

BIOSORPTION OF Cd (II), Cu (II), Fe (III) AND Pb (II)  
FROM WATER SYSTEM USING *MORINGA*  
*OLEIFERA* LEAVES

SABREEN RAMZI ALFARRA

Thesis submitted in fulfilment of the requirements  
for the award of the degree of  
Master of Engineering (Chemical Engineering)

Faculty of Chemical and Natural Resources Engineering  
UNIVERSITI MALAYSIA PAHANG

NOVEMBER 2015

## ABSTRACT

This study was an attempt to use *Moringa oleifera* leaves as a natural alternative for synthetic sorbents to reduce the presence of Cd (II), Cu (II), Fe (III) and Pb (II) from water. In this study synthetic water was used to determine the optimum conditions for Cd (II) removal from synthetic water using the biosorbent as first stage of the study. The effect of biosorbent dosage and particle size, contact time, and pH as well as the initial concentration of Cd (II) was studied. Atomic Absorption Spectroscopy (AAS) was used to monitor the experimented ions' concentration before and after using the biosorbent. Fourier Transform Infrared Spectroscopy (FTIR) was used to monitor biosorbent structure changes before and after loading with Cd (II). The parameters studied were biosorbent dosage 2 to 20 g/l, contact time used was from 2 min to 120 min, biosorbent particle sizes used were 2 mm, 1 mm, 500 $\mu$ m, 250 $\mu$ m, and < 250 $\mu$ m, pH ranges started from 4-10, and the Cd (II) initial concentrations were 1, 3, 5, and 7 ppm. Results revealed that the optimum parameters to reduce 81% of Cd (II) were 12 g/l of biosorbent, 60 min of contact time, <250  $\mu$ m biosorbent particle sizes with Cd (II) initial concentration of 1 ppm and 50 NTU. The optimized parameters obtained in the study for Cd (II) removal, were applied for Fe (III), Pb (II) and Cu (II) removal, as an attempt to experiment the effect of the optimum parameters of Cd (II) on the other heavy metals. Results showed that the removal efficiency of *Moringa oleifera* leaves was 81% for Cd (II), 78% for Cu (II), 63.6% for Pb (II) and 62% for Fe (III). It was clear that the achieved optimum conditions give the best removal efficiency percentage on Cd (II) removal. Student *t-test* results showed that the investigated parameters have an effect on Cd (II) removal with *p* values <0.05. Biosorption kinetic data were properly fitted with the pseudo-second-order kinetic model. FTIR presented changes in the peaks of the main functional groups and fingerprint area of *Moringa oleifera* leaves after Cd (II) adsorption experiments; results of FTIR indicated the reactivity of Cd (II) with the biosorbent chemical ingredients and its surface. The SEM results showed that there were differences on the morphological characteristics of the biosorbent, which also indicates the binding process of Cd (II) on the *Moringa oleifera* leaves. Again, the optimum condition was applied on drainage water, and showed removal efficiency of 83.6% for Cd (II), 73% for Cu (II), 65% for Pb (II) and 52% for Fe (III). Although the results of *Moringa oleifera* leaves on other heavy metals showed that *Moringa oleifera* as a biosorbent could reduce the other metals with less percentages which could suggest that *Moringa oleifera* is a good biosorbent for all the investigated ions generally and Cd (II) particularly. As a conclusion, *Moringa oleifera* leaves can be a potential and effective, low cost and environmentally friendly biosorbent for the removal of Cd (II) from water systems and reduce the Cu (II), Pb (II) and Fe (III) as well.

