biosorbent
- To remove heavy metal (Zinc(II)) from aqueous solution
- To identify the optimum condition for the parameter involved

## 1.4 Scopes of Study

There are four parameter involved in this study:-

- Effect of dose
- Effect of initial concentration
- Effect of pH
- Effect of time

## 1.3 Rational and Significant

The rational of this research is as we can see that recently, there are so many environmental pollutions occur. Therefore, removal of toxic heavy metals from industrial wastewater is essential from the standpoint of environmental pollution control (Yuan *et al.*, 2001). Besides, by doing this research we can also settle problems that caused by water hyacinth to the environment such as the blockage of canals and rivers can even cause dangerous flooding. This research can also replace conventional treatment methods to treat wastewater because this method are: low cost, high efficiency of metal removal from dilute solutions, no additional nutrient requirements, regeneration of biosorbent, and possibility of metal recovery (Kaustubha Mohanty *et al*., 2005).

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Heavy Metal

### 2.1.1 Introduction

Heavy metal such as lead, mercury, nickel, zinc, cadmium, chromium and manganese metals are a cause of environmental pollution (heavy-metal pollution) (Harvey Stewart *et al*., 1975). The commonest sources of heavy metal pollution are industrial and mining activities, petroleum exploration, exploitation, processing and effluent management, atmospheric condensation and sewage disposal. Removal of toxic heavy metals from industrial wastewater is essential from the standpoint of environmental pollution control (Yuan *et al*., 2001).

In order to mitigate the heavy metal pollution, there are many processes like adsorption, precipitation, coagulation, ion exchange, cementation, electro-dialysis, electro-winning, electro-coagulation and reverse osmosis have been developed. But all these method have many disadvantages such as they may be ineffective or extremely expensive especially when the metals in solution are in the range of 1–100 mg $l^{-1}$ (Nourbakhsh *et al*., 1994). Likewise, ion exchange and membrane systems could be expensive, especially in small-scale processes, with the resins or membranes prone to fouling or oxidation. Similarly, activated carbon, the most widely used adsorbent in the treatment of waste water, is expensive and may also require complexing agents to improve its ability to remove inorganic matter (Bebel and Kurniawan., 2002). Through these processes, the production of toxic chemical sludge and its disposal/treatment becomes a costly affair and is not eco-friendly.

Therefore, removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance.

### 2.1.2 Zinc (II)

#### 2.1.2.1 Characteristic

Zinc, also referred to in nonscientific contexts as spelter, is a moderately reactive bluish-grey metal that tarnishes in moist air. It can also burn in air with a bright bluish-green flame, giving off fumes of zinc oxide. It reacts with acids, alkalis and other non-metals. (Holleman, Arnold F *et al.*, 1985) If not completely pure, zinc reacts with dilute acids to release hydrogen. The one common oxidation state of zinc is +2 (Gmelin, Leopold *et al.*, 1853). From 100 °C to 210 °C (212 °F to 410 °F) zinc metal is malleable and can be easily beaten into various shapes. Above 210 °C (410 °F), the metal becomes brittle and can be pulverized by beating (Scoffern, John et al., 1861). Zinc is nonmagnetic.

## 2.2 Biosorption

Recently, biosorption is gaining considerable importance as an alternative technology for the treatment of heavy metal waste. Biosorption, which is the ability of certain biomaterials to bind and concentrate heavy metals from even the most dilute aqueous solutions, offers a technically feasible and economically attractive alternative to the conventional technologies for removal of heavy metal from the contaminated effluents (Davis *et al*., 2000; De Carvalho *et al*., 2001; Esposito et al., 2001; Demir and Arisoy., 2007). The major advantages of biosorption over other conventional treatment methods are: low cost, high efficiency of metal removal from dilute solutions, no additional nutrient requirements, regeneration of biosorbent, and possibility of metal recovery (Kaustubha Mohanty *et al*., 2005).

### 2.2.1 Choice of metal for biosorption process

The appropriate selection of metals for biosorption studies is dependent on the angle of interest and the impact of different metals, on the basis of which they would be divided into four major categories:

i. toxic heavy metals
ii. strategic metals
iii. precious metals and
iv. radio nuclides

In terms of environmental threats, it is mainly categories (i) and (iv) that are of interest for removal from the environment and/or from point source effluent discharges. Apart from toxicological criteria, the interest in specific metals may also be based on how representative their behaviour may be in terms of eventual generalization of results of studying their biosorbent uptake. The toxicity and interesting solution chemistry of elements such as chromium, arsenic and selenium make them interesting to study. Strategic and precious metals though not environmentally threatening are important from their recovery point of view.

