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

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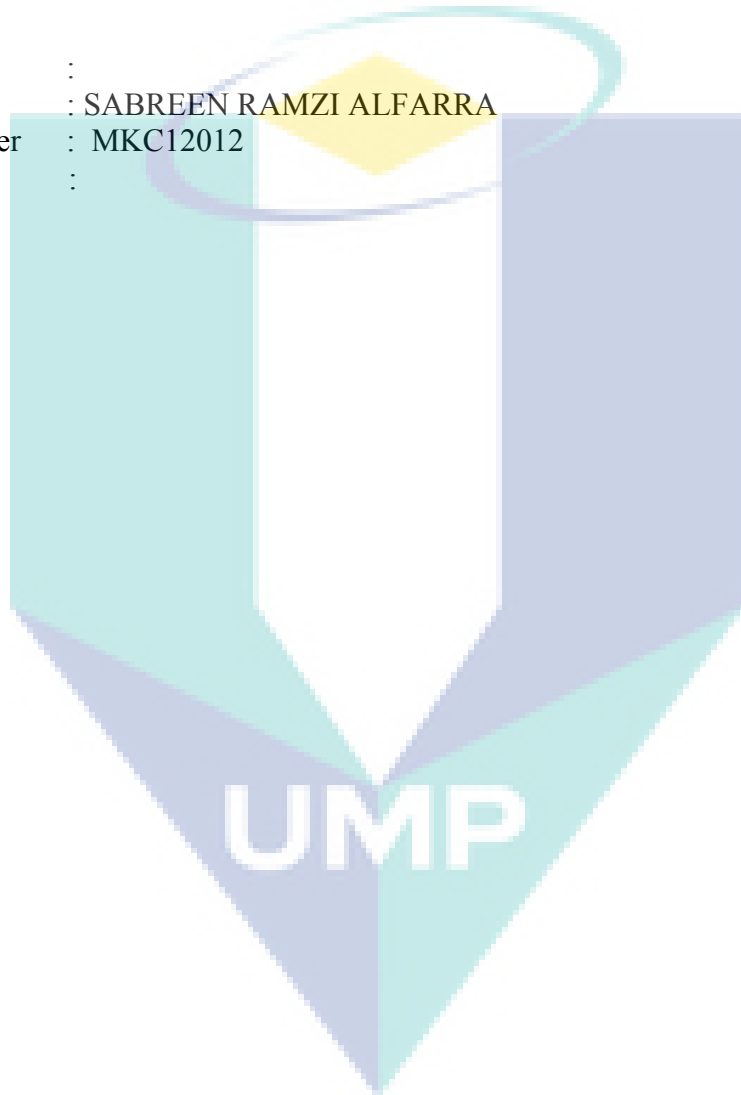Date   :
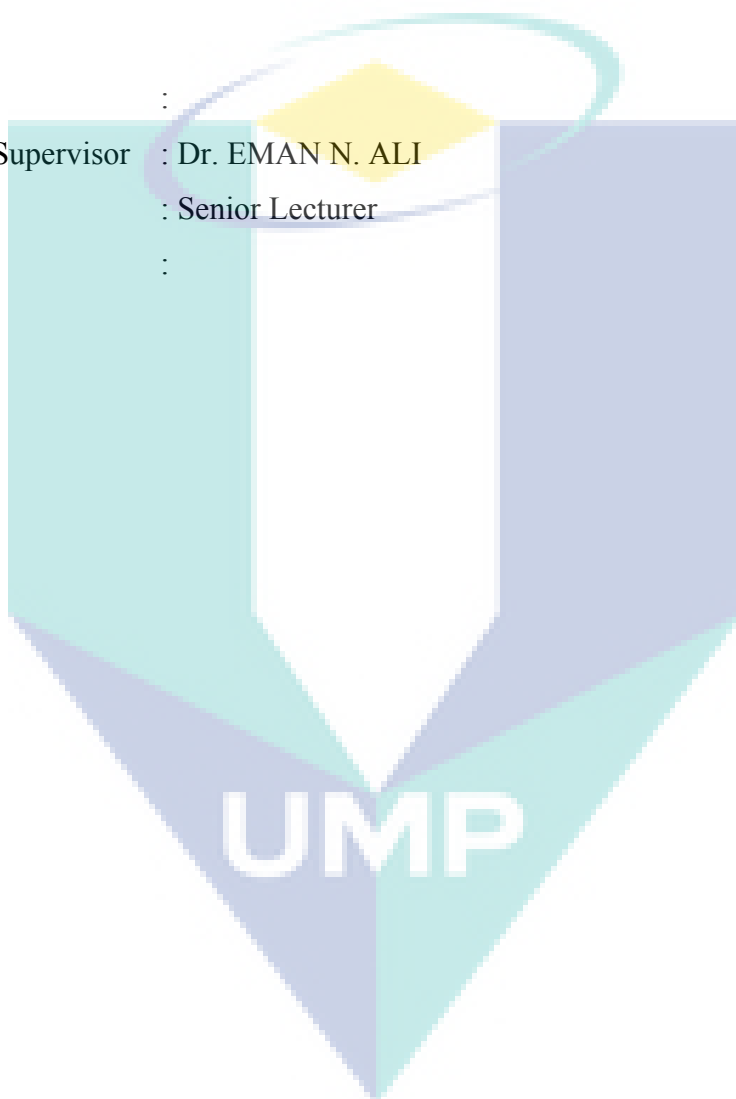
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To my beloved parents, words of all languages are not enough to thank you & to tell you
love you

To my fabulous sisters Mariam, Mona and Mai, thanks Allah for a beautiful gift

To the honourable person in my life, the source of motivation and inspiration, without him
I couldn't reach my goals, the one and only, my husband

Helmi

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To the people who touch my heart

To my father & mother in law, my sisters & brothers in law the symbol of love & giving.

To my best friend Rama

To my homeland Palestine

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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, 500μm, 250μm, and < 250μm, 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 μm 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 oleifora* (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, 500µm, 250µm, dan -250µm, 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 µm 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.

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LIST OF ABBREVIATIONS AND SYMBOLES

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

Metal	Source	Toxic effect	WHO Permissible limit mg/l	MOH permissible limit mg/l	Reference
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 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., 20 Ali et al., 201 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., 201 Rao et al., 201 Singh et al., 2(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., 2(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, 20 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 a 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

Method	Advantages	Disadvantages	References
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

Factors	Effects
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 ºC (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 Bhanger, 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, β - carotene, amino acids and various phenolic. The *Moringa oleifera* plant provides a rich and rare combination of zeatin, quercetin, β - 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.
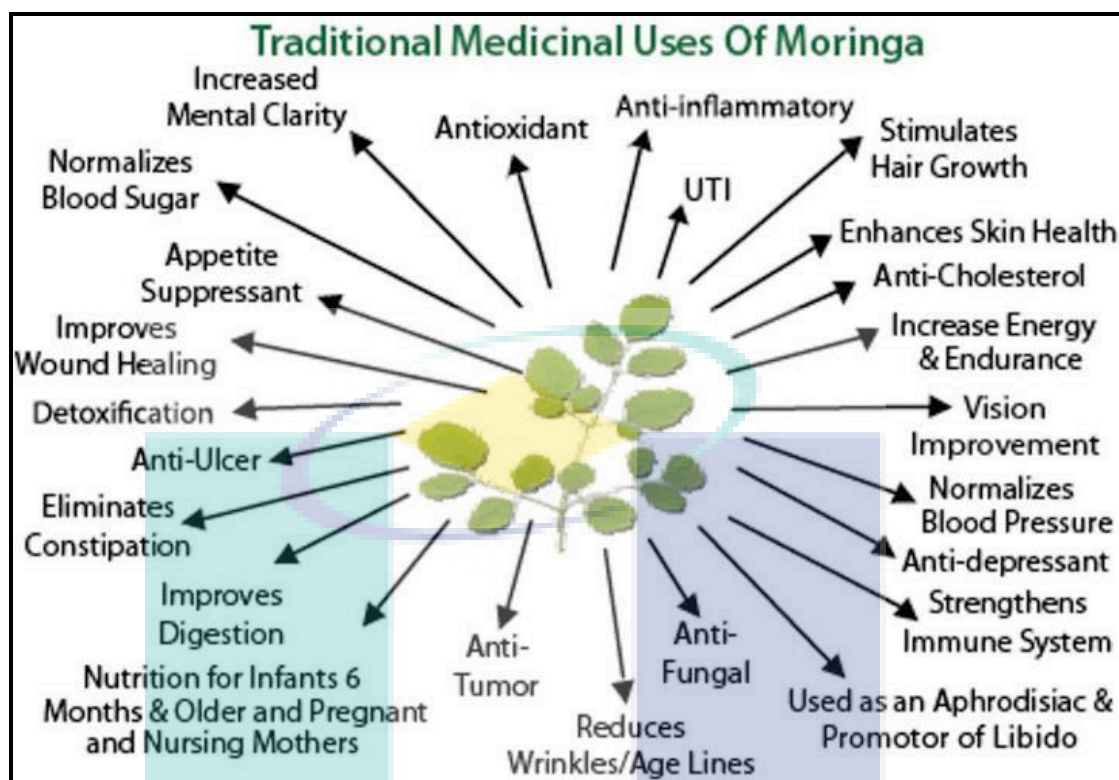
Figure 2.1: Traditional Medicinal Uses of *Moringa oleifera* leaves (Anwar et al., 2007)

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.

2.1.4 Biosorption of Cadmium

Cadmium occurs naturally 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 (Rao et al., 2010). The best-known Cd (II) mineral is greenockite, or cadmium sulphide (77.6% Cd). Other minerals are otavite, cadmium carbonate (61.5% Cd) and pure cadmium oxide (87.5% Cd). Greenockite (CdS) is nearly always associated with sphalerite (ZnS) (Rao et al., 2010) as a consequence; Cd (II) is produced mainly as a by-product from mining, smelting, and refining of sulphide ores of zinc (Rao et al., 2010). Cd (II) 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 fraction, and destruction of red blood cells (Drasch, 1983). The metal has a special concern because it is non-degradable and therefore persistent. Cd (II) enters the environment via wastes from industrial processes such as electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, dyes, textile operations and refining (Momodu and Anyakora, 2010; Rao et al., 2010; Sharma and Bhattacharyya, 2005; Singh et al., 2005). All over the world cadmium contaminated wastewaters are being generated either directly due to Cd (II) production or through secondary sources. A major past disaster 'Itai-Itai' due to contamination of cadmium in the Jintsu river of Japan is well known. According to WHO's recommendation Cd (II) limit in drinking water is 0.005 mg/l (Rao et al., 2010). Meanwhile, Ministry of Health Malaysia recommends that Cd (II) limits in drinking water should not exceeding 0.003 mg/l .The solubility of Cd (II) in water is influenced to a large degree by its acidity; suspended or sediment-bound Cd (II) may dissolve when there is an increase in acidity (IARC, 1976). In natural waters Cd (II) is found mainly in bottom sediments and suspended particles. It is also present in ambient air in the form of particles in which cadmium oxide is probably an important constituent.

Crops grown in polluted soil or irrigated with polluted water may contain high concentrations, as well as meat from animals grazing on contaminated pastures (IARC, 1976).

2.1.4.1 Microorganisms used for Cd (II) removal from water

Fungi (Xiao et al., 2010), bacteria (Kalkan et al., 2013), yeast (Göksungur et al., 2005), micro and macro-algae (Sarada et al., 2014; Anastopoulos and Kyzas, 2015), and other microorganisms have been investigated for Cd (II) uptake from water. Waste biomass *Sargassum* species was studied to remove Cd (II) from water (Esteves et al., 2000). Different microorganism-derived materials have also been used as biosorbents which includes, brown algae *Fucus vesiculosus* (Mata et al., 2008), green algae *Chlorella emersonii* (Arkipo et al., 2004), red algae *Ceramium virgatum* (Sarı and Tuzen, 2008), *Sargassum muticum* (Lodeiro et al., 2004), and *Ascophyllum sargassum* . It is reported that *Aspergillus Niger* (fungus) is effective in removing Cd (II) (Barros et al., 2003). Yeast species (*Saccharomyces cerevisiae* and *Kluyveromyces fragilis*) were also used to remove Cd (II) from industrial effluents (Göksungur et al., 2005). A newly developed deep-sea bacterium, *Pseudo alteromonas* was investigated as a biosorbent for Cd (II) removal from water (Zhou et al., 2013).

2.1.4.2 Biosorption with agro-industrial waste materials

A number of adsorbents obtained from agro-industrial waste materials were used to remove Cd (II) from wastewaters which include: Tea industry waste (Cay et al., 2004), waste tea leaves (Tee and Khan, 1988), Areca-food waste (Zheng et al., 2008), sugarcane bagasse (Putra et al., 2014) and grape waste (Sardella et al., 2015). Kaikake et al. (2007) have investigated degreased coffee beans for removing Cd (II) from aqueous solution. Modified cassava waste is another industrial waste which has been used for removal of Cd (II) from solutions (Abia et al., 2003).

Furthermore, agro based waste have also been reported for removal of heavy metals (Qaiser et al., 2007). More research works have been done using other waste materials by many researchers as follow:

2.1.4.2.1 Saw dust as biosorbent

Saw dust has been widely studied to remove metal ions from wastewater. Memon et al. (2007) carried out a detailed study on treated and untreated saw dust for

Cd (II) uptake from water and the removal efficiency of Cd (II) was 97%. Pinus sylvestris saw dust has been investigated by Taty-Costodes et al. (2003) for Cd (II) and Pb (II) removal from aqueous solution. Naiya et al. (2009) have studied the ability of sawdust and neem bark for removal of zinc and Cd (II) ions from aqueous solutions. Popular wood sawdust was examined for adsorption of Cu (II), zinc and Cd (II) from electroplating wastewater (Šćiban et al., 2007), papaya wood (Saeed et al., 2005) and modified hardwood saw dust (Sciban et al., 2006) were also investigated. Furthermore, popular Romanian fir tree (Abies alba) sawdust was investigated as biosorbent for Cd (II) removal from synthetic aqueous solution and showed good results (Nagy et al., 2013). Moreover, Agave sisalana (sisal fiber) was proposed as a biosorbent for Pb (II) and Cd (II) ions from natural waters (dos Santos et al., 2011).