## ABSTRAK

Kajian ini merupakan percubaan untuk menyelidik penggunaan daun *Moringa oleifera* (penjerap bio) sebagai satu kaedah alternatif semulajadi yang bertindak seumpama penjerap sintetik untuk mengurangkan kehadiran Kadmium (Cd (II)), Kuprum (Cu (II)), Ferum (Fe (III)) dan Plumbum (Pb (II)) dalam air. Dalam kajian ini, air sintetik telah digunakan untuk menentukan keadaan optimum bagi penyingkiran Cd (II) daripada air sintetik menggunakan penjerap bio. Kesan dos penjerap bio, saiz zarah, masa sentuh, pH serta kepekatan awal turut dijalankan. Spektroskopi Penyerapan Atom (AAS) telah digunakan untuk memantau kepekatan ion-ion yang dikaji sebelum dan selepas penggunaan penjerap bio. Spektroskopi Inframerah Transformasi Fourier (FTIR) pula digunakan untuk memantau perubahan struktur penjerap bio sebelum dan selepas proses memuatkan dengan Cd (II). Antara parameter yang dikaji ialah dos penjerap bio (2 hingga 20 g/l, masa sentuh yang digunakan antara 2 minit hingga 120 minit, saiz zarah yang digunakan ialah 2 mm, 1 mm, 500 $\mu$ m, 250 $\mu$ m, dan -250 $\mu$ m, pH dalam kadar 4-10, dan kepekatan awal Cd (II) ialah 1, 3, 5, dan 7 ppm. Hasil kajian menunjukkan bahawa dos optimum ialah 12gm/l; masa sentuh ialah 60 minit; saiz zarah ialah -250  $\mu$ m dan kepekatan awal ialah 1 ppm manakala kekeruhan ialah 50 NTU. Parameter optimum yang dicapai dalam kajian penyingkiran Cd (II) ini telah diuji dalam kajian penyingkiran logam berat yang lain seperti Fe (III), Pb (II) dan Cu (II). Hasil kajian telah menunjukkan kecekapan penyingkiran daun *Moringa oleifera* ialah sebanyak 81 % untuk Cd (II), 78 % untuk Cu (II), 63.6 % untuk Pb (II) dan 62 % untuk Fe (III). Ini jelas menunjukkan bahawa keadaan optimum yang dicapai sangat berkesan bagi peratusan penyingkiran logam Cd (II). Analisis dengan ujian T juga menunjukkan bahawa parameter yang dikaji mempunyai kesan terhadap penyingkiran Cd (II) dengan nilai  $p < 0.05$ . Keputusan FTIR menunjukkan perubahan dalam paruh kelompok fungsian utama dan juga kawasan cap jari *Moringa oleifera* selepas ujian penjerapan Cd (II). Sekali lagi keadaan optimum telah diuji kesannya terhadap air sisa saliran dan hasil kajian menunjukkan peratusan kecekapan penyingkiran logam berat ialah 83.6% untuk Cd (II), 73% untuk Cu (II), 65% untuk Pb (II) dan 52% untuk Fe (III). Hasil kajian daun *Moringa oleifera* ke atas logam-logam berat yang lain menunjukkan bahawa ia mampu mengurangkan bahan-bahan logam dengan peratusan yang lebih rendah dan ini menandakan bahawa daun ini sangat sesuai sebagai penjerap bio untuk Cd (II) khususnya dan logam berat lain amnya. Kesimpulannya, daun *Moringa oleifera* sangat berpotensi dan efektif, mempunyai kos yang rendah dan juga penjerap bio yang mesra alam bagi menyingkirkan Cd (II) dari sistem pengairan.

## TABLE OF CONTENTS

<b>SUPERVISOR'S DECLARATION</b>	<b>ii</b>
<b>STUDENT'S DECLARATION</b>	<b>iii</b>
<b>DEDICATION</b>	<b>iv</b>
<b>ACKNOWLEDGEMENT</b>	<b>v</b>
<b>ABSTRACT</b>	<b>vi</b>
<b>ABSTRAK</b>	<b>vii</b>
<b>TABLE OF CONTENTS</b>	<b>viii</b>
<b>LIST OF TABLES</b>	<b>xi</b>
<b>LIST OF FIGURES</b>	<b>xii</b>
<b>LIST OF APPENDICES</b>	<b>xiii</b>
<b>LIST OF ABBREVIATIONS AND SYMBOLES</b>	<b>xiv</b>
<b>CHAPTER 1 INTRODUCTION</b>	
1.1 Background	1
1.2 Problem statements	3
1.3 Research questions	4
1.4 Specific objectives	4
1.5 Research hypothesis	5
1.6 Significance	5
1.7 Dissertation summary	5
<b>CHAPTER 2 LITERATURE REVIEW</b>	
2.1 Background	7
2.1.1 Heavy metals	7
2.1.2 Water treatment	9
2.1.3 Biosorption of heavy metals	11
2.1.3.1 Agricultural waste biosorbents	12
2.1.3.2 <i>Moringa oleifera</i> as biosorbents	13

2.1.4	Biosorption of Cadmium	15
2.1.4.1	Micororganisms used for Cd (II) removal from water	16
2.1.4.2	Biosorption with agro-industrial waste materials	16
2.1.5	Biosorption of Iron	21
2.1.6	Biosorption of Copper	22
2.1.7	Biosorption of Lead	22

### CHAPTER 3 METHODOLOGY

3.1	Introduction	25
3.2	Analytical techniques	25
3.2.1	Atomic Absorption Spectrometry (AAS)	25
3.2.2	Fourier Transform Infrared Spectroscopy (FTIR)	25
3.2.3	Flocculator (Jar Test)	26
3.2.4	Brunauer-Emmett-Teller (BET) Surface Area Analysis	27
3.2.5	Scanning Electron Microscope	27
3.2.6	Chemicals	28
3.2.7	Equipment	28
3.3	Methods	28
3.3.1	Preparation of Biosorbents	28
3.3.2	Preparation of stock solution	29
3.3.3	Preparation of synthetic water	29
3.3.4	Biosorption Batch Experiments	30
3.3.5	Application of <i>Moringa oleifera</i> leaves on Pb(II), Cu(II), and Fe(III)	30
3.3.6	Preparation of 1D and 2D Fourier transform infrared spectroscopy (FTIR) sample	31
3.3.7	Preparation for SEM analysis	31
3.3.8	Preparation for Surface area analysis	31
3.3.9	Preparation for Heavy Metal Removal Analysis	31
3.3.10	Preparation for Turbidity Measurement	32
3.3.11	Biosorption kinetics procedures	32

