

REMOVAL OF CADMIUM FROM AQUEOUS SOLUTION BY DRIED WATER
HYACINTH, (*EICHHORNIA CRASSIPES*)

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DECLARATION

I declare that this thesis entitled “Removal of Cadmium from Aqueous Solution by Dried Water Hyacinth, (*Eichhornia Crassipies*)” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Date : 14th May 2008

DEDICATION

To my love, Khairul Azmil Adzmi and my dearest family
May Allah bless us all....

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ABSTRACT

Water hyacinth (*E. crassipes*) approaches being a scourge in many parts of the world, choking waterways and hindering transport upon them. At the same time it is known to readily abstract heavy metal ions from water and, thus, aids in the removal of heavy metals found in such waters. This study considers the possibility of using dried parts of the plant as an inexpensive adsorbent for the removal of heavy metals from cadmium solution. Water hyacinth is dried and used as biosorbent as removal of cadmium in aqueous solution. Parameters that are used for these studies are dosage of biosorbent, contact time, pH and temperature. The analysis was done by using Atomic Absorption Spectroscopy where initial concentration was 20 mg/L; the amount of biosorbent was from 0.4 to 4 g/L, pH range between 2 to 10, contact time between 10 until 50 min, and temperature range between 25 until 60 degree celcius. The best conditions were found to be biosorbent at dose of 2 g/L, pH of 7, and contact time of 40 min and 35°C for temperature. The results obtained show that the dried Water Hyacinth performed well for the removal of cadmium as heavy metals. As a low cost adsorbent, Water Hyacinth can preferable for removal of heavy metals from wastewaters.

ABSTRAK

Keladi bunting (*E. crassipes*) merupakan tumbuhan yang sedang menular ke seluruh dunia, menyumbat saluran air dan juga menghalang pengangkutan di air terutamanya. Pada masa yang sama, keupayaan keladi bunting sebagai alat untuk menyerap cas logam berat dari air, dan seterusnya membantu menyerap segala logam berat yang ditemui di dalam air. Tesis ini juga mempertimbangkan keupayaan keladi bunting dalam bentuk yang kering atau serbuk sebagai alat penyerap logam berat yang murah khasnya untuk menyerap ion logam kadmium dalam air penyahkumbahan. Keladi bunting dikeringkan dan digunakan sebagai penyerap logam kadmium dalam larutan cecair. Parameter yang dikaji di dalam tesis ini ialah dos penyerapan keladi bunting, masa, pH dan suhu. Di mana, nilai optimum yang diperoleh daripada hasil kajian dianalisa menggunakan “Atomic Absorption Spectroscopy” dengan nilai awal kepekatan 20 mg/L; dengan dos 0.4 kepada 4 g/L, pH diantara 2 hingga 10, masa diantara 10 hingga 50 minit dan juga suhu diantara 25 hingga 60 darjah celcius. Hasil kajian menunjukkan keputusan nilai yang optimum iaitu pada dos 2 g/L, pH 7, masa pada 40 minit dan suhu optimum pada 35 darjah celcius. Ekperimen yang telah dijalankan telah menunjukkan keputusan yang baik iaitu keladi bunting sebagai alat penyerapan logam berat yang berkesan.

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LIST OF SYMBOLS

g	-	Gram
mol	-	Molar
cm	-	Centimeter
°C	-	Degree Celcius
nm	-	Nanometer
kJ	-	Kilo Joule
V	-	Voltan
in	-	Inch
T	-	Tonne
μ	-	micro
λ	-	Wavelength
ξ	-	Energy State
λ _E	-	Characteristic Wavelength
A	-	Absorbance
e	-	Molar Absorptivity
b	-	Path Length
μL	-	Micro Liter
ppm	-	part per million
<i>m</i>	-	Mass
<i>V</i>	-	Volume
M	-	Molarity
i	-	Initial
f	-	Final

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, Water Hyacinth or in scientific name *Eichhornia crassipes* have been disturbing mankind ecosystem especially making pollute to the lake, river and etc. Water hyacinth is believed has a potential to remove heavy metals from water such as Cadmium (Cd). Zhu *et al.* (1999) have studied the ability of water hyacinth to take up and translocate six trace elements namely As(V), Cd(II), Cr(VI), Cu(II), Ni(II) and Se(VI) under controlled conditions.

Nevertheless, the mobilization of heavy metals in the environment due to industrial activities is of serious concern due to the toxicity of these metals in human and other forms of life (Vieira and Volesky, 2000; Esterves *et al.*, 2000). Removal of toxic heavy metals from industrial wastewater is essential from the standpoint of environmental pollution control (Yuan *et al.*, 2001). Many industries, especially electroplating, battery and plastic manufacturing release heavy metals such as cadmium and zinc in wastewater (Olguin and Hurnandoz, 1998; Prasad and Pandey, 2000).

However, heavy metals such as Cd^{2+} , Zn^{2+} , Fe^{2+} are essential micronutriens for plants but when it present in excess, they can become extremely toxic. Cd is one of the most toxic heavy metals and is considered non-essential for living organisms. Cd has been recognized for its negative effect on the environment where it accumulates

throughout the food chain posing a serious threat to human health. Science Asia, 2004, also quote that Cd pollution has induced extremely severe effects on plants.

Recently, researcher has shown an interest in treating wastewater with benefit of cost effective and environmentally friendly technologies for the remediation of soil and wastewater polluted with heavy metals elements (ScienceAsia 30, 2004). Plants which have the ability to absorb and accumulate nonessential metals such as Cd and Pb, and this ability could contribute to environment by removing pollutant metals (Holan and Volesky , 1994).