2.1.4.2.2 *Peels as biosorbent*

Several researchers have studied the fruit peels for cadmium removal. Orange peel was studied by Gupta and Nayak (2012) for cadmium removal. Modified jackfruit peel was investigated for the removal of Cd (II) from aqueous solution (Inbaraj and Sulochana, 2004). Also Benaissa (2006) has investigated the capacity of four inexpensive materials which are peels of peas, broad bean, medlar and fig leaves, to remove cadmium from aqueous solutions. It was noted that the broad bean peel was the most effective to remove Cd (II) ions with a maximum sorption capacity about 147.71 mg/g. Moreover, mango peels (Iqbal et al., 2009) and banana peel (Memon et al., 2008) has been studied for cadmium adsorption. In addition, different cortex fruit wastes including banana (*Musa aradisiaca*), lemon (*Citrus limonum*) and orange (*Citrus sinensis*) peel were investigated for Cd (II) removal from water (Kelly-Vargas et al., 2012).

2.1.4.2.3 *Barks, stems, straw and stalks as biosorbent*

Tan and Xiao (2009) have examined the ability of ground wheat stems to remove Cd (II) and they noted that blocking of the functional groups decreased the binding capacity of Cd (II) whereas increasing functional groups improved the binding capacity. In addition, Ghodbane et al. (2007) studied the effectiveness of

eucalyptus bark as an inexpensive adsorbent for removing Cd (II) ions from aqueous solution and stated that the bark is an excellent adsorbent for removing metals ions from wastewater with efficiency as good as conventional used adsorbents with less cost. Farooq et al. (2011) studied the effect of pH, contact time and temperature on wheat straw and modified wheat straw for Cd (II) removal. They found that the maximum sorption occurred at pH of 6 by both the material and the biosorption with the modified wheat straw is faster (equilibrium time 10 min) than by the wheat straw (equilibrium time 20 min). Han et al. (2013) have investigated the use of rice straw for Cd (II) removal from water. Chemically modified maize straw was also used for Cd (II) removal (Guo et al., 2015). *Calotropis procera,* a perennial wild plant, was investigated by Pandey et al. (2008) for Cd (II) removal, and the result showed that the maximum removal was obtained at pH 5.0 and 8.0 with maximum biosorption capacity in batch and column mode was found to be 40 and 50.5 mg/g. respectively. *Hybrid Eucalyptus* wood based activated carbon was investigated for Cd (II) removal and they found that the optimum dosage to remove 80 mg/l of cadmium from aqueous solution was 1.0 g/150 ml and the optimum contact time was 30 min.(Venkatesan et al., 2014). Sunflower Head Carbon (SHC) and Sunflower Stem Carbon (SSC) were reported for removal of cadmium from wastewater in batch mode The results of batch experiment showed that the highest cadmium adsorption was found at pH = 6.0, initial Cd (II) concentration = 100 mg /l, adsorbent dose = 20 g/l, contact time = 120 min at temperature = 25±1°C and at 180 rpm (Jain et al., 2015). *Scolymus hispanicus* L. plant was studied under several conditions of particle size, pH, biosorbent dosage, contact time, initial metal concentration and temperature for Cd (II) removal from water. Result showed that the maximum biosorption occurred at pH 6.5 with maximum biosorption capacity of 54.05 mg/g (Barka et al., 2010). The effect of pH, adsorbent concentration, contact time, and initial metal concentration studied on Cd (II) removal using coffee ground and wheat straw, and the optimum condition were achieved in less than 30 min with maximum adsorption capacity of coffee ground and wheat straw 16.2 and 31.6 mg/g respectively (Dutta et al., 2015)

2.1.4.2.4 Husks, hull and shells as biosorbent

The husk of a black gram (*Cicer arientinum*) was investigated as a new biosorbent of Cd (II) from low concentration aqueous solutions (Saeed and Iqbal, 2003). Moreover, the removal and recovery of Cd (II) from waste waters using a rice husk have studied by Ajmal et al. (2003). Also, Untreated and phosphate-treated rice husk (PRH) studied for Cd removal and the result showed that adsorption of Cd (II) was greater when PRH was used and Cd (II) sorption was dependent on contact time, ion concentration, temperature, adsorbent doses and pH of the solution (Ajmal et al., 2003). Chemically modified onion skin (CMOS) for Cd (II) removal from aqueous solution was investigated at different conditions of initial Cd (II) concentration, contact time, pH, and temperature, and the result showed that the maximum biosorption capacity of 18.34 mg/g was obtained for CMOS as compared with 11.90 mg/g for a raw onion skin (Agarry et al., 2015). The sorption of Cd (II) from aqueous solution by Raw Rice Husk (RRH) and epichlorohydrin treated rice husk (ERH), NaOH treated rice husk (NRH) and sodium bicarbonate treated rice husk (NCRH) were investigated. Modifications resulted in increasing the sorption capacity of (RRH) from 8.58 mg/g to 11.12, 20.24, 16.18 mg/g and reducing the equilibrium time from 10 h of RRH to 2, 4 and 1 h, of (ERH), (NRH) and (NCRH), respectively (Kumar and Bandyopadhyay, 2006). Green coconut shell was studied for Cd (II) biosorption and it was found that the maximum biosorption of 94.44% for Cd (II) was attained at pH 6.5, 120 min and biosorbent dosage, 5g/l (Pino et al., 2006).

2.1.4.2.5 Brans and grains as biosorbent

Rice bran was evaluated for its potential use as a biosorbent for Cd (II), Cu (II), Pb (II) and Zn (II) (Montanher et al., 2005). Rice polish has been examined by Singh et al. (2005) for the removal of Cd (II) from wastewater with maximum removal of Cd (II) 9.72 mg/ g at pH 8.6, initial Cd (II) concentration of 125 mg/l at 20°C. Low et al. (2000) studied the use of spent grain a by-product of the brewing industry as adsorbent to remove Cd (II) and Pb (II) from aqueous solutions. The effects of solution pH, initial concentration, and temperature were studied in batch experiments with maximum sorption capacities of 17.3 and 35.5 mg/g of cadmium and lead on

spent grain, respectively. By-product lignin from paper production has been investigated for cadmium removal (Mohan et al., 2014).

2.1.4.2.6 Seeds as biosorbent

Jantropha curcas L. Seed's hull has been investigated for Cd (II) and Zn (II) ions removal from aqueous solution (Mohammad et al., 2010). Saif et al. (2012) have investigated *Strychnos potatorum* seeds to remove Cd (II) from aqueous solution. *Moringa stenopetala* and *Moringa oleifera* seed powder were investigated for Cd (II) removal from water. The results showed that *Moringa stenopetala* was more effective than *Moringa oleifera* in removing Cd (II) from water (p < 0.05) and the maximum Cd (II) removals were 82.7% for *Moringa stenopetala* and 70.7% for *Moringa oleifera* (Mataka et al., 2010). Obuseng et al. (2012) examined removal of Pb (II), Cu (II) and Cd (II), by *Moringa oleifera* seeds. Also Nand et al. (2012) results showed that the percentage removal by *Moringa oleifera* seeds was 60% for Cd (II) investigated *Moringa oleifera* seeds.

2.1.4.2.7 Leaves as biosorbent

A batch adsorption study of Cd (II) ions from aqueous solution by *Hevea brasiliensis* (HB) rubber tree leaf powder has also been reported (Hanafiah et al., 2006). Sharma and Bhattacharyya (2005) have studied *Azadirachta indica (Neem)* leaf powder for Cd (II) adsorption, and the result showed that 2g of *Azadirachta indica* (Neem) leaf powder could remove 86% of Cd (II) in 100 ml solution at pH 9.5. In addition, the leaves of the olive tree (*Olea europaea*) were proposed as a novel adsorbent for the removal of Cd (II) from solutions (Hamdaoui, 2009). Ulmus leaves and their ash have been investigated for Cd (II) removal from wastewaters. The study showed that Cd (II) uptake was found to be rapid and reached to 85-92% of equilibrium capacity of biosorption in 15min at optimum pH=6 and initial concentration 2 mg/l for both Ulmus leaves and their ash, respectively (Mahvi et al., 2008). Chemically modified *Moringa oleifera* leaves powder has been used for the removal of Cd (II), Cu (II) and Ni (II) (Reddy et al., 2012). It has been observed that *Eichhornia crassipes* (Water hyacinth) aquatic plants were able to remove Cd (II)

from the municipal contaminated water, where the average removal efficiency for Cd (II) was 71.28% (Satya et al., 2011). *Prunus avium* (sweet cherry) leaves was used to remove Cd (II) from aqueous solutions(Salem et al., 2012). The effect of contact time, pH, Cd (II) initial concentration and adsorbent dosage for Cd (II) removal from water were studied by using Quetta pine leaves, result revealed that the optimum pH was 7.0 at 30 min with adsorbent dose of 10 g and maximum adsorption efficiency of 98.50% for Cd (II) (Rahman et al., 2015). *Psidium guajava* leaves powder was studied to remove Cd (II) from water and the result showed that the maximum uptake capacity is 4.28 mg/g at pH = 4, in 50 mL of the aqueous solution for 20 g/l dosage and 38μm particle size of the biosorbent (Varma et al., 2010). Biosorption of Cd (II) onto loquat leaves (LL) powder and loquat leaves ash (LA) from aqueous solution has been investigated, result showed that the maximum capacity of LL and LA was 29.240 mg /g and 21.322 mg/ g for Cd (II) ions, respectively.(Al-Dujaili et al., 2012).

2.1.5 Biosorption of Iron

Iron is one of the most abundant elements on earth. It is an essential element in human nutrition and plant metabolism, and it is used in a variety of industrial processes. In industry, 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 entering the water bodies in the form of ferrous ion (Fe), which can be oxidized to ferric ion Fe (III) by oxygen dissolved in water (Ahalya et al., 2003). Many investigations have been studied on the ability of some agricultural waste and natural biosorbent to remove Fe (III) from water which includes bark of a tree (Rose and Rajam, 2012), wooden charcoal (Ahamad and Jawed, 2010), pomegranate peel (Moghadam et al., 2013) and *Moringa oleifera* seeds (Mancy et al., 2013). Oil palm bark (OPB) was investigated for iron (III) removal from aqueous solutions and the optimum conditions was 5 to 6 pH range, 200 μm particle size, 1 g/l adsorbent dosage, and 40 min agitation time to remove 78 % of Fe (III) (Khosravihaftkhany et al., 2013). Also Fe (III) removal was studied using chemically treated leaves of *Melia azedarach* L.

(MAL) and the optimum conditions of this metal with NaOH and HCl treated MAL biosorbents was observed at 5–7 pH of solution, 0.09 g of adsorbent dose, 250 rpm shaking speed, 75 μm biosorbent sizes, 60 min of contact time and 5 mg /l initial metal ion concentration.The maximum sorption capacity by NaOH treated biosorbent for Fe(III) was 38.46 mg /g, and by HCl was 28.57 mg /g (Khokhar et al., 2015).

2.1.6 Biosorption of Copper

Copper is an essential nutrient and a drinking water contaminant. It is an important element required by humans in traces, used by human body for enzyme synthesis, tissues and bones development (Nand et al., 2012). However, the excessive amount of it is toxic and carcinogenic. Deposition of copper in body causes health problems such as Wilson disease, liver and kidney failure and gastrointestinal bleeding (Bilal et al., 2013). The excessive amounts of Cu (II) in fresh water resources and aquatic ecosystem damage the osmoregulatory mechanism of the freshwater animals. Large quantities of copper are released by the disposal of untreated industrial waste (Bilal et al., 2013). According to the World Health Organization (WHO) the permissible limit of Cu (II) in drinking water should not exceed 1.5 mg/l (Bilal et al., 2013). Several conventional methods have been used to remove Cu (II) from water. Though, the used methods have many disadvantages. Adsorption by agricultural wastes and natural biosorbent has more benefits than the conventional methods. Several biosorbent have been investigated for Cu (II) removal which include cassava waste (Abia et al., 2003) wheat shells (Basci et al., 2004), hazelnut shells (Demirbaş et al., 2008), cashew nut shells (SenthilKumar et al., 2011), orange peel (Feng et al., 2009), pomegranate peel (El-Ashtoukhy et al., 2008), Grape seeds (Al Bsoul et al., 2014), *Cinnamomum camphora* leave's (Chen et al., 2010), loquat leaves (Al-Dujaili et al., 2012) and *Moringa oleifera* wood (Helen and Miranda, 2010). .

2.1.7 Biosorption of Lead

Lead in water arises from a number of industrial and mining sources and is the most widely distributed of all toxic metals (Shafaghat et al., 2014). The excess amount of lead in water causes serious problems such as anaemia, encephalopathy, hepatitis,

and kidney disease and affects the nervous system (Shafaghat et al., 2014). Conventional methods used for removing Pb (II) from water have many disadvantages. On the other hand biosorption of the metal by natural biosorbent is more advantageous than the used method. Several studies have been conducted on Pb (II) removal from water using natural biosorbents which include mango peels (Iqbal et al., 2009), *Agave sisalana* (sisal fiber) (dos Santos et al., 2011), *Cinnamomum camphora* leave's (Chen et al., 2010) and *Moringa oleifera* leaves (Reddy et al., 2010). Also chemically treated leaves of *Melia azedarach* L. (MAL) was carried in batch mode on Pb (II) biosorption and the optimum conditions with NaOH and HCl treated MAL biosorbents was observed at 5–7 pH of solution, 0.09 g of adsorbent dose, 250 rpm shaking speed, 75 μm biosorbent sizes, 60 min of contact time and 5 mg /l initial metal ion concentration with maximum sorption capacity by NaOH treated biosorbent for Pb (II) was 35.06 mg/g and by HCl treated biosorbent was 28.5 mg/g, respectively (Khokhar et al., 2015). Oil palm bark (OPB) was studied on lead (II) removal from aqueous solutions. The proper pH range, particle size, adsorbent dosage, and agitation time for Pb (II) removal was 5 to 6, 200 μm, 1 g/l, and 40 min, respectively. With removal efficiency of 80 % for Pb (II) (Khosravihaftkhany et al., 2013).