**CHAPTER 4 RESULTS AND DISCUSSIONS**

4.1	Introduction	34
4.2	Effect of parameters on Cd (II) removal	34
4.2.1	Biosorbent dose effect	34
4.2.2	Contact time effect	37
4.2.3	Biosorbent particle size effect	40
4.2.4	Water turbidity effect on Cd (II) removal	41
4.2.5	Biosorption kinetics	42
4.2.5.1	Pseudo-first order kinetics	42
4.2.5.2	Pseudo-second order kinetics	43
4.2.6	FTIR analysis	45
4.2.7	SEM analysis	47
4.2.8	Biosorption of Pb(II), Cu(II) and Fe(III) from water by <i>Moringa oleifera</i> leaves	48
4.3	Effect of <i>Moringa oleifera</i> on heavy metal removal from drainage water	50
4.4	Conclusion	51

**CHAPTER 5 CONCLUSION AND RECOMMENDATIONS**

5.1	Conclusion	52
5.2	Recommendations and future work	53

<b>REFERENCES</b>	<b>55</b>
-------------------	-----------

<b>APPENDICES</b>	<b>68</b>
-------------------	-----------

**LIST OF TABLES**

<b>TABLE NO.</b>	<b>TITLE</b>	<b>PAGE</b>
2.1	Heavy metals sources and its toxicity	8
2.2	Advantages and disadvantages of some techniques to remove heavy metal from water	10
2.3	Advantages and disadvantages of used biosorbents	11
2.4	Factors affecting biosorption	12
4.1	The removal efficiency percentage at different times with different Cd (II) concentration	39
4.2	The effect of <i>Moringa oleifera</i> leaves particle sizes on the Cd (II) removal efficiency	40
4.3	The different turbidity and the optimum RE% for each Cd (II) concentration	41
4.4	Kinetic constant for Cadmium (II) biosorption onto <i>Moringa oleifera</i> leaves.	42

## LIST OF FIGURES

FIGURES NO.	TITLE	PAGE
2.1	Traditional Medicinal Uses of <i>Moringa oleifera</i> leaves	14
3.1	Sample running in the Jar test	26
3.2	Flow chart of the experimental work involved in this study	28
3.3	AAS standard curve of the Cd (II) concentrations (0.5, 1, 1.5 ppm).	31
4.1	The removal efficiency of different dose at different Cd (II) concentrations at 200 rpm, 60 min contact time, <250 $\mu$ particle size and 200 NTU	35
4.2	The amount of Cd (II) removed by different doses of <i>Moringa oleifera</i> at the different initial concentration, 200 rpm, 60 min contact time, < 250 $\mu$ particle size and 200 NTU	35
4.3	The pseudo-first order kinetic plot for the adsorption of cadmium ions onto <i>Moringa oleifera</i> leaves	40
4.4	The pseudo-second order kinetic plot for the adsorption of cadmium ions onto <i>Moringa oleifera</i> leaves	45
4.5	2D FTIR spectrum of <i>Moringa oleifera</i> leaves before and after biosorption of Cd	46
4.6	1D FTIR of <i>Moringa oleifera</i> leaves contents before and after biosorption of Cd	44
4.7	Scanning electron micrographs of <i>Moringa oleifera</i> leaves before and after Cd (II) adsorption, where (a) represents the morphology before and (b) represents the morphology after Cd (II) adsorption	45
4.8	The removal efficiency of <i>Moringa oleifera</i> leaves on different heavy metals from synthetic water	46
4.9	The removal efficiency of <i>Moringa oleifera</i> leaves on heavy metal removal from waste water	48

**LIST OF APPENDICES**

<b>APPENDIX NO.</b>	<b>TITLE</b>	<b>PAGE</b>
1	List of publications and exhibition	68
2	Atomic Absorption Spectroscopy	69
3	Flocculator (jar test) used for coagulation - flocculation process	70
4	<i>Moringa oleifera</i> tree leaves	71
5	Drying <i>Moringa oleifera</i> leaves under the sun	72
6	Preparation of the sample for the experiment before and after filtration	73
7	Surface area analyser instrument results	74
8	AAS data	75

## LIST OF ABBREVIATIONS AND SYMBOLES

1D	One Dimensional
2D	Two Dimensional
WHO	World Health Organization
Cd	Cadmium
Pb	Lead
Cu	Copper
Fe	Iron
MO	<i>Moringa oleifera</i>
RE	Removal Efficiency
$K_1$	Pseudo-first-order rate constant of biosorption ( $\text{min}^{-1}$ )
$K_2$	Pseudo-second-order rate constant of biosorption ( $\text{gmg}^{-1}\text{min}^{-1}$ )
$q_t$	Metal ion adsorbed on biosorbent at a given time ( $\text{mg g}^{-1}$ )
$q_e$	Metal ion adsorbed on biosorbent at equilibrium ( $\text{mg g}^{-1}$ )
$R^2$	Regression correlation coefficient

## CHAPTER 1

### INTRODUCTION

#### 1.1 BACKGROUND

Every day, there are thousands of chemicals discharged directly and indirectly into water bodies without further treatment for elimination of the included harmful compounds (Salim et al., 2008). Heavy metals are without doubt well thought-out as the most hazardous and harmful metals even if they are present as traces, since they accumulate in the tissue of living organisms (Rao et al., 2010; Khairy et al., 2014).