### 2.2.2 Biosorption Mechanism

The complex structure of microorganisms implies that there are many ways for the metal to be taken up by the microbial cell. The biosorption mechanisms are various and are not fully understood. They may be classified according to various criteria.

According to the dependence on the cell's metabolism, biosorption mechanisms can be divided into:

i. Metabolism dependent and
ii. Non -metabolism dependent.

According to the location where the metal removed from solution is found, biosorption can be classified as

i. Extra cellular accumulation/ precipitation
ii. Cell surface sorption/ precipitation and Intracellular accumulation.

Transport of the metal across the cell membrane yields intracellular accumulation, which is dependent on the cell's metabolism. This means that this kind of biosorption may take place only with viable cells. It is often associated with an active defense system of the microorganism, which reacts in the presence of toxic metal.

During non-metabolism dependent biosorption, metal uptake is by physico-chemical interaction between the metal and the functional groups present on the microbial cell surface. This is based on physical adsorption, ion exchange and chemical sorption, which is not dependent on the cells' metabolism. Cell walls of microbial biomass, mainly composed of polysaccharides, proteins and lipids have abundant metal binding groups such as carboxyl, sulphate, phosphate and amino groups. This type of biosorption, i.e., non-metabolism dependent is relatively rapid and can be reversible (Kuyucak and Volesky, 1988).

In the case of precipitation, the metal uptake may take place both in the solution and on the cell surface (Ercole, *et al*. 1994). Further, it may be dependent on the cell's' metabolism if, in the presence of toxic metals, the microorganism produces compounds that favor the precipitation process. Precipitation may not be dependent on the cells' metabolism, if it occurs after a chemical interaction between the metal and cell surface.

#### 2.2.2.1 Transport across cell membrane

Heavy metal transport across microbial cell membranes may be mediated by the same mechanism used to convey metabolically important ions such as potassium, magnesium and sodium. The metal transport systems may become confused by the presence of heavy metal ions of the same charge and ionic radius associated with essential ions. This kind of mechanism is not associated with metabolic activity. Basically biosorption by living organisms comprises of two steps. First, a metabolism independent binding where the metals are bound to the cell walls and second metabolism dependent intracellular uptake, whereby metal ions are transported across the cell membrane. (Nourbaksh *et.al.,* 1994)

### 2.2.2.2 Ion Exchange

Ion exchange is a reversible chemical reaction wherein an ion in a solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion-exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. Synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications.
Ion exchange reactions are stoichiometric and reversible, and as such they are similar to other solution-phase reactions. For example, in the reaction

$$NiSO_4 + Ca(OH)_2 \rightarrow Ni(OH)_2 + CaSO_4$$

The nickel ions of the nickel sulfate (NiSO4) are exchanged for the calcium ions of the calcium hydroxide Ca(OH)2 molecule.

### 2.2.2.3 Complexation

The metal removal from solution may also take place by complex formation on the cell surface after the interaction between the metal and the active groups. (Aksu *et al*., 1992) hypothesized that biosorption of copper by C. vulgaris and Z. ramigera takes place through both adsorption and formation of coordination bonds between metals and amino and carboxyl groups of cell wall polysaccharides. Complexation was found to be the only mechanism responsible for calcium, magnesium, cadmium, zinc, copper and mercury accumulation by Pseudomonas syringae. Microorganisms may also produce organic acids (e.g., citric, oxalic, gluonic, fumaric, lactic and malic acids), which may chelate toxic metals resulting in the formation of metallo-organic molecules. These organic acids help in the solubilisation of metal compounds and their leaching from their surfaces. Metals may be biosorbed or complexed by carboxyl groups found in microbial polysaccharides and other polymers.

#### 2.2.2.4 Precipitation

Precipitation may be either dependent on the cellular metabolism or independent of it. In the former case, the metal removal from solution is often associated with active defense system of the microorganisms. They react in the presence of toxic metal producing compounds, which favor the precipitation process. In the case of precipitation not dependent on the cellular metabolism, it may be a consequence of the chemical interaction between the metal and the cell surface. The various biosorption mechanisms mentioned above can take place simultaneously.

### 2.2.3 Factors affecting Biosorption

The investigation of the efficacy of the metal uptake by the microbial biomass is essential for the industrial application of biosorption, as it gives information about the equilibrium of the process which is necessary for the design of the equipment. The metal uptake is usually measured by the parameter 'q' which indicates the milligrams of metal accumulated per gram of biosorbent material and 'qH' is reported as a function of metal accumulated, sorbent material used and operating conditions.

The following factors affect the biosorption process:

1. Temperature seems not to influence the biosorption performances in the range of 20-35 0C (Aksu *et al*., 1992)
2. pH seems to be the most important parameter in the biosorptive process: it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Friis and Myers-Keith, 1986, Galun *et al*., 1987)