Literature review showed that consumption of low-cost sorbents has been studied as a substitution for current costly techniques of removing heavy metals from solution. Biomaterials with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost.

In this review, a wide list of biosorbent literature has been collected to provide a summary of available information on a wide range of potentially low-cost sorbents, including bark, leaves, husk, microorganisms and others. Some of the maximum adsorption abilities reported for cadmium,

The literature review has shown that in most of the situations, biosorption experiments were done either in stirred tank using flocculation or column adsorption. Generally the various adsorption parameters studied to assess their effects on Cd (II) elimination efficacy are: contact time, pH, biosorbent and ion concentrations. Several low-cost biosorbents have been proposed as possible candidates for elimination of cadmium from water systems. And in conclusion it can be said that Cd (II) is amongst

the most toxic ions hazardous to living organism and its permissible limit in drinking water is 0.005 mg/l according to WHO. Though there are few studies in literature for the use of *Moringa oleifera* leaves to remove Cd (II) from water. Thus this study targeted *Moringa oleifera* leaves was used to assist its capability in Cd (II) from water.
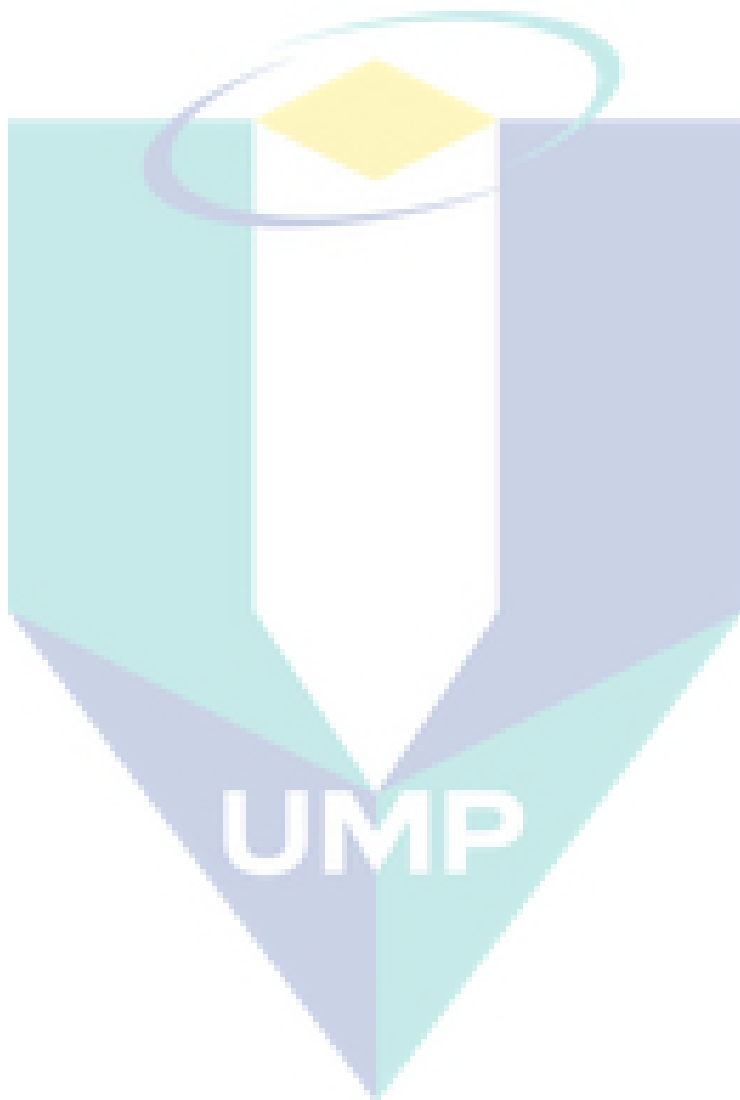
CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This chapter illustrates the experimental procedure, preparation of the biosorbent and synthetic water. Also encloses the application of *Moringa oleifera* leaves on Cd (II) and other heavy metals Pb (II), Cu (II) and Fe (III). The analytical techniques used in this study were the Atomic Absorption Spectroscopy (AAS), Flocculator (Jar test), Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) surface area analyser.

3.2 ANALYTICAL TECHNIQUES

3.2.1 Atomic absorption spectrometry (AAS)

It is an analytical technique that measures the concentrations of elements. In this study (AAS, Perkin Elmer 400) was used to analyse Cd (II), Pb (II), Fe (III) and Cu (II) in synthetic water before and after absorption by *Moringa oleifera* leaves. The heavy metals were measured at wavelength of 228.8, 248.3, 283.31and 324.8 for Cd (II), Fe (III), Pb (II) and Cu (II), respectively.

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

It is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information. FTIR has been used in this study to identify the different functional groups present in the *Moringa oleifera* leaves before and after removing Cd (II). FTIR analysis is also used to determine the functional

groups that are responsible for the Cd (II) binding with *Moringa oleifera* leaves. The analysis was carried out using KBr pellet and the spectral range varying from 4000 to 400 cm^{-1}. Furthermore, another type of FTIR has been used in this study called two-dimensional infrared (2D IR) spectroscopy. It is an exciting technique with many advantages over standard linear infrared spectroscopies like infrared absorption spectroscopy and FTIR spectroscopy. In 2D IR, infrared spectra are spread into a second dimension, providing information on vibrational couplings and separating the effects of homogeneous and inhomogeneous dynamics. This provides a powerful tool for studying molecular structures, environmental dynamics, and structural kinetics.

3.2.3 Flocculator (Jar Test)

This is a general laboratory procedure that simulates water treatment plants, by coagulation-flocculation process (Kawamura, 1991). The coagulation-flocculation test is carried out to determine the chemical, dosages, mix speed and settling time to estimate the conditions required to achieve optimum results. This jar test permits the evaluation of various coagulants and coagulant aids used in the treatment of water and wastewater for the same water and the same experimental conditions. The effects of concentration of the coagulants and coagulant aids and their order of addition can also be evaluated by this practice. Figure 3.1, shows the jar test apparatus.
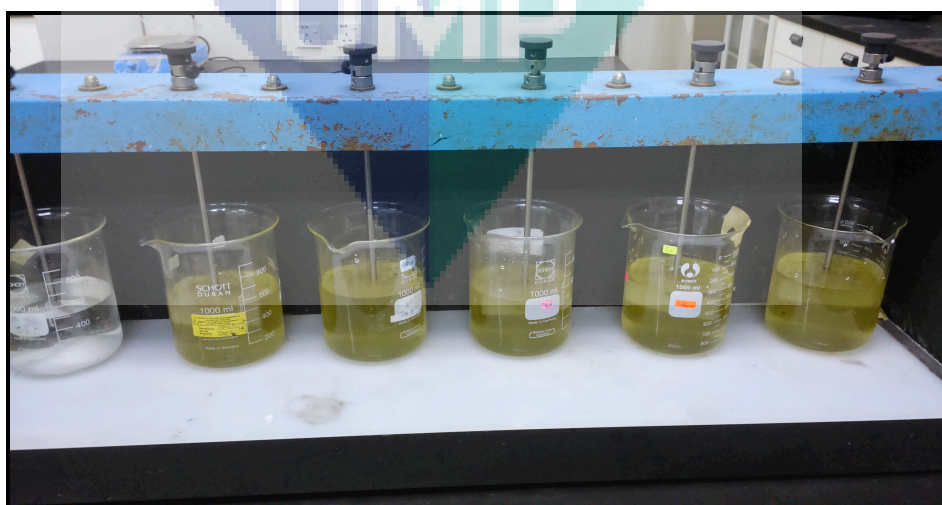
Figure 3.1: Sample running in the Jar test

3.2.4 Brunauer-Emmett-Teller (BET) Surface Area Analysis

Surface Area Analysis/ BET offer precise specific surface area assessment of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The method includes external area and pore area evaluations to determine the total specific surface area in m^2/g yielding significant information in studying the effects of surface absorbency and particle size in many purposes.

To analyse the surface area, solid samples are pre-treated by applying some combination of heat, vacuum, and /or flowing gas to remove adsorbed contaminants acquired (typically water and carbon-dioxide) from atmospheric exposure. The solid is then cooled, under vacuum, usually to cryogenic temperature (77K= -196.15 C). An adsorptive (typically nitrogen) is dosed to the solid in controlled increments. After each dose of adsorptive, the pressure is allowed to equilibrate and the quantity adsorbed is calculated. The quantity adsorbed at each pressure (and temperature) defines an adsorption isotherm, from which the quantity of gas required to form a monolayer over the external surface of the solid is determined. With the area covered by each adsorbed gas molecule known, the surface area can be calculated (Brunauer et al., 1938).

3.2.5 Scanning Electron Microscope

Scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the coated sample, producing various signals that can be detected and that contain information about the sample's surface structure and composition (Jaishankar et al., 2014). SEM is used for the high magnification of most biomaterials. (ZEISS Evo50 Germany) SEM was used in this study for *Moringa oleifera* leaves structure analysis.

3.2.6 Chemicals

Cadmium, Copper, Iron and Lead were purchased from Merck (Germany). Sodium bicarbonate, sodium hydroxide (0.1N) and hydrochloric acid (0.1N) were purchased from HmbG Chemicals (Germany). Kaolin was purchased from (Sigma-Aldrich).

3.2.7 Equipment

Magnet stirrer (Favorit), pH meter and Electrical balance (Metler Toledo) Turbidity meter (Hach2100 Q), Electrical grinder (Philips) and Sieve shaker (Endecotts) from United Kingdom.

3.3 METHODS

3.3.1 Preparation of Biosorbents

Moringa oleifera leaves were collected from nearby area of University Malaysia Pahang, Gambang, Kuantan, Pahang, Malaysia. Leaves were dried under sunlight for 2 days (Appendix 5). Then leaves were ground using an electrical grinder, followed by sieving to different particle size (2 mm, 1 mm, 500 μm, 250 μm, and -250 μm) using a sieve shaker (Endecotts, UK) then kept in plastic bags at room temperature to be used in the study. Figure 3.2 shows flow chart summarizes the experimental works involved in this study.
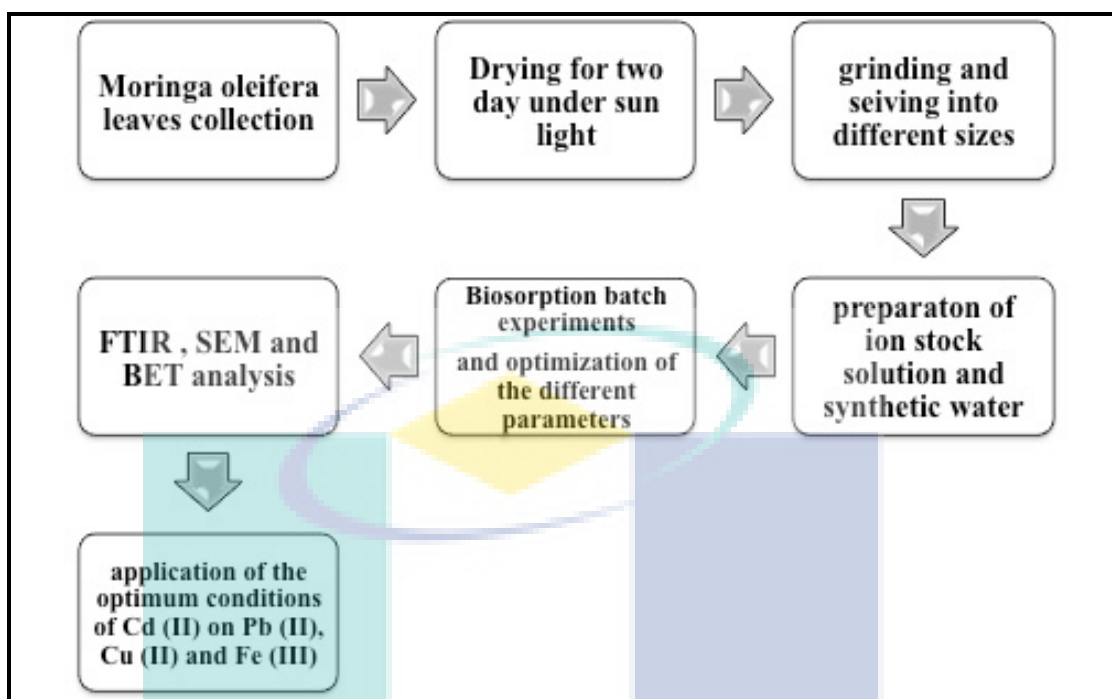
Figure 3.2: Flow chart of the experimental work involved in this study

3.3.2 Preparation of stock solution

The metal solution used in this study for Cd (II) was prepared from ready standard stock solution (1000 mg/l) (Merck). Few dilutions were prepared from the stock solution to prepare the calibration curve for each heavy metal.

3.3.3 Preparation of synthetic water

A weight of 5 g of kaolin, laboratory grade (k7375-500G Sigma- Aldrich), was dissolved with 500 ml of distilled water. Sodium bicarbonate (Hamburg Chemicals) solution with concentration of 100 mg/l was prepared by adding 100 mg of sodium bicarbonate to 1000 ml of distilled water; Adding 500 ml of the sodium bicarbonate solution to the kaolin. The suspension was stirred for about 1 hour at 200 rpm to achieve a uniform dispersion of kaolin particles. Then it was left for at least 24 hours for complete hydration of the kaolin (Eman et al., 2010). The synthetic turbid water was used for biosorption test on Cd (II) removal from water by *Moringa oleifera* leaves. This stock was diluted a few times to get the turbidity needed for each particular test.