Conventional processes for removal of metals from water include chemical precipitation oxidation-reduction, filtration, electrochemical methods and other complicated separation procedures using membranes. Such methods showed to be not effective and not economically possible for the treatment of low heavy metals concentrations (Kelly-Vargas et al., 2012; Lim and Aris, 2014). Therefore, new alternative methods are needed to find the best ecological and economical techniques for biosorption of heavy metals from water.

Biosorption describes any system which includes a sorbate working together with a biosorbent resulting in an accumulation at the sorbate–biosorbent interface, and therefore a decrease of sorbent concentration in the solution (Sasaki et al., 2013). Biosorption is a property of both living and dead organisms, and has been exploited as a promising biotechnology because of its simplicity (Bilal et al., 2013). Accordingly, biosorption can be defined as the removal of substances from solution by biological materials (Gadd, 2001).

*Moringa oleifera* is a native tree of the sub-Himalayan parts of Northwest India, Pakistan and Afghanistan. It is now widely cultivated across Africa, South America, most parts of South - East Asia for example: Malaysia, Indonesia and Thailand (Reddy et al., 2011).

*Moringa oleifera* is a multipurpose tree with most of its parts being useful for a number of applications. It is generally used in a number of developing countries as a vegetable, medical plant and a source of vegetable oil. It has an impressive range of medicinal uses with high nutritional value (Anwar et al., 2007). On the other hand, *Moringa oleifera* seeds have been found to be a natural coagulant, flocculants, softener, disinfectant, and sludge conditioner (Jahn et al., 1986; Suarez et al., 2003; Nand et al., 2012), heavy metal remover in water and wastewater treatment (Alves and Coelho, 2013; Obuseng et al., 2012).

One of the heavy metals in water is Cadmium (II); it is naturally present in the environment by the gradual process of erosion and abrasion of rocks and soils, and from singular events such as forest fires and volcanic eruptions. It is therefore naturally present everywhere in air, water, soils and foodstuffs (Mahvi et al., 2008).

Cadmium is one of the heavy metals which is highly toxic to humans, plants and animals and it is responsible for causing kidney damage, renal disorder, high blood pressure, bone fractures, and destruction of red blood cells (Drasch, 1983; Purkayastha et al., 2014). According to the World Health Organization (WHO), the maximum accepted level of Cd (II) in water is 0.005 mg/l (Abaliwano et al., 2008). Meanwhile, Ministry of Health Malaysia (MOH) recommends that Cd (II) limits in drinking water should be 0.003 mg/l (MOH, 2015).

Another heavy metal is iron, which is the most plentiful element on earth. It is an essential element in human nutrition and plant metabolism, and it is used in a variety of industrial processes. In industries, it is used as a construction material and to create pigments. For humans, it is required for haemoglobin to transport oxygen from lungs to cells. However, high levels of iron can be fatal. Iron is commonly found in many industrial wastewaters. Generally, it is present in the water in the ferric state and enters the water bodies in the form of ferrous ion Fe (II), which can be oxidized to ferric ion Fe (III) by oxygen dissolved in water (Ahalya et al., 2003). The maximum accepted level of Fe (III) in water is 0.3 mg/l (Colter and Mahler, 2006). Meanwhile, Ministry of Health Malaysia recommends that Fe (III) limits in drinking water should be 1 mg/l (MOH, 2015).

Copper is both an essential nutrient and a drinking water contaminant. It is an important trace element required by humans for its role in enzyme synthesis, tissue

and bone development (Nand et al., 2012). However, excessive amounts of copper consumed is toxic and carcinogenic and it leads to its deposition in the liver and causes many diseases such as Wilson disease, liver and kidney failure and finally gastrointestinal bleeding (Al Bsoul et al., 2014).

The excessive amounts of Cu (II) in fresh water resources and aquatic ecosystem damage the osmo-regulatory mechanism of the freshwater animals and cause mutagenesis in humans (Bilal et al., 2013). Large quantities of copper are released to the environment by discarding industrial waste without further treatment (Demirbaş et al., 2008). According to World Health Organization (WHO) the permissible limit of Cu (II) in water is 1.5 mg/l (Bilal et al., 2013). According to the Ministry of Health Malaysia the acceptable limits of Cu (II) in drinking water should be 1 mg/l (MOH, 2015).

Lead occurs in water due to numerous industrial and mining sources and is the most widely spread of all toxic metals. The overload amount of lead in water causes severe problems such as anaemia, encephalopathy, hepatitis and kidney disease (Shafaghat et al., 2014; Putra et al., 2014). According to World Health Organization (WHO) the highest desirable limit of Pb (II) is 0.05 mg/l (Mataka et al., 2006). Meanwhile, Ministry of Health Malaysia recommends that Pb (II) limits in drinking water should be 0.01 mg/l (MOH, 2015).