3.3.4 Biosorption Batch Experiments

The jar test has been designed for use in water treatment to evaluate coagulation- flocculation processes (Kawamura, 1991). The experiment carried out using Paddle Jar Test apparatus equipped with six paddles rotating in a set of six beakers filled with 500 ml of the synthetic water and known quantity of Cd (II) (0.5, 1.5, 2.5, and 3.5 ml of 1000 mg/l stock solution) were added to 500 ml of synthetic water to get the Cd (II) concentration of (1, 3, 5, and 7 ppm). A different dose of *Moringa oleifera* leaves of (2 to 20 g/l) was added to the synthetic water, the sample was mixed with biosorbent at 200 rpm for 60 minutes, the suspension was allowed to settle for 30 minutes then the biosorbent was filtered using Whatman filter paper No. 42. The pH of the solution was measured with a (Mettler Toledo) pH meter using combined glass electrode. Turbidity of the water was measured by using a 2100Q (HACH) turbidity meter for synthetic water used in the experiments. The residual Cd (II) in the water was analyzed using AAS at wavelength of 228.8 using an acetylene air flame. Removal Efficiency (RE) of Cd (II) was calculated using the equation:

$$RE\% = [(C_o - C_e) / C_o] * 100,$$

Where: C_o and C_e are the initial and equilibrium concentration of Cd (II) in water (mg/l), respectively (Al-Dujaili et al., 2012)

Adsorption of Cd (II) in synthetic water on *Moringa oleifera* leaves were examined by different parameters such as dose concentration (2 -20 g/l), contact time (2 - 120 min), particle size (2 mm, 1 mm, 500 μm, 250 μm, and < 250 μm) and Cd (II) concentration (1, 3, 5, and 7 ppm). The water pH varied from 4 to 10, the pH of the water was adjusted by using 0.1N HCl or 0.1N NaOH without changing the volume of the sample. Multi diluted standards of 1, 3, 5 and 7 ppm of Cd (II) in this study were prepared from standard stock solution (1000 mg/l).

3.3.5 Application of *Moringa oleifera* leaves on (Pb (II), Cu (II), and Fe (III))

Pb (II), Cu (II), and Fe (III) have been investigated using the optimum condition achieved in the previous experiment. This experiment was conducted to show the ability of *Moringa oleifera* leaves for several heavy metal removals.

3.3.6 Preparation of 1D and 2D Fourier transform infrared spectroscopy (FTIR) sample.

To prepare the sample for 1 and 2D FTIR, a small amount of *Moringa oleifera* leaves (MOL) powder before adding Cd (II) and after adding Cd (II) were ground separately using a pestle and mortar and mixed with Potassium Bromide (KBr) (1:10 ratio) to reduce its water content. After that, the fine mixtures of MOL/KBr powder and MOL with Cd (II)/KBr were placed in a die set and a pressure of 10 tons was applied for 20 seconds to the mixture. The pellet was transferred to a 2D FTIR set fixed to the instrument. After background reading and sample scanning was performed at temperatures of 40, 50, 60, until 120 °C the results were processed using 2D FTIR software to obtain the results. The result of 1D FTIR were analysed using FTIR between ranges of 400 - 4000 cm^{-1}.

3.3.7 Preparation for SEM analysis

For the scanning electron microscopy (SEM), proper amount of *Moringa oliefera* leaves powder placed on the carbon tape on the stump of the SEM. After that the stump placed in the coating machine until the vacuum reached to the standard level. The samples were analysed, the magnification was 1000x, probe equal 50 Pa. The picture was captured at 1000x for the sample with and without Cd (II).

3.3.8 Preparation for Surface area analysis

To prepare the sample for BET analysis 0.3-0.5g of *Moringa oliefera* leaves was added to the sample tube then the sample burette installed in the degasser port. The instrument switched on the slow mode until the pressure reached 10^4 Pa, and the desired temperature 50°C. After that the results were collected and analysed.

3.3.9 Preparation for Heavy Metal Removal Analysis

Using a PerkinElmer AAnalyst TM 400 High-Performance Atomic Absorption Spectrometer (AAS) the heavy metal removal test was done. A series of calibration solutions, such as Cadmium, Iron, Copper, and Lead, were prepared from standard

stock solution (1000 mg/l). Each of the elements was prepared with 4 different concentrations of 1, 3, 5 and 7 ppm. Each water sample was diluted before analysing by AAS. AAS equipment operated according to the manufacturer instructions and laboratory assistant guidance. Equipment was turned on and the flame started on the proper ion lamp. When energy reached the standard level, the prepared standard solutions of ions were analysed to give the standard curve as shown in Figure 3.3. After that the samples were analysed using same procedure.
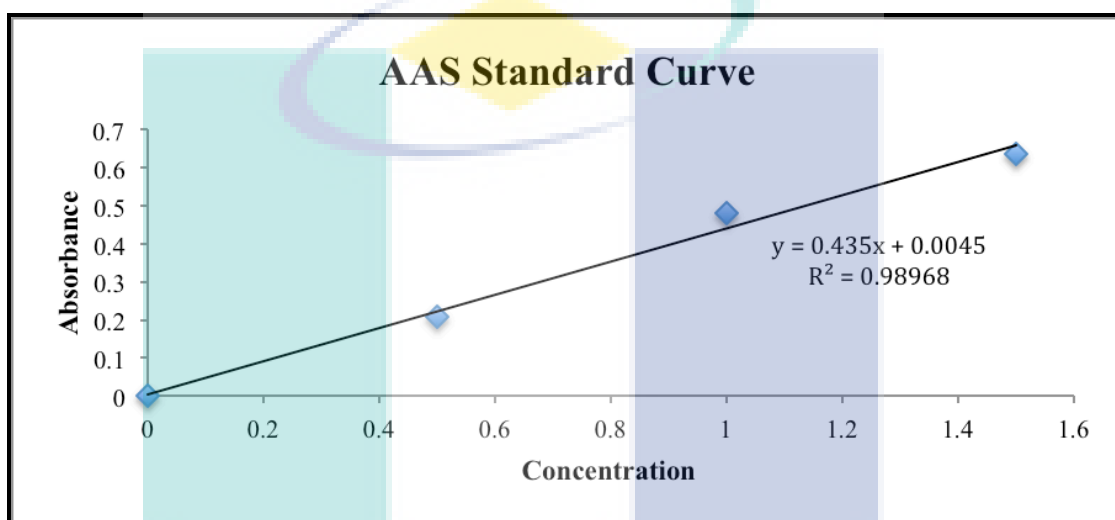
Figure 3.3: AAS standard curve of the Cd (II) concentrations (0.5, 1, 1.5 ppm).

3.3.10 Preparation for Turbidity Measurement

Turbidity of water was measured by using a 2100q (HACH) turbid meter. Turbidity of the water sample was analysed before and after treatment to monitor the performance of *Moringa oleifera* leaves.

3.3.11 Biosorption kinetics procedures

As shown in Table 3.1, according to the absorbance values, ion-remaining concentrations (C_t) was calculated.

Table 3.1: Data for kinetic biosorption analysis

Time	Abs	C_t mg/l	C_0-C_t	q_t	q_e-q_t	$\log(q_e-q_t)$	time/q_t
20	0.355	0.806	0.194	0.0162	0.0192	-1.718	1235.5
40	0.288	0.652	0.348	0.0290	0.0063	-2.199	1378.2
60	0.26	0.587	0.413	0.0344	0.0010	-3.019	1744.8
80	0.26	0.587	0.413	0.0344	0.0010	-3.019	2326.5
100	0.255	0.576	0.424	0.0353	0		2829.3
120	0.255	0.576	0.424	0.0353			3395.1

(C_0-C_t) was calculated by subtracting C_t value from the initial concentration C_0, which was 1 ppm.

After that q_t was calculated as $q_t = (C_0 - C_t/M) * V$

After that q_e-q_t was calculated by subtracting the q_t values from the q experimental (q_e), where q_e is the last value in the q_t column.

Then the collected values were applied in the pseudo-first order (1) and pseudo-second order (2) equations respectively.

$$\log(q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303}t \qquad (1)$$

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t \qquad (2)$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 INTRODUCTION

In this study, *Moringa oleifera* leaves (biosorbent) was used for Cd (II) removal from water as a natural alternative for synthetic sorbents. Synthetic water was used to find optimum conditions for water treatment using biosorbent. Atomic Absorption Spectroscopy (AAS) was used to monitor the Cd (II) concentration before and after treatment with biosorbent. Moreover, Fourier Transform Infrared Spectroscopy (FTIR) was used to monitor biosorbent structure changes before and after loading with Cd (II). This chapter focuses on the effect of different parameter conducted for Cd removal from water by *Moringa oleifera* leaves. In addition, enclosed in this chapter are the results of other heavy metals removed by *Moringa oleifera* leaves and the removal efficiency percentage (RE %) for each metal.

4.2 EFFECT OF PARAMETERS ON CD (II) REMOVAL

4.2.1 Biosorbent Dose Effect

The biosorbent dosage is an important parameter to determine the capacity of a biosorbent for a given initial concentration. Biosorption of Cd (II) onto *Moringa oleifera* leaves was studied by adding different dosage of *Moringa oleifera* leaves from 2 to 20 g/l in the synthetic water sample using different initial Cd (II) concentration of (1, 3, 5, and 7 ppm) and constant contact time of 60 min. The control sample contains Cd (II) and Kaolin has no effect on the adsorption process because the result of the AAS before and after treatment was same. *t-test* results showed that the dose has an effect on the removal of Cd (II) with different concentrations from

synthetic water. *P* value for 1 ppm, 3 ppm, 5 ppm, and 7 ppm were 0.00078, 0.000716, 0.000571and 0.000629, respectively which is <0.05. Figure 4.1, shows the removal efficiency for Cd (II) adsorbed by *Moringa oleifera* leaves at different Cd (II) concentrations. It was observed that when the initial concentration of Cd (II) increased the removal amount increased at the same dose of *Moringa oleifera.* As in Figure 4.1 slight ascending in the removal efficiency was observed at 7 ppm more than 5 ppm, it is assumed because of the instrumental errors that could make these changes during the experimental analysis, and it could be because the experiments were not done at the same time and the same day so this could make some variations. Figure 4.2 shows that *Moringa* could remove 0.8 ppm at 12 g/l with the initial concentration 1 ppm, while it could remove 5.2 ppm at 12 g/l with the initial concentration 7 ppm. It could be concluded that at higher concentrations the removed amount is higher.
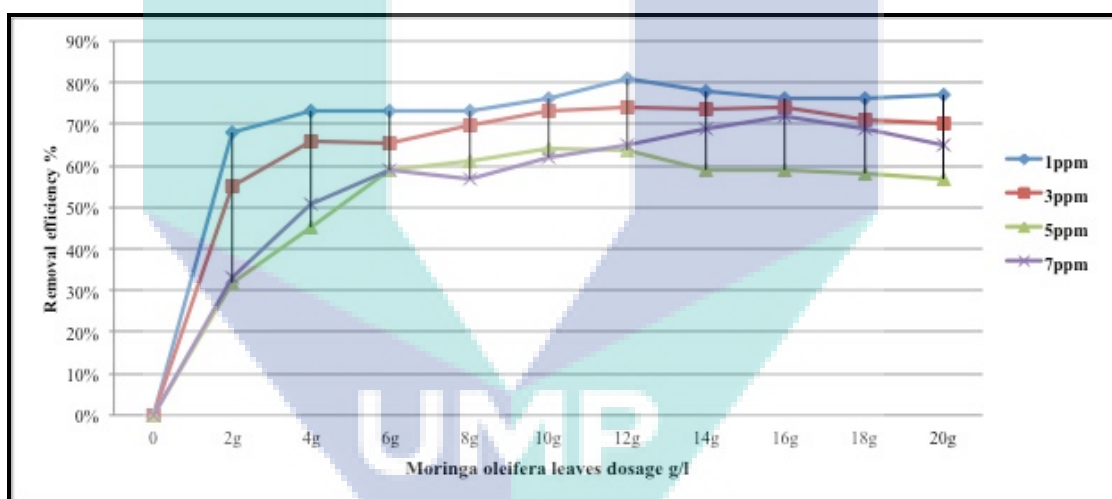
Figure 4.1: The removal efficiency of the different dose on the different Cd (II) concentrations at 200 rpm, 60 min contact time, < 250μ particle size and 200 NTU

The maximum RE for 1 ppm was 81% with optimum dosage of 12 g/l, while it was 74%, 64% and 72% for the Cd (II) concentration of 3 ppm, 5 ppm, and 7 ppm, with optimum dosage of biosorbent 12g/l, 10g/l, and 16g/l, respectively. It was clear that the percentage of the metal biosorption sharply increased when the biosorbent dosage increased. This result might be explained by the fact that the numbers of active sites increases by increasing the biosorbent dosage; this is in agreement with the results reported by different authors. However, further increase in sorbent mass

beyond 12g/l did not result in significant improvement in the percentage removal of metal ion by *Moringa oleifera* leaves. Therefore the best biomass concentration was taken as 12g/l for further batch experiments. Mataka et al. (2010) have studied the potential of *Moringa stenopetala* seeds and *Moringa oleifera* seeds in the removal of Cd (II) ions from water. They reported that the maximum Cd (II) removal by *Moringa stenopetala* seeds was 82.7 and by *Moringa oleifera* seeds was 70.7% when the optimum dose was 2.5g/l. Mataka et al. (2010) suggested that *Moringa stenopetala* and *Moringa oleifera* seeds have potential in Cd (II) reduction. Nand et al. (2012) studied the effect of *Moringa oleifera* seeds on different heavy metal removal and they reported that *Moringa oleifera* seeds were capable to reduce Cd (II); the percentage removal of Cd was 60 %.