Since Malaysia is widely recognized as one of the centres of biological diversity, rich with wild plants, it will be beneficial for the researchers to further screen the valuable biosorbent. All of these resources could provide renewable useful products not only for the current generation but also for the future generations to come. Hence, this study is initiated to target the miracle tree *Moringa oleifera* to be used as a potent biosorbent for the Cd (II), Pb (II), Cu (II) and Fe (III) ions. To help in finding an alternative methods to treat water, which could be economically and environmental friendly techniques.

## **1.2 PROBLEM STATEMENTS**

Cadmium and other heavy metals present in water are harmful and poisonous and need to be removed from water; using natural biosorbent is one of the solutions.

In aquatic ecosystems water contamination by heavy metals is one of the main types of pollutions that may stress the biological systems. Great amount of several heavy metals including Cd (II) are discharged into water systems as contaminants by anthropogenic activities (Ebrahimpour and Mushrifah, 2008; Sany et al., 2013). In Malaysia there are different industrial resources for Cd (II) and heavy metals. Petroleum refinery could be a source of many heavy metals including Cd (II) (Wuyep et al., 2007). Few studies reported the removal of some heavy metals from water by *Moringa oleifera*, however the use of *Moringa oleifera* leaves to adsorb cadmium from water still not too much targeted and minimally used in this field, thus more research is needed. Therefore, this project is an investigation of removing mainly cadmium and other heavy metals from water, which will be carried out.

### 1.3 RESEARCH QUESTIONS

1. Can *Moringa oleifera* leaves used as a biosorbent?
2. Do *Moringa oleifera* leaves have the ability to remove Cd (II) from water systems?
3. Does Cd (II) affect the phytochemistry of *Moringa oleifera* leaves?
4. What is the effect of Cd (II) on the morphological characteristics of *Moringa oleifera*?
5. What are the optimum conditions that give the maximum removal of Cd (II) by *Moringa oleifera* leaves?
6. Could the *Moringa oleifera* leaves remove the other heavy metals from water systems?

### 1.4 SPECIFIC OBJECTIVES

1. To remove cadmium from water using *Moringa oleifera* leaves and to find the best conditions that can be used for Cd (II) removal from water.
2. To know the effect of Cd (II) adsorption on *Moringa oleifera* leaves phytochemistry structure.
3. To examine the effect of Cd (II) on the morphological properties of *Moringa oleifera* leaves.

4. To study the biosorption kinetics of Cd (II) up taken by *Moringa oleifera* leaves.
5. To apply the optimum conditions for the removal of Cd (II) on other heavy metals such as Fe (III), Cu (II) and Pb (II) from drainage water.

## **1.5 RESEARCH HYPOTHESIS**

*Moringa oleifera* leaves could remove the Cd (II) from the contaminated water system, which will be useful in drinking and wastewater treatment. This leaves was chosen because *Moringa oleifera* tree can be of great benefit to Malaysia as new crop for producing different product from all parts of the tree and the leaves is one of the parts that can be a good source of raw material such as adsorbent.

## **1.6 SIGNIFICANCE**

The results of this project will serve in treating water by removing cadmium and other heavy metals using natural and environmentally friendly materials which can be used in many countries especially Malaysia.

## **1.7 DISSERTATION SUMMARY**

This dissertation includes five chapters. Chapter one is the introduction chapter, which included the background of the study, problem statement, research questions, specific objectives, research hypothesis and significance.

Chapter two the literatures review chapter, which included the review of the previous reports and studies that related to the heavy metals and biosorbent of heavy metals.

Chapter Three the methodology chapter covered different stages, which included collecting the leaves from the available sources around Kuantan, Pahang, Malaysia. Preparing leaves, biosorbent tests and investigating the optimum conditions for Cd (II) removal from synthetic water.

The first stage, reported in Chapter Three, covered the preparation of *Moringa oleifera* leaves, which included the leave drying, grinding and sieving to different sizes, in addition to the synthetic water and heavy metal's stock solutions preparation.

Then, the second stage was continued with the optimization of the different parameters started with biosorbent dosage, contact time, particle size, pH effect, water turbidity and initial heavy metal concentrations.

Optimization of the parameters started with dosage optimization. After getting the optimum dosage, it was maintained in the other experiment and other parameters were targeted and optimized. Atomic Absorption spectroscopy (AAS) was used to determine the heavy metals before and after biosorption by *Moringa oleifera* leaves. FTIR was used to investigate the functional groups of *Moringa oleifera* leaves and change in the structure before and after loading with Cd (II). In addition to that Electron Scanning Microscopy was done to follow the changes occurred on *Moringa oleifera* leaves morphology after the biosorption process. Surface Area Analyser (BET test) was used to investigate the effect of the particle size on the biosorption process. Lastly, the optimized parameters achieved in the study for Cd (II) removal, were applied on Fe (III), Pb (II) and Cu (II) in one experiment to test the optimized parameters on these ions and to compare the ability of *Moringa oleifera* leaves biosorption of these ions.

At the end, it can be concluded that the study answered the main research questions, which can summarize that *Moringa oleifera* leaves could be a potential biosorbent for Cd (II) and the other targeted heavy metals from water systems. It also answered the question that Cd (II) could make changes on the structure and the morphological characteristics of *Moringa oleifera* leaves.

Chapter four covered the results and discussion. The last chapter in this dissertation chapter five includes the conclusion and recommendations.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 BACKGROUND**

##### **2.1.1 Heavy metals**

This entire review revised the most recent studies on biosorbents used for heavy metals removal such as plant leaves, seeds, barks, agricultural wastes and biological material and their efficiency on heavy metals adsorption, such as: lead, cadmium, iron and copper. This literature revision also mentioned the conventional methods used for heavy metals removal and the advantages and disadvantages of them. Furthermore, it represents the advantages and disadvantages of common biosorbents and the effect of several factors that influence the biosorption process.

Every day, there are thousands of chemicals discharged directly and indirectly into water bodies as industrial waste causing serious air, soil, and water contamination without further treatment for elimination of the included harmful compounds (Salim et al., 2008; Khairy et al., 2014). Heavy metals are without doubt well thought-out as the most hazardous and harmful metals even if they are present as traces, since they accumulate in the tissue of living organisms (Rao et al., 2010; Khairy et al., 2014). Most of the metals are carcinogenic, teratogenic and cause severe health problems like organ damage, reduced growth and development, nervous system impairments and oxidative stress. Heavy metals introduced into water by several industries such as mining, electroplating, petroleum refining (Rao et al., 2010) and other industries with its toxicity which is presented in Table 2.1.

**Table 2.1:** Heavy metal sources and toxicity

<b>Metal</b>	<b>Source</b>	<b>Toxic effect</b>	<b>WHO Permissible limit mg/l</b>	<b>MOH permissible limit mg/l</b>	<b>Reference</b>
Cadmium	Electroplating, smelting, alloy manufacturing, pigments, plastic and mining	Itai–Itai disease, carcinogenic, renal disturbances, lung insufficiency, bone lesions, cancers, hypertension, weight loss	0.005	0.003	(Sharma and Bhattacharyya 2005; Momodu and Anyakora 2010; Singh et al. 2005; MOH, 2015)
Lead	Manufacturing of batteries, pigments Electroplating, ammunition	Anaemia, brain damage, anorexia, malaise, loss of appetite	0.05	0.01	(Low et al., 2010; Ali et al., 2011; Mataka et al., 2006; MOH, 2015)
Chromium	Electroplating, paints and pigments, metal processing, steel fabrication and canning industry	Epigastric pain, nausea, vomiting, severe diarrhoea, lung tumours, Carcinogenic, mutagenic, teratogenic	0.03	0.05	(Ali et al., 2011; Rao et al., 2011; Singh et al., 2011; MOH, 2015)
Copper	Electronics plating, paint manufacturing, wire drawing, copper polishing, and printing operations	Reproductive and developmental toxicity, neurotoxicity, and acute toxicity, dizziness, diarrhoea	1.5	1	(Bilal et al., 2010; MOH, 2015)
Arsenic	Smelting, mining, energy production from fossil fuels, rock sediment's	Bone marrow depression, haemolysis, liver tumours, gastrointestinal symptoms, cardiovascular and nervous system functions disturbances,	0.02	0.01	(Momodu and Anyakora, 2010; MOH, 2015)
Mercury	Volcanic eruptions, forest fires, battery manufacturing	Corrosive to skin, eyes, muscles, neurological and renal disturbances,	0.002	0.001	(Farooq et al., 2010; MOH, 2015)
Nickel	Copper sulphate manufacture, electroplating, non-ferrous metal, mineral processing,	Reduced lung function, lung cancer, chronic bronchitis, dermatitis, and chronic asthma.	0.03	0.02	(Febrianto et al. 2009; Öztürk, 2007; MOH, 2015)
Zinc	Mining and manufacturing processes	Causes short term “metal-fume fever,” gastrointestinal distress, nausea and diarrhoea	4	3	(Farooq et al., 2010; MOH, 2015)

### **2.1.2 Water treatment**

Inorganic coagulants for water treatment are used in a wide-range. Aluminium sulphate is an examples of the inorganic coagulant, which is the most commonly used coagulant in the developing countries (Farooq et al., 2010). However, aluminium sulphate is reported to cause some neurological diseases for instance pre-senile dementia or Alzheimer's disease (Othman et al., 2010).

The currently used techniques contain several constraints in the removal of heavy metals from water (Abaliwano et al., 2008), such methods showed to not be effective and not economically possible for the treatment of low concentrations (Kelly-Vargas et al., 2012). Therefore new alternative methods need to be explored to find the best ecological and economical techniques to remove the heavy metals from water. A number of effective biosorbents from plant resources have been investigated which will be mentioned in this chapter. Table 2.2, illustrates the advantages and disadvantages of some techniques to remove heavy metals.