Sharma and Bhattacharyya (2005) also investigated *Moringa oleifera* shelled seed powder for Cd (II) removal; they reported that the removal efficiency of Cd (II) was 85.10% when they used 20g/l biomass dosage. Other researchers used different plant resources as a biosorbent. Salem et al. (2012) studied sweet cherry leaves for Cd (II) removal, they reported that the removal efficiency of using 5g/l dosage was 94.44%. Varma et al. (2010) Studied *Psidium guajava* leaves for Cd (II) removal. It was reported that the percentage removal of Cd (II) was 94.89% at the optimum dose of 20g/l. To the best of our knowledge, in our study we report for the first time the removal of Cd (II) by *Moringa oleifera* leaves without any modification on the leaves - *Moringa oleifera* was used as it is in nature and we observed that *Moringa oleifera* leaves with lower dosage (12g/l) could be more effective on the Cd (II) removal up to 81%.
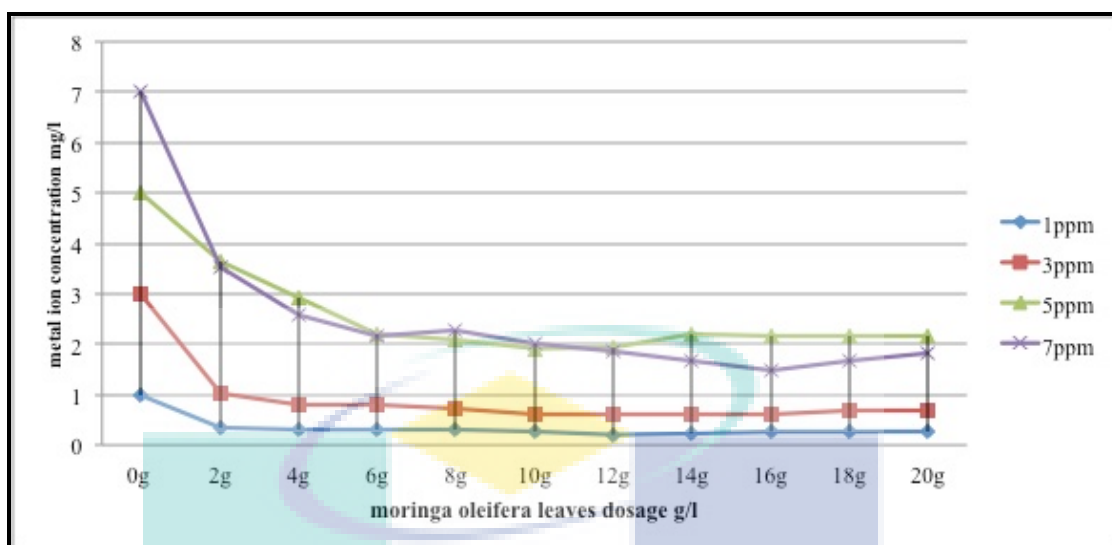
Figure 4.2: The amount of Cd (II) removed by different doses of *Moringa oleifera* at the different initial concentration, 200 rpm, 60 min contact time, < 250µ particle size and 200 NTU

4.2.2 Contact Time Effect

The speed of biosorption is essential for designing batch biosorption experiments. The effect of contact time on the biosorption process was studied within a time range from 2 to 120 min at the optimum doses mentioned above for the different Cd (II) concentrations. It can be seen from Table 4.1, that the RE % was increased by increasing the contact time.

RE% of 79.5% was achieved for Cd (II) removal with concentration of 1 ppm at a contact time of 60 min. It was observed that the removal efficiency at contact time 60 minutes was the highest among the other contact time as the RE % was 79.5%. Accordingly, because 60 minutes gave the maximum RE % then it was decided to start sorption within 60 minutes. It was observed that RE% was increasing by increasing the contact time; in contrast further increase in contact time did not show considerable change on Cd (II) biosorption. It was observed that 60 minutes was enough to reach biosorption equilibrium. As contact time increases metal uptakes increase initially and then become almost stable, denoting attainment of equilibrium. these changes in ion uptake may be due to the fact that, initially, all active sites were vacant and the solute concentration was high. After that period, only a very low increase in the metal uptake was observed because there were few surface active sites

on the cell wall of *Moringa oleifera* leaves. Therefore, the best contact time was selected as 60 min for the rest of the experiments as shown in Table 4.1.

While we found in our study 60 minutes was the optimum contact time of *Moringa oleifera* leaves for Cd (II) biosorption, Mataka et al. (2010) reported that the contact time for Cd (II) removal was 30 minutes when they used *Moringa oleifera* seeds. Sharma and Bhattacharyya (2005) reported that the removal efficiency of Cd (II) was 85.10% when the contact time was 40 minutes. Other researchers studied other types of plants and they reported that the best contact time was up to 120 minutes (Al-Dujaili et al., 2012; Salem et al., 2012). It could be concluded that *Moringa oleifera* leaves could give a good result within an acceptable contact time, which means it could be more economic as less energy is needed.
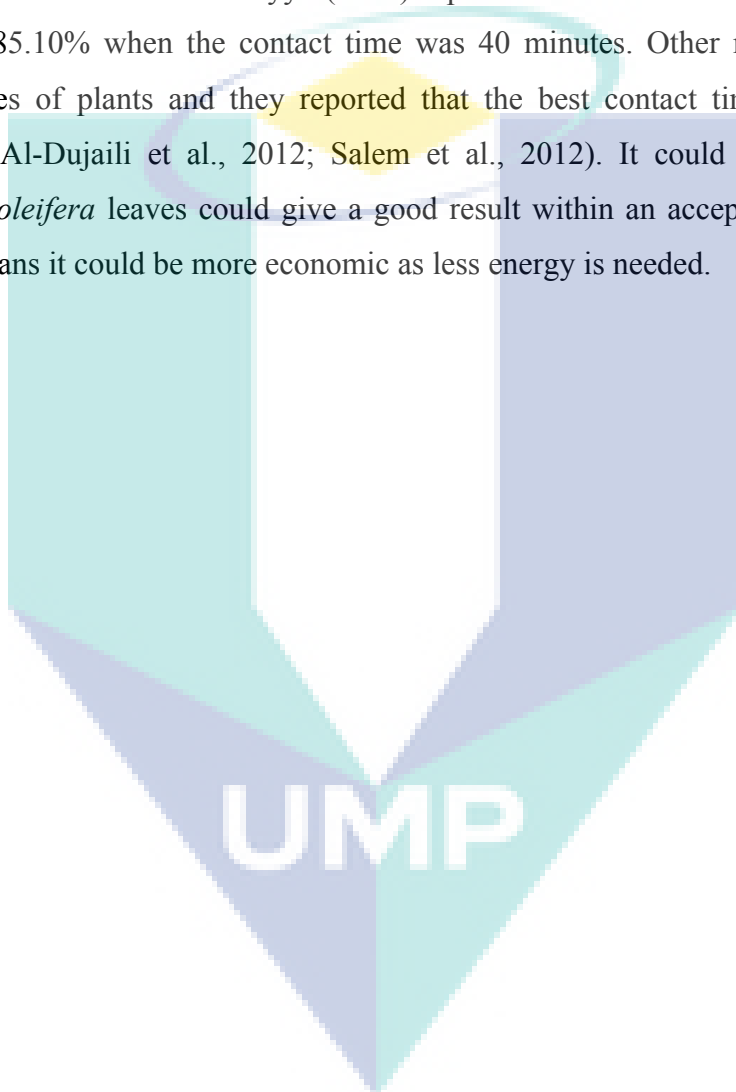
Table 4.1: The removal efficiency percentage at different times with different Cd (II) concentration using 6 g dosage, 200 rpm, 200 NTU and <250 μm particle size

Time	Conc. 1ppm	3ppm	5ppm	7ppm
2	26%	23%	13%	22%
4	18%	27%	17%	24%
6	20%	11%	18%	23%
8	23.3%	11%	14%	18%
10	20%	19%	18%	21%
12	29.4%	25%	55.5%	14%
14	69%	66%	67%	63%
16	71%	65.5%	65.4%	64%
18	72.1%	72%	68%	71%
20	70%	64%	66.4%	65%
40	75%	70.92%	59%	57.67%
60	79.5%	63.44%	61.31%	65.12%
80	73.60%	63.65%	62.26%	61.12%
100	73.40%	59.35%	61.34%	62.20%
120	74.89%	62.26%	61.73%	60.17%

4.2.3 Biosorbent Particle Size Effect

Another important parameter was reported to have an important effect on the uptake of Cd (II). The effect of the biosorbent particle size on the biosorption process was studied using different sizes of *Moringa oleifera* leaves. The particle sizes used in this experiment were (2 mm, 1 mm, 500 μm, 250 μm, and < 250 μm). It was noted that the RE% was very low when 2 mm and 1 mm material were used, and this was probably due to smaller surface area of the biosorbent. On the other hand, analysis showed that particle sizes of 500 μm, 250 μm, and < 250 μm have an effect on Cd (II) removal with *p* values < 0.05. It can be observed that the highest RE% was achieved by applying *Moringa oleifera* leaves with a particle size of < 250 μm to remove 81% of Cd (II) in water due to higher surface area. It was observed that a decrease in particle size exhibited a favourable effect on ion sorption and by using BET test it was confirmed that the more fine particles are better adsorbent due to higher surface area (Appendix 7). Results of this section may be ascribed to the fact that an increase in the surface area of the biomass occurs with as decrease of its particle size and therefore, providing more reactive sites on biomass available for the sorption of metal ion. The results of this parameter were in agreement with what reported by other scientists. Previously Pino et al. (2006) reported that the decrease in the coconut shell particle size show an increase in Cd (II) removal. Kelly-Vargas et al. (2012) reported that smaller particle size had the highest biosorption effect. Thus our results agreed with the reported hypothesis. To sum up, it can be concluded that higher metal adsorption from these particles is attributed to mass transport inside the sorbent particles (Chojnacka, 2010). Table 4.2, shows the RE% using different particle sizes.

Table 4.2: The effect of *Moringa oleifera* particle sizes on the Cd (II) removal efficiency using 12 g/l dosage, 200 rpm, 200 NTU and 60 min contact time

Particle Size	RE%1ppm	RE%3ppm	RE%5ppm	RE%7ppm	Surface area m^2/g
2mm	9.10%	9.11%	5.15%	8%	13.34
1mm	10.20%	5.23%	4.57%	13%	15.45
500	75.00%	72%	71.00%	66%	14.91
250	76.7%	71.2%	76%	76%	17.02
<250	81%	74%	64%	72%	27.69

4.2.4 Water Turbidity Effect on Cd (II) Removal

Previous researches targeted *Moringa oleifera* reduce water turbidity (Abaliwano et al., 2008), while other reported the effect of turbidity levels and *Moringa oleifera* concentration to remove treat water from *Escherichia coli* (Nkurunziza et al., 2009). In the current study the turbidity effect on the adsorption of Cd (II) by *Moringa oleifera* was studied. To the best of our knowledge there were no disclosed reports about the effect of turbidity on the Cd (II) biosorption.

Moringa oleifera leaves as a biosorbent for Cd (II) removal was also investigated on different water turbidity using the optimum doses mentioned above for each concentration of Cd (II). Table 4.3, shows the different turbidity and the optimum RE% for each Cd (II) concentration. The removal efficiency at 50 NTU for the different concentration was 83.4%, 61.6%, 61.5% and 60.6% for 1ppm, 3ppm, 5ppm and 7ppm respectively, whereas the removal efficiency of 200 NTU was 81% for 1ppm, 74% for 3ppm, 64% for 5 ppm and 72% for 7ppm, while the removal efficiency of 400 NTU for 1ppm, 3ppm, 5ppm and 7ppm were 62%, 62.6%, 48.3% and 48.3 in that order. It is assumed that *Moringa oleifera* worked best at the lowest turbidity because the biosorbent interaction with the Cd (II) is higher according to the less competition between the *Moringa oleifera* and the Kaolin particles. It was also observed that at the higher turbidity the biosorption of Cd (II) was lesser and this might be because the competition between the biosobent and the Kaolin is higher, as the Kaolin particles works like a barrier between the *Moringa oleifera* and Cd (II) contact.

Table 4.3: The different turbidity and the optimum RE% for each Cd (II) concentration at 200 rpm, 60 min, 12g/l, <250μ particle size

Turbidity	1ppm	3ppm	5ppm	7ppm
50 NTU	83.4	61.6	61.5	60.6
200 NTU	81	74	64	72
400 NTU	62	62.6	48.3	48.3

4.2.5 Biosorption kinetics

Biosorption rate gives important information for designing batch biosorption systems. The kinetic data was analysed using two kinetic models, pseudo-first-order model and pseudo-second-order model to examine the biosorption kinetics of Cd (II) uptake by *Moringa oleifera* leaves powder with initial concentration of 1ppm.