**Table 2.2:** Advantages and disadvantages of several techniques used currently to remove heavy metal from water

<b>Method</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>References</b>
Chemical Precipitation	Inexpensive. Simple. Most of the metals can be removed.	Disposal problems. High solid waste produced.	(Abaliwano et al., 2008)
Ion-exchange	Metal selective. High regeneration of Materials.	Fewer numbers of metal ions removed. High cost	(Rao et al., 2010)
Chemical coagulation	De watering. Sludge settling.	Large consumption of chemicals. High cost.	(Abaliwano et al., 2008)
Membrane process and ultra filtration	High efficiency (>95) Less solid waste produced Less chemical consumption.	High running cost. Low flow rates.	(Fu and Wang, 2011)
Natural zeolite	Relatively less costly materials. Most of the metals can be removed.	Low efficiency.	(Fu and Wang, 2011)
Electrochemical methods	Pure metals can be achieved. No consumption of chemicals.	High running cost. High capital cost.	(Rao et al., 2010)

### 2.1.3 Biosorption of heavy metals

Biosorption is a property of both living and dead organisms (and their components), and has been exploited as a promising biotechnology because of its simplicity (Bilal et al., 2013). Accordingly, Biosorption can be defined as the removal of substances from solution by biological materials (Gadd, 2001); Table 2.3 represents the advantages and disadvantages of common biosorbents.

**Table 2.3:** Advantages and disadvantages of common biosorbents

Advantages	Disadvantages
Low operation costs if low-cost sorbents are used. (Fu and Wang, 2011)	Shorter lifetime of biosorbents when compared with conventional sorbents. (Fu and Wang, 2011)
Low quantity of sewage sludge disposed. (Gadd, 2008)	Fast saturation i.e. when metal interactive sites are occupied.(Gadd, 2008)
COD of wastewater does not increase. (Sahmoune et al., 2011)	Recyclable and decomposable properties of biomass are delaying their long-term applications in adsorption processes. (Sahmoune et al., 2011)
The process is simple in operation and very rapid. (Sahmoune et al., 2011)	
Biosorbents are selective and regenerable. (Fu and Wang, 2011)	The characteristics of the biosorbents cannot be biologically controlled.(Ahalya et al., 2003)

Biosorption describes any system that includes a sorbate (an atom, molecule, a molecular ion) working together with a biosorbent (a solid surface of a biological matrix) resulting in an accumulation at the sorbate–biosorbent interface, and therefore a decrease of sorbent concentration in the solution (Sasaki et al., 2013).

Since biosorption is determined by equilibrium, several factors have an impact on heavy metals removal is summarized in Table 2.4 (Chojnacka, 2010).

**Table 2.4:** Factors affecting biosorption

<b>Factors</b>	<b>Effects</b>
Biosorbent dosage	It decreases the quantity of biosorbed pollutant per unit weight of biosorbent, but increases its removal efficiency
Initial pollutant Concentration	It increases the quantity of biosorbed pollutant per unit weight of biosorbent, but decreases its removal efficiency
Solution pH	It enhances biosorptive removal of cationic metals or basic dyes, but reduces that of anionic metals or acidic dyes
Biosorbent size	It is favourable for batch process due to higher surface area of the biosorbent, but not for column process due to its low mechanical strength and clogging of the column
Other pollutant Concentration	If coexisting pollutant competes with a target pollutant for binding sites or forms any complex with it, higher concentration of other pollutants will reduce biosorptive removal of the target pollutant

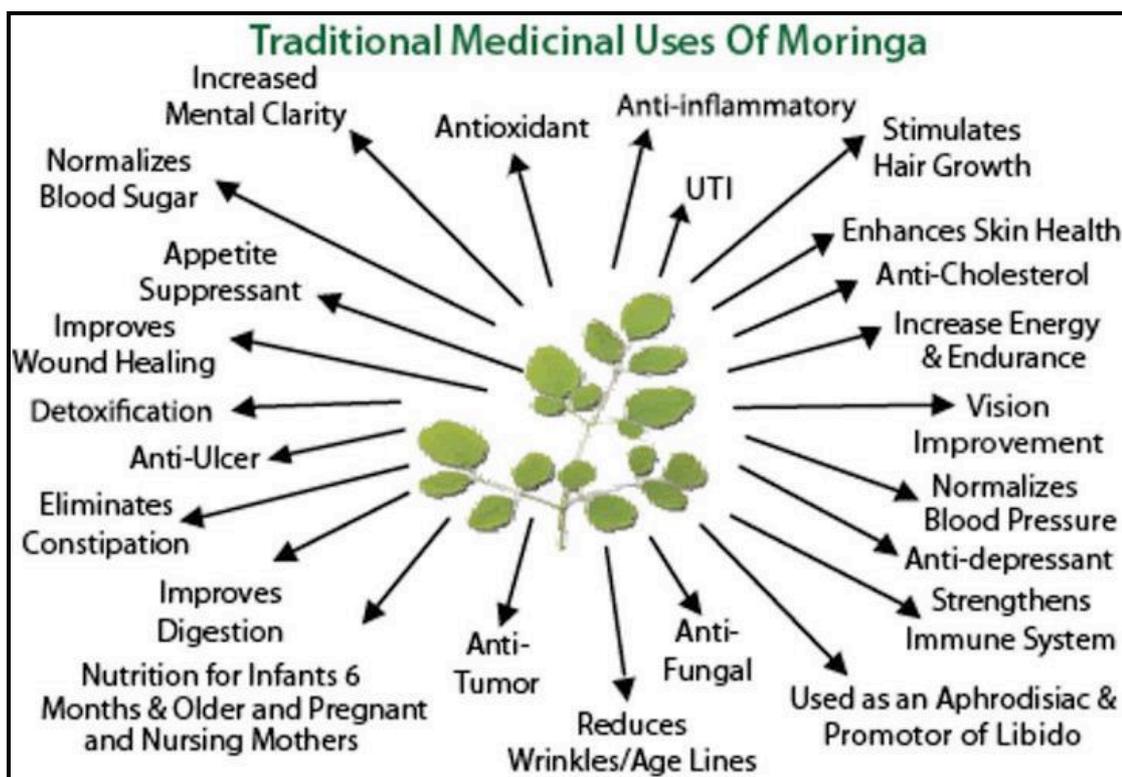
### ***2.1.3.1 Agricultural waste Biosorbents***