4.2.5.1 Pseudo First-Order Kinetics

The pseudo-first order equation of Lagergren (Salem et al., 2012) could be expressed as shown in eq. (1):

$$\log (q_{eq} - q) = \log q_{eq} - \frac{k_1}{2.303}t \qquad (1)$$

The pseudo first order rate constant K_1 can be obtained from the slope of graph of log ($q_e - q_t$) against time, t. The pseudo-first order kinetic graph for the adsorption of Cadmium ions onto *Moringa oleifera* leaves powder is shown in Figure 4.3 and the K_1 value, the correlation coefficients, R^2, the calculated and experimental q_e values are given in Table 4.4.
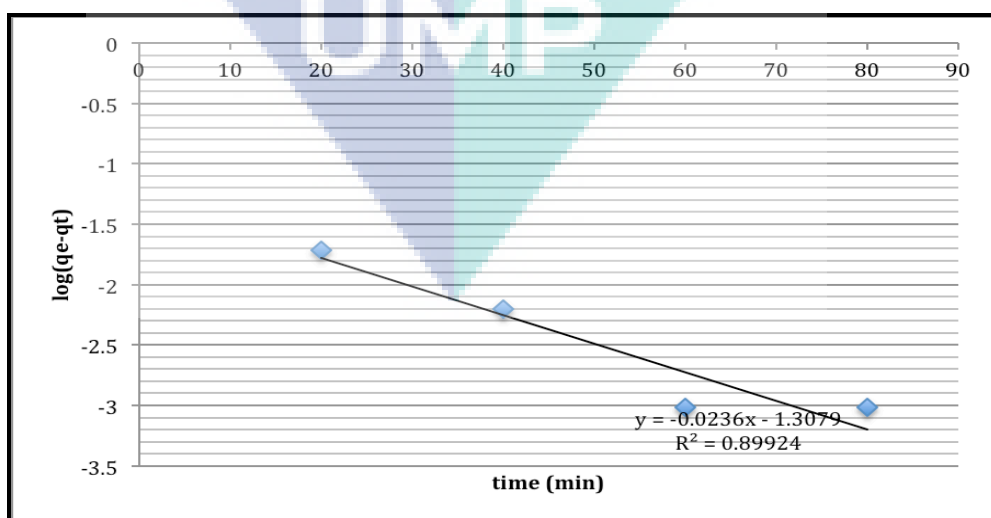

Figure 4.3: The pseudo-first order kinetic plot for the adsorption of cadmium ions onto *Moringa oleifera* leaves

Based on Table 4.4, the correlation coefficient R^2 were found to be low and the values of calculated adsorption capacities (q_e, calculated) were far much lower than experimental ones (q_e, experimental), suggesting that the adsorption process did not fit the pseudo-first order model. Therefore pseudo-second order kinetics was performed to get better fit of the data.

4.2.5.2 Pseudo-Second Order Kinetics

The pseudo second-order model was used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorptions (Barka et al., 2010; Ho and McKay, 1998). The pseudo-second-order model is generally expressed as in eq. (2):

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t \qquad (2)$$

Where t is the contact time (min), q_e (mg/g) and q_t (mg/g) are the amount of the solute adsorbed at equilibrium and at time, t.

If pseudo-second order kinetics is applicable, the plot of t/q_t versus t should give a linear relationship, from which q_e and K_2 can be determined from the slope and intercept of the plot, Figure 4.4. The pseudo-second order rate constant K_2, the calculated q_e value, the experimental q_e value and the correlation coefficient R^2 value are given in Table 4.4. The table shows that the correlation coefficient for the pseudo-second-order kinetic model is nearly equal to 1 and the calculated value of q_e is quite close to the experimental values, q_e, experimental. This suggests that the pseudo second order model fits very well with the kinetic data.
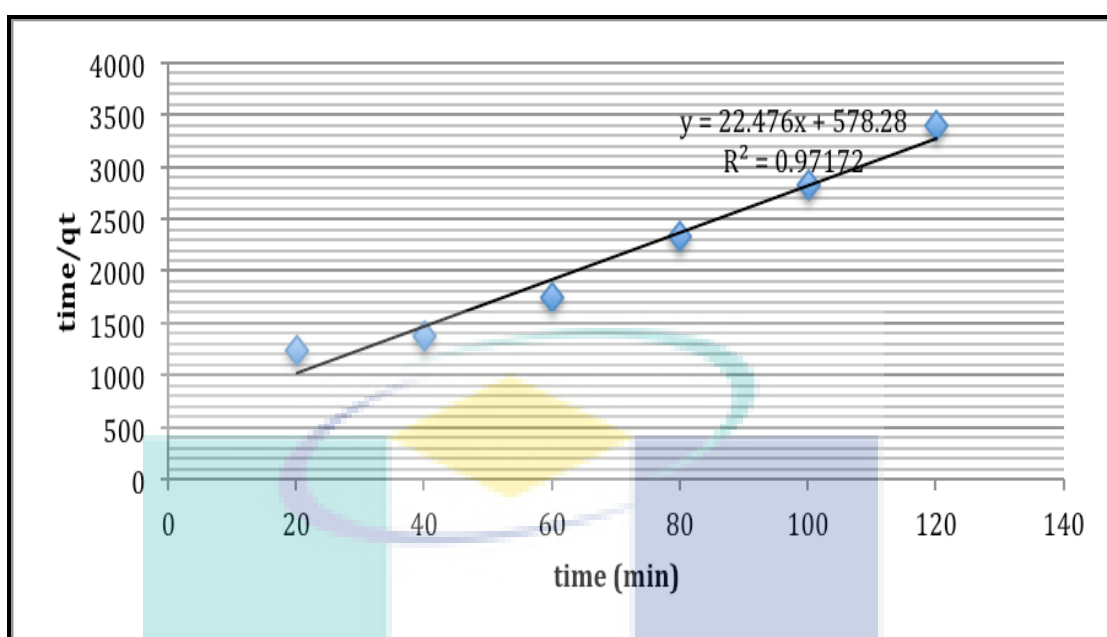
Figure 4.4: The pseudo-second order kinetic plot for the adsorption of Cadmium (II) onto *Moringa oleifera* leaves

Table 4.4: Kinetic constant for Cadmium (II) biosorption onto *Moringa oleifera*

	Pseudo-first-order	Pseudo-second-order
k	0.0529	11.44
q_e (calculated)	0.0493	0.0445
q_e (experimental)	0.0353	0.0353
R^2	0.899	0.971

4.2.6 FTIR Analysis

FTIR was used to investigate the functional groups of *Moringa oleifera* leaves and Cd (II) loaded on *Moringa oleifera* leaves. FTIR study was carried out and the spectra are shown in Figure. 4.4 and 4.5. The *Moringa oleifera* leaves display a number of absorption peaks, reflecting their complex nature. The 2D FTIR spectrum shows the *Moringa oleifera* leaves before and after biosorption of Cd (II) (Figure 4.4).
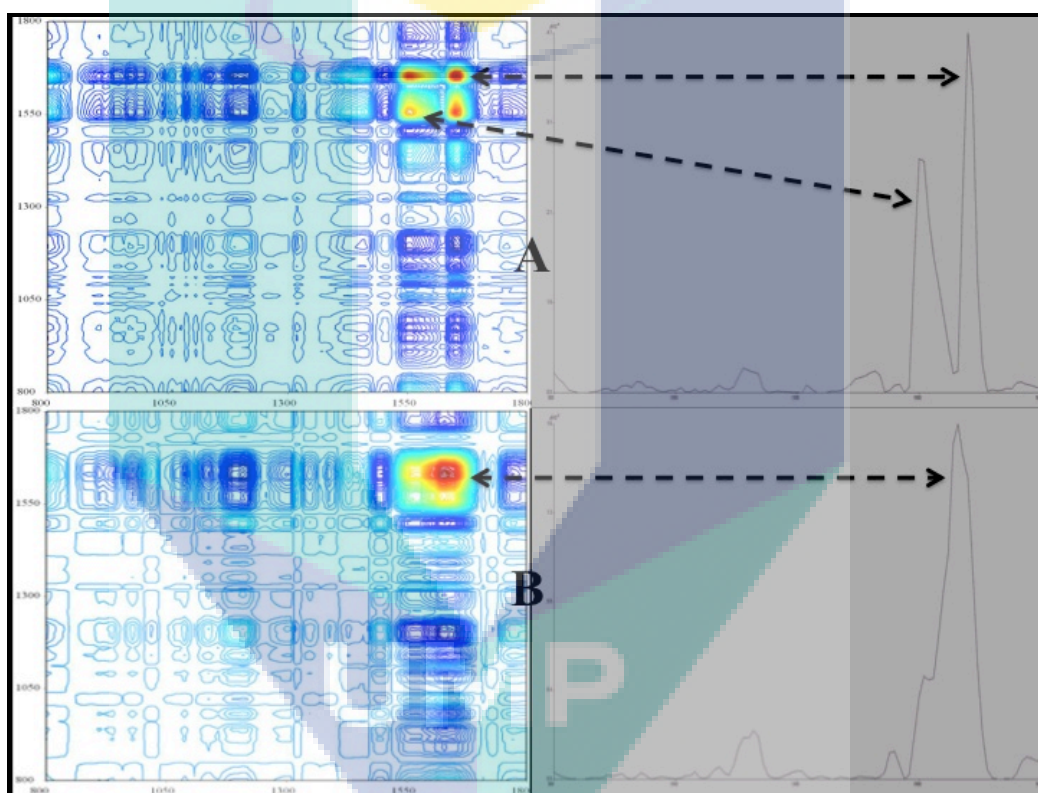
Figure 4.5: 2D FTIR of *Moringa oleifera* before and after biosorption of Cd (II)

Figure 4.5(a) shows that *Moringa oleifera* leaves in nature has two peaks which is considered as the finger print of *Moringa oleifera* leaves, while Figure 4.5 (b) shows those peaks after biosorption of Cd (II) are merged to be one strong peak, which means that Cd (II) is affecting the *Moringa oleifera* leaves structure. Figure 4.6 shows 1D FTIR for a comparison of the transmittance of *Moringa oleifera* leaves

content before and after biosorption of Cd (II), the lower graph is the original peaks of MO leaves while the upper is the MO leaves loaded with Cd (II).
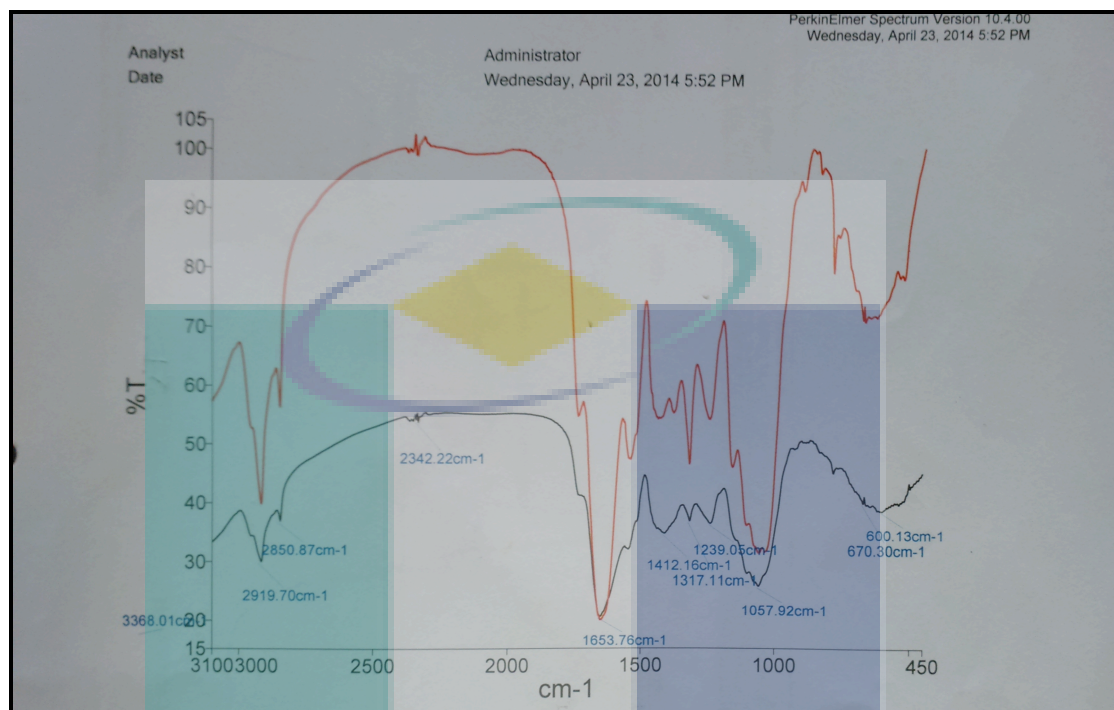
Figure 4.6: 1D FTIR of *Moringa oleifera* contents before and after biosorption of Cd (II)

Figure 4.6 shows the absorption peaks at 2919.70 cm^{-1} and 2850.87 cm^{-1} were elongated and sharpened, this could be because of the C-H stretching off –C=O and/or –CH3 of functional groups. At absorption peak 1653.76 cm^{-1} there was elongation in the peak due to the stretch in the C=O functional group of the carboxylic acids. It was noted also that the peak at 1412.16 cm^{-1} was shifted to 1436.01 cm^{-1} and the peak at 1239.05 cm^{-1} shifted to 1243.19 cm^{-1}, this was due to the stretching of C-O of the functional groups. The peak at 1317.11 cm^{-1} also has an elongation and this might be because of the N=O bending in the functional groups. Another change was noted on the natural composition of *Moringa oleifera* leaves, which the existence is of peaks at wave number of 1378.01 cm^{-1}, 1155.9 cm^{-1}, and 1032 cm^{-1}. The repeated shift due to the C-O stretching suggests that C-O might be a functional group that Cd (II) can bind and react with it.

In addition, it could be said that the shift in the absorption peaks generally observed and might indicate the existence of Cd (II) binding process on the surface of

the *Moringa oleifera* leaves. The obtained results were in agreement with (Al-Dujaili et al., 2012) results with some differences, and this might be because of different source of *Moringa oleifera* leaves.