Agricultural waste materials are usually composed of lignin and cellulose as the main constituents (Beveridge and Murray, 1980). Other components are hemicelluloses, lipids, proteins, simple sugars, starches, water, hydrocarbons, ash and many more compounds that contain a variety of functional groups present in the binding process; for example carboxyl, amino, alcohol and esters (Gupta and Ali, 2000). These groups are assumed to have the ability to bind heavy metal by replacement of hydrogen ions for metal ions in solution or by donation of an electron pair from these groups to form complexes with the metal ions in solution. Researchers reported the relation between the presence of various functional groups and their binding with heavy metals during the biosorption process (Tarley and Arruda, 2004). A number of studies have highlighted the potential of inexpensive adsorbents prepared from an agricultural by-product (Bailey et al., 1999; Babel and Kurniawan, 2003; Kurniawan et al., 2006; Sud et al., 2008; Reddy et al., 2009). Moreover heavy metal removal by agro based waste material was reported by (Qaiser et al., 2007) and agricultural waste okra biomass (Singha and Guleria, 2015).

### 2.1.3.2 *Moringa oleifera* as biosorbents

*Moringa oleifera* is a fast growing tree which can tolerate drought, bacteria and fungi (Karmakar et al., 2010). It can also tolerate rainfall ranging from 25 to 300 cm with temperatures ranging from 19 to 28 °C (Karmakar et al., 2010). The tree ranges in height from 5-12 meters and sometimes even 15 meters (Tsaknis et al., 1999). In some parts of the world *Moringa oleifera* is referred to as the ‘drumstick tree’ or the ‘horse radish tree’, and kelor tree (Anwar and Bhangar, 2003). While in the Nile valley, the name of the tree is ‘Shagara al Rauwaq’, which means ‘tree for purifying’ (Anwar et al., 2007). In Pakistan, *Moringa oleifera* is locally known as ‘Sohanjna’ and is grown and cultivated all over the country (Anwar et al., 2007). In the Philippines, it is known as ‘mother’s best friend’ because of its utilization to increase the woman’s milk production and is sometimes prescribed for anaemia (Estrella et al., 2000; Siddhuraju and Becker, 2003).

*Moringa oleifera* is a multi purposes tree with most of its parts being useful for a number of applications. It is generally used in a number of developing countries as a vegetable, medical plant and a source of vegetable oil. It has an impressive range of medicinal uses with high nutritional value (Anwar et al., 2007). Each part of this plant contains a profile of important minerals, and is a good source of protein, vitamins,  $\beta$  - carotene, amino acids and various phenolic. The *Moringa oleifera* plant provides a rich and rare combination of zeatin, quercetin,  $\beta$  - sitosterol, caffeoylquinic acid and kaempferol (Siddhuraju and Becker, 2003). The fresh leaves are rich in vitamin A and C. The leaves extract has therapeutic potential for the prevention of some diseases (Anwar et al., 2007), Figure 2.1, shows some traditional medicinal uses of *Moringa oleifera* leaves.



**Figure 2.1:** Traditional Medicinal Uses of *Moringa oleifera* leaves (Anwar et al., 2007)

*Moringa oleifera* seeds have been found to be a natural coagulant, flocculants, softener, disinfectant, and sludge conditioner (Muyibi and Evison, 1995; Jahn et al., 1986; Abaliwano et al., 2008; Suarez et al., 2003), heavy metal remover in water and wastewater treatment (Alves and Coelho, 2013; Obuseng et al., 2012; Reddy et al., 2011; Reddy et al., 2010). The *Moringa oleifera* seeds also have antibacterial activity (Broin et al., 2002). Extracted seed oil is a good edible oil, lubricant oil and as feedstock for biodiesel (Karmakar et al., 2010; Mani et al., 2007; Rashid et al., 2008). The seed husk and pods left over can be steamed activated to produce a high quality activated carbon (Nadeem et al., 2006). The flower and fruits are used as vegetables and the trunk is used in the paper industry (Tsaknis et al., 1999). The roots are used for medicinal purposes (Karadi et al., 2006).

The residual solids left from oil extraction and filtration process can be considered as animal feed with high nutritional value, and as soil fertilizer.