4.2.7 SEM Analysis

Scanning electron microscopy evaluated the morphological characteristics of *Moringa oleifera* leaves before and after Cd (II) adsorption. The SEM micrographs of *Moringa oleifera* before and after metal uptake at 1k magnifications are shown in Figure 4.7 (a and b) respectively. It was observed that there were significant changes in the surface morphology of *Moringa oleifera* leaves, as well as the formation of discrete aggregates on their surfaces following metal ion adsorption. SEM micrograph shows a quite irregular and porous material. As appears in Figure 4.7 (b) interactions with Cd (II) ion changed the surface morphology of *Moringa oleifera* to rough texture, Cd (II) made a significant effect to the surface of the biosorbent as the surface became irregular following Cd (II) adsorption. Figure 4.7 (b) also shows accumulation of spherical shapes on the surface of the *Moringa oleifera* leaves. Meanwhile there was no accumulation on the *Moringa leaves* in the control sample, which contains only the Kaolin synthetic water. Thus it was assumed that these spherical shapes are the adsorbed Cd (II) ion.
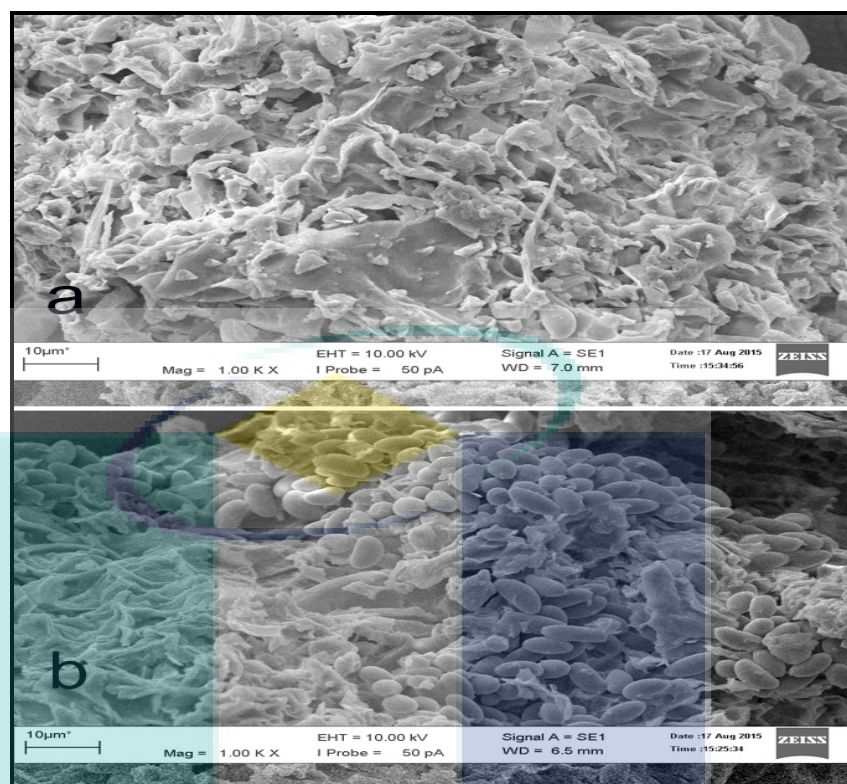
Figure 4.7: Scanning electron micrographs of *Moringa oleifera* leaves before and after Cd (II) adsorption, where (a) represents the morphology before and (b) represents the morphology after Cd (II) adsorption.

4.2.8 Biosorption of Pb (II), Cu (II) and Fe (III) from water by *Moringa oleifera* leaves

Biosorption of Pb (II), Cu (II) and Fe (III) onto *Moringa oleifera* leaves was studied using the optimum condition which have been achieved in the previous experiments as dosage was 12 g/l, contact time 60 min and metal ions initial concentration1 ppm. Figure 4.8 shows the removal efficiency for heavy metal biosorption by *Moringa oleifera* leaves at 1ppm initial concentration.
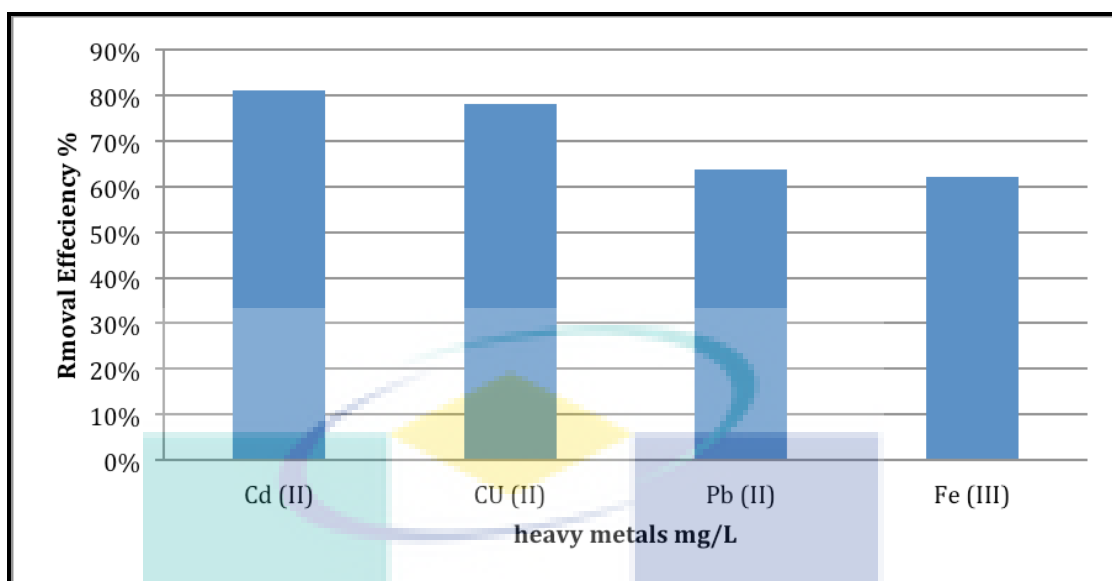
Figure 4.8: The removal efficiency of *Moringa oleifera* on different heavy metals at 60 min, 200 rpm, 200 NTU, 12g/l dosage, <250μm particle size and 1ppm initial concentration.

The results of our study on Pb (II) showed that *Moringa oleifera* leaves could reduce the Pb (II) ion, and the RE% was 63.6%. Literature showed some studies on the effect of *Moringa oleifera* on the removal of Pb (II). Nand et al. (2012) reported that RE% of *Moringa oleifera* seeds on Pb (II) were 80%. On the other hand there was another study by Meneghel et al. (2013) which concluded that *Moringa oleifera* seeds could adsorb Pb (II) from water systems and the maximum adsorption capacity was 12.24 mg/g. There was another study by Reddy et al. (2010) but this study investigated the effect of the chemically modified *Moringa oleifera* bark and leaves on the removal efficiency of Pb (II) in aqueous systems and they found that the modified *Moringa oleifera* could remove the Pb (II) with a biosorption capacity of 209.54 mg/g.

To conclude, it can be said that the optimum conditions of this study could also be used to reduce Pb (II) from the water systems. However it is recommended to make more investigations and optimizations to confirm that the optimum conditions that gave the maximum removal of Cd (II) could give the maximum removal of Pb (II). In a recent report Ali et al. (2014) also investigated the impact of *Moringa oleifera* Cake Residue on waste water treatment and it was concluded that the reduction of Pb (II) also achieved 82.17%.

Experiments on Cu (II) found that *Moringa oleifera* leaves could remove the Cu (II) from the water systems with RE 78%. It was reported in literature that *Moringa oleifera* seeds was also used to remove the Cu (II) from water systems and to improve the quality of drinking water. The results showed that *Moringa oleifera* seeds were capable of absorbing the Cu (II) with a percentage removal of 90 % (Nand et al., 2012). In addition there was another study by (Ali et al., 2014) they reported that the *Moringa oleifera* Cake Residue could remove the Cu (II) from the waste water with RE 98%. Farrokhzadeh et al. (2013) also reported that *Moringa oleifera* seeds could remove the Cu (II) with 24.98 mg/l.

As a conclusion, it can be reported that the optimum conditions of this study suggest *Moringa oleifera* to remove Cu (II) from the water systems. Nevertheless it is recommended to conduct more examination and research to confirm that the optimum conditions that gave the maximum removal of Cd (II) could give the maximum removal of Cu (II). To the best of our knowledge it can also be said that *Moringa oleifera* leaves was not reported to remove Cu (II) from water systems, and this study could be the first report on the use of *Moringa oleifera* leaves as a Cu (II) biosorbent with RE of 78 %.

The effect of *Moringa oleifera* leaves on Fe (III) removal was also studied, it was observed that *Moringa oleifera* could reduce the Fe (III) from water with RE 62%. *Moringa oleifera* seeds were used by Mancy et al. (2013) to remove Fe (III); they reported that it could remove the Fe (III) up to 72%.

In another study the *Moringa oleifera* cake residue was reported to remove the Fe (III) totally from the wastewater (Ali et al., 2014).

According to the findings, *Moringa oleifera* leaves can be regarded as a relative efficient absorbent for Fe (III) removal from solution with RE of 62 %.

4.3 EFFECT OF MORINGA OLEIFERA ON HEAVY METAL REMOVAL FROM DRAINAGE WATER

In this experiment the effect of *Moringa oleifera* on the different heavy metal in the drainage water were studied. Water was collected from the drainage of the environmental laboratory in University Malaysia Pahang. This experiment conducted to investigate that *Moringa oleifera* could remove other heavy metals with the same

condition of Cd (II) removal. The water does not contain heavy metals, though amounts of Cd (II), Cu (II), Fe (III) and Pb (II) were added to the water properly.

The results of our study showed that the effect of *Moringa oleifera* on heavy metals removal was in accordance to the result of the preliminary experiments in the optimization process. As is shown in Figure 4.9 RE% using *Moringa oleifera* leaves to remove Cd (II) was the highest among the other heavy metals as it was 83.6%. Results also showed that *Moringa oleifera* leaves could absorb Pb (II), Cu (II) and Fe (III) with a removal efficiency of 65%, 73% and 52% respectively.
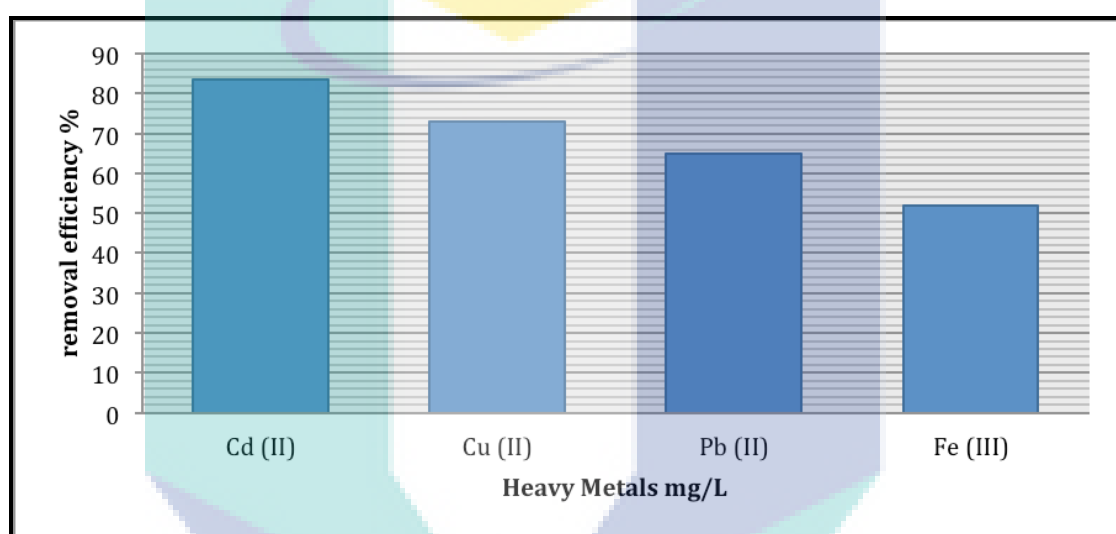
Figure 4.9: The removal efficiency of *Moringa oleifera* on heavy metals in the drainage water at 60min, 12g/l dosage, <250μm particle size, 1ppm initial concentration, 200 rpm and 200 NTU

4.4 CONCLUSION

The results of this study proved that *Moringa oleifera* leaves could remove Cd (II). Furthermore, it was concluded that the optimum conditions that achieved the maximum RE percentage on Cd (II) could be applied to remove other heavy metals and ions such as Pb (II), Cu (II), and Fe (III). Although the best conditions of Cd (II) removal achieved good results on other ions, however, it is recommended to make further optimization for each ion to confirm that the optimum conditions of Cd (II) removal could be the optimum for all ions to give the maximum removal efficiency.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The results of this study revealed that 12g/l achieved the optimum Cd (II) removal with RE 81%. It was also observed that the optimum contact time was at 60 min with RE 79.5%. Particle size experiments showed that the particle size <250 μm was the best in the adsorption process with RE 81%. The surface area analyser result (BET test) confirmed that the more fine particles are better adsorbent due to higher surface area. It was also observed that *Moringa oleifera* leaves worked best with Cd (II) initial concentration of 1 ppm, as the RE was 81%. The experiment of the turbidity investigations revealed that the best turbidity of synthetic water was 50 NTU as RE was 83.4% compared to 200, and 400 NTU with RE% of 81% and 62%, respectively.

FTIR was used to investigate the functional groups of *Moringa oleifera* leaves and Cd (II) effect on *Moringa oleifera* leaves chemical structure. The FTIR analysis of *Moringa oleifera* leaves showed a number of absorption peaks, reflecting its complex phytochemical nature. However, from the FTIR observations it can be said that the repeated shifts in the spectra due to the C-O stretching suggest that C-O could represent the target functional group of Cd (II) and Cd (II) adsorbed on the *Moringa oleifera* leaves surface. In addition, it can be assumed that the shift in the peaks generally observed and might indicate the existence of Cd (II) binding process on the surface of the *Moringa oleifera* leaves. Moreover, the effect of Cd (II) was investigated on the phytochemical fingerprint of *Moringa oleifera* leaves by using the 2D FTIR technique. The results of 2D FTIR revealed that *Moringa oleifera* leaves fingerprint zone in nature has two peaks, and the original peaks after biosorption

process of Cd (II) were merged to be one strong peak that also could suggest effect of Cd (II) on *Moringa oleifera* leaves structure and its biochemical structure.

The investigation of the optimum conditions on Cd (II) and other heavy metals in one batch under the same conditions showed that the removal efficiency of *Moringa oleifera* leaves were 81 %, 78 %, 63.6 % and 62 % for Cd (II), Cu (II), Pb (II) and Fe (III), respectively.

The experiments also showed that the achieved optimum conditions gave the best results in the Cd (II) removal experiments. Though the results of *Moringa oleifera* leaves investigations on other heavy metals showed that *Moringa oleifera* leaves as a biosorbent could remove the other metals with different removal efficiency percentages that could be recommend *Moringa oleifera* leaves as a good biosorbent for all the used heavy metal in general and Cd (II) in particular.

To sum up, it can be concluded that the objectives of this study were successfully achieved, and the study answered the main research questions. It also can be concluded that *Moringa oleifera* leaves could be an effective natural biosorbent for Cd (II) and the other targeted heavy metals from water systems. It also could be said that the chemical structure of *Moringa oleifera* react and bind with Cd (II) during the biosorption process that suggests *Moringa oleifera* could have a unique structure, which might help in Cd (II) removal from water systems. It could be concluded that Particle size plays a big role in the biosorption process according to the BET test results.

5.2 RECOMMENDATION AND FUTURE WORK

The major challenge realized by biosorption scientists is to select the most hopeful sorts of biomass from a very huge collection of freely available and cheap biomaterials. Additional exploration for better and more selective biosorbents is essential. Factors other than the accessibility and costs of biomass, particularly the biosorptive capability, need to be considered when choosing the biomass. More research is necessary to eliminate the whole price for pre-treatments or develop new approaches that are both cheap and effective. It is also essential to optimize biosorption parameters and methods.

Future directions of this project are proposed in line with current development water treatment methods. These directions include looking into finding alternative inexpensive and healthy methods for water treatments. It is recommended to make further studies to optimize the biosorption conditions for each single metal to prove that all the metals could be removed at the maximum removal efficiency.

Most of the research achieved in the last decade has focused on batch experimentation while examining diverse bioadsorbents, Therefore it is recommended to solve this problem by studying the possibility of using columns enclosing *Moringa oleifera* leaves for the treatment of drinking water and wastewaters.

Since most of the existing research is focused on single metal ion treatment, it is recommended to study the heterogeneous nature of wastewaters. Additionally, more research to understand the chemical properties of the *Moringa oleifera* leaves could help in finding successful solutions in the field of wastewater recovery.

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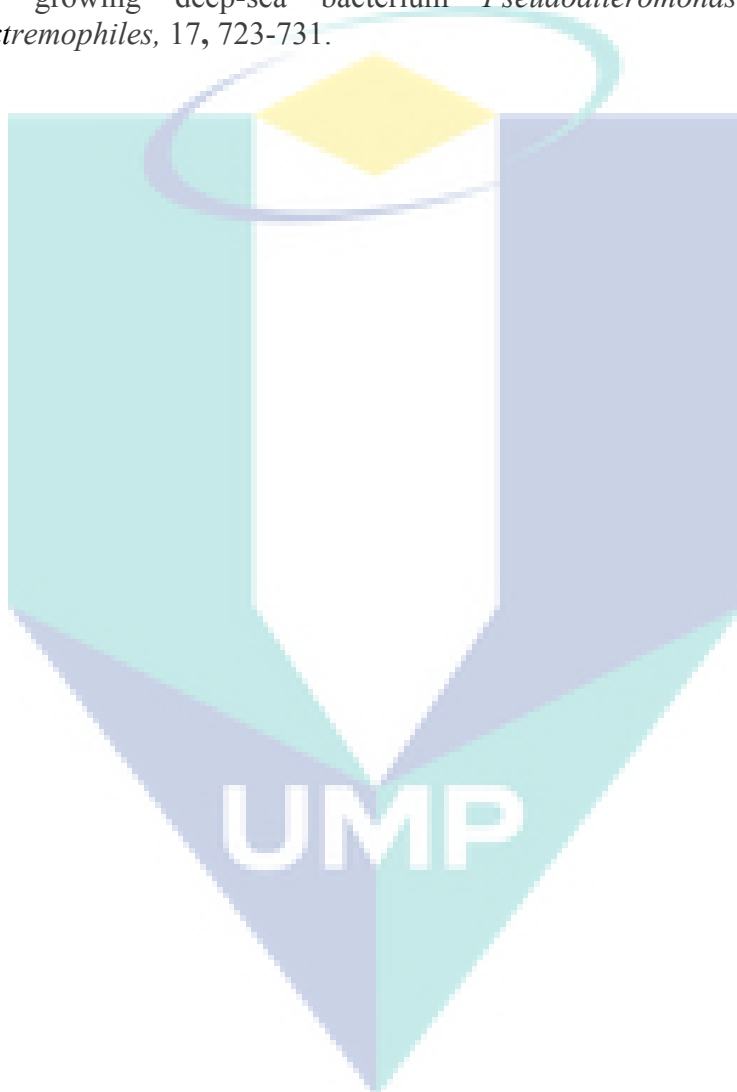
APPENDICES

APPENDIX 1

LIST OF PUBLICATIONS AND EXHIBITIONS

Publications

1.   **Alfarra, R. S**., Ali, N. E., & Yusoff, M. M. (2014). **Removal of heavy metals by natural adsorbent**: review. *International Journal of Biosciences (IJB)*, *4*(7), 130-139.

2.   Ali, E. N., **Alfarra, S. R**., Yusoff, M. M., & Rahman, M. L.2015. **Environmentally Friendly Biosorbent from *Moringa oleifera* Leaves for Water Treatment**. *International Journal of Environmental Science and Development,* 6**,** 165-169

Awards

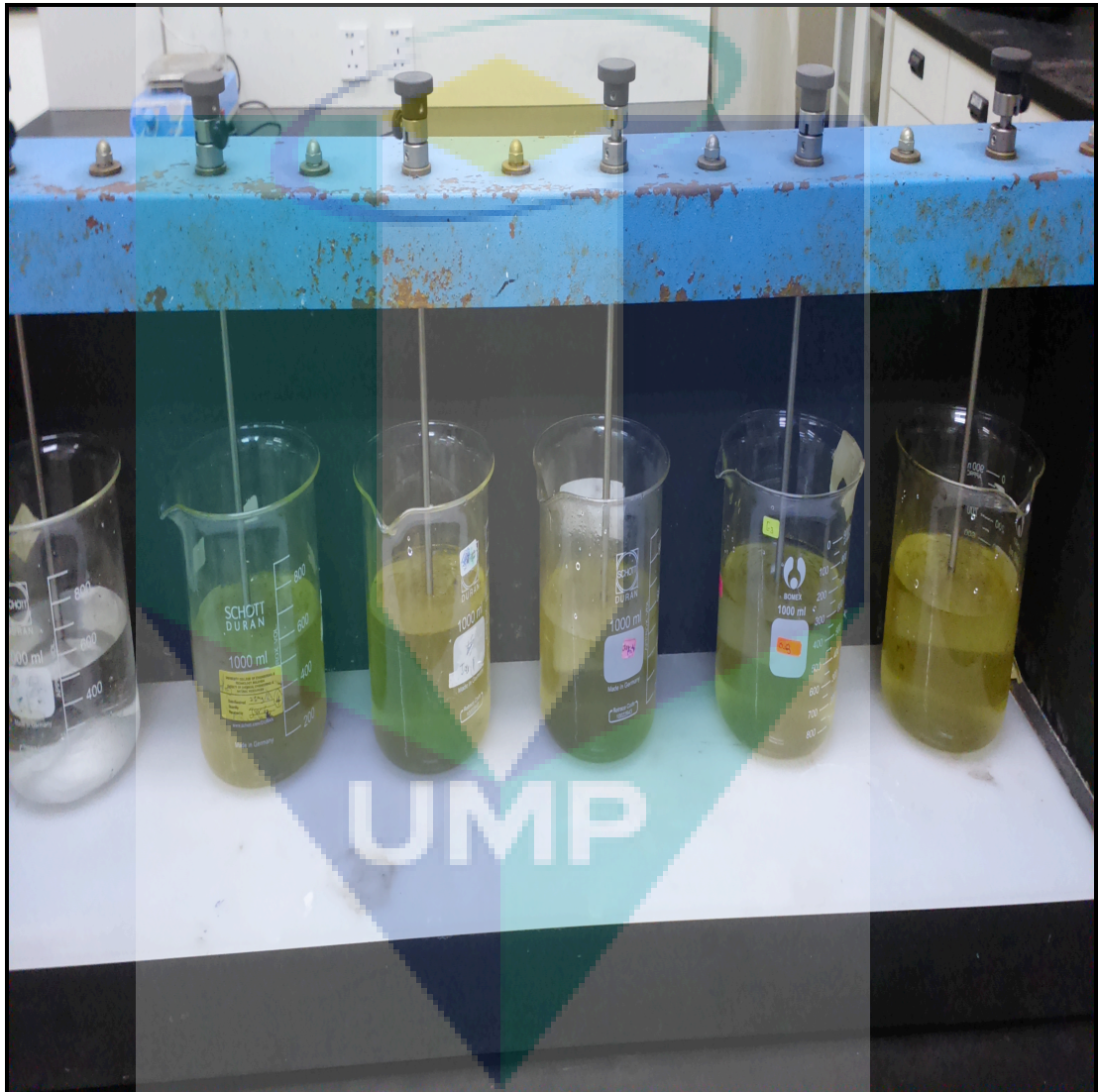Bronze medal, **Biosorption of heavy metals from water using *Moringa oleifera* leaves**, CITREX 2015
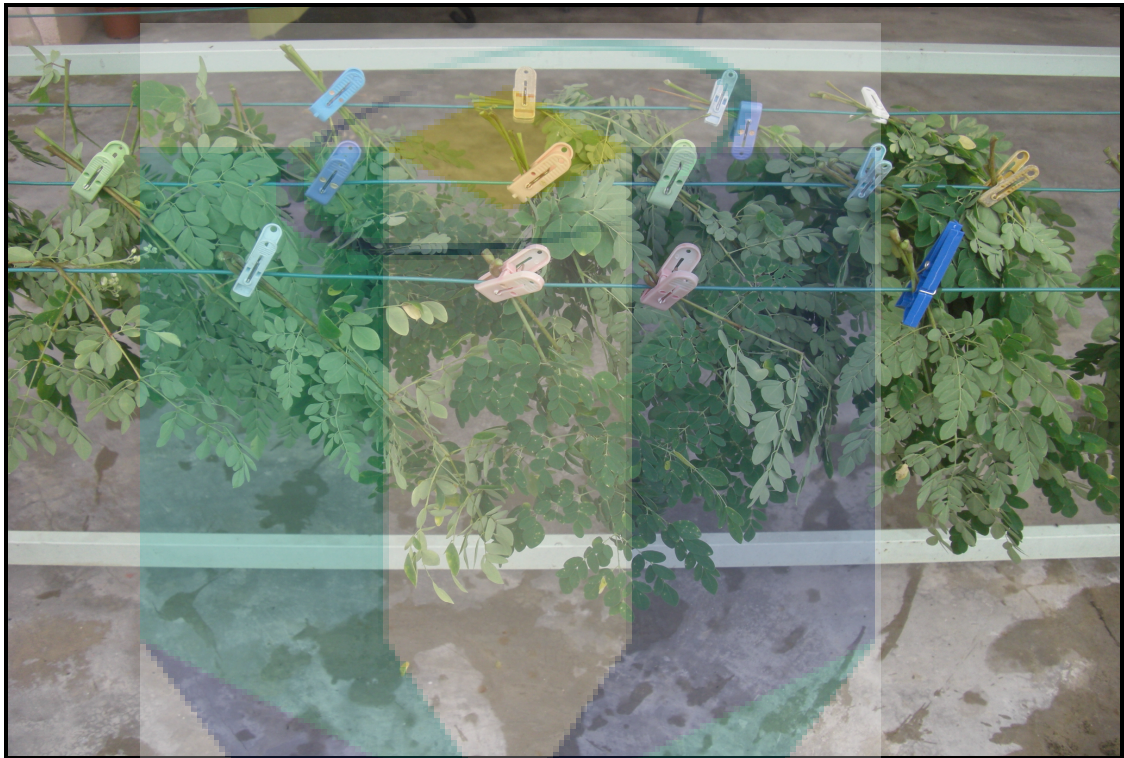
APPENDIX 2

ATOMIC ABSORPTION SPECTROSCOPIC

APPENDIX 3

FLOCUULATOR (JAR TEST) FOR COAGULATION FLOCCULATION PROCESS

APPENDIX 4

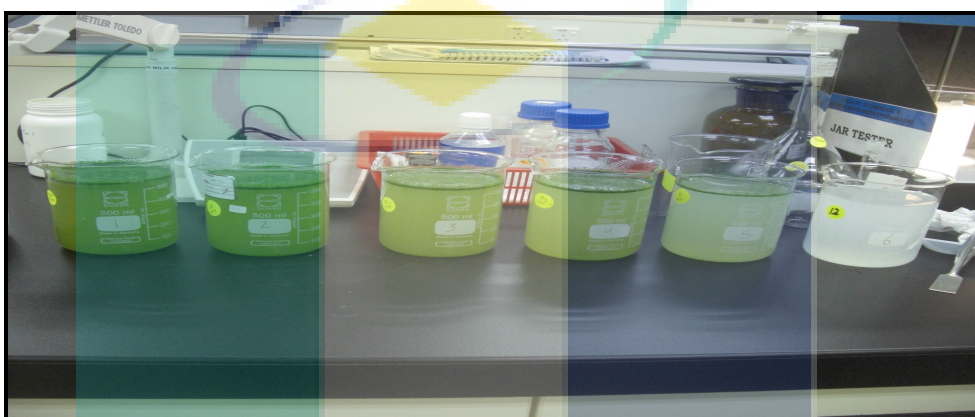## *MORINGA OLEIFERA* TREE LEAVES

APPENDIX 5

DRYING *MORINGA OLEIFERA* LEAVES UNDER THE SUN

APPENDIX 6

PREPARATION OF THE SAMPLE FOR THE EXPERIMENTS BEFORE AND AFTER FILTRATION

BEFORE FILTRATION

AFTER FILTRATION

APPENDIX 7

Surface Area Analyser results

APPENDIX 8

AAS data