Water hyacinth is a free floating aquatic plant well known for its production abilities and removal of pollutants from water (A. Malik *et al.*, 2007). It has been discovered that water hyacinth's quest for nutrients can be turned in a more useful direction. The plant has been shown to accumulate trace elements such as Ag, Pb, Cd and Zn. The focus on water hyacinth as a key step in wastewater recycling is due to the fact that it forms the central unit of a recycling engine driven by photosynthesis and therefore the process is sustainable, energy efficient and cost efficient under a wide variety of rural and urban conditions (ScienceAsia 30, 2004).

1.2 Objective of Study

The objectives of this study are to study the potential of water hyacinth as a wastewater treatment method to remove cadmium from aqueous solution.

1.3 Scope of Study

The scope of this study is to study the effects of biosorbent dosage, contact time, pH and temperature in the removal of cadmium from aqueous solution.

1.4 Problem Statement

Water hyacinth is listed as one of the most productive and active plants on earth and it are considered as one of the world's worst aquatic plants. It cans double its size in 5 days and a mat of medium sized plants may contain 2 million plants per hectare that weigh 270 to 400T (A. Malik, 2007). However, it is also known to be an accumulator of heavy metal ions and has been widely studied as such (Wolverton, 19751; Blake *et. al.*, 1987; Pinto *et. al.*, 1987). However, two main disadvantages emerge from this practice. First, ponds have to be constructed if they are not available in place and, second, heavy metals produce phytotoxic effects on plants resulting in inhibition of chlorophyll synthesis and necrosis (Blake *et. al.*, 1987; Satyakala *et al.*, 1992; Delgado *et. al.*, 1993). Additionally, the metal sorption capacity of the dried biomass of aquatic plants has been recently investigated (Scheinder *et. al.*, 1994). Compared to living systems, dried biomass presents advantages for conservation, transport and handling, being able to be applied in waste water treatment plants as a simple sorbent material. To date, however, the individual parts of *E. crassipes* (stems, roots, leaves of the plants) have not been studied. Also, there has been little direct comparison of the relative heavy metal biosorption by *E. crassipes* and its parts to biosorption by various other biosorbents.

CHAPTER 2

LITERATURE REVIEW

2.1 Background Study of Cadmium



Figure 2.1: Cadmium metal solid

Cadmium is a lustrous, silver-white (as shown in Figure 2.1), ductile, very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but insoluble in alkalis. It has similar in many physical to zinc but it forms more complex compounds. More details on properties of cadmium are shown in Table 2.1.

Cd has been recognized for its negative effect on the environment where it accumulates throughout the food chain posing a serious threat to human health (Holan and Volesky, 1994). Chronic dust or fume exposure can give permanently damage to the

lungs, producing shortness of breath and emphysema. The risks of absorption via dermal contact are negligible.

In every year, a very large amount of cadmium is released into the environment, about 25,000 tons. Cadmium is one of the most toxic metals affecting the environment. Mining and metallurgy of cadmium, cadmium electroplating, battery and accumulator manufacturing, pigments and ceramic industries waste waters contain undesired amounts of Cd^{2+} ions (G.H. Pino *et al.*, 2006)

While, in aquatic ecosystems cadmium can bio accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms. Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms. Mean time, animals that eating or drinking cadmium also sometimes gets high blood-pressures, liver disease and nerve or brain damage. This scenario shows that the damage affects of cadmium not only to environment but to animals and aquatic.

Meantime, when humans expose to cadmium exposure, kidneys and lungs are the most effected organs. As mentioned above, cadmium poisoning may be acute by ingestion or inhalation or the poisoning may be chronic at lower levels, which can cause kidney damage by the mechanism described above. In chronic exposure, cadmium accumulates in the body, particularly the kidneys and liver.

Other health effects that can be caused by cadmium are:

- 1) Diarrhoea, stomach pains and severe vomiting
- 2) Bone fracture
- 3) Reproductive failure and possibly even infertility
- 4) Damage to the central nervous system
- 5) Damage to the immune system
- 6) Psychological disorders

- 7) Possibly DNA damage or cancer development
 8) muscle cramps

Table 2.1: Chemical properties of cadmium

Items	Properties
Atomic number	48
Atomic mass	112.4 g.mol ⁻¹
Electronegativity according to Pauling	1.7
Density	8.7 g.cm ⁻³ at 20°C
Melting point	321 °C
Boiling point	767 °C
Vanderwaals radius	0.154 nm
Ionic radius	0.097 nm (+2)
Isotopes	15
Electronic shell	[Kr] 4d ¹⁰ 5s ²
Energy of first ionisation	866 kJ.mol ⁻¹
Energy of second ionisation	1622 kJ.mol ⁻¹
Standard potential	-0.402 V
Discovered	Fredrich Stromeyer in 1817

2.1.1 Cadmium in Water

WHO, 1992 said that the average cadmium content in the world's oceans has variously been reported as low as <5 ng/L and 5-20 ng/L by OECD (1994), Jensen and Bro-Rasmussen (1992), to as high as 110 ng/L (CRC 1996), 1 00 ng/L (Cook and Morrow 1995) and 10 to 100 ng/L (Elinder 1985). These high levels have been noted found by Elinder (1985), around certain coastal areas and meanwhile WHO (1992), and OECD (1994), found that the variations of cadmium concentration with the ocean depth, presumably due to patterns of nutrient concentrations, have also been measured. Even greater variations are quoted for the cadmium contents of rainwater, fresh waters, and surface waters in urban and industrialised areas. Levels from 10 ng/L to 4000 ng/L have been quoted in the literature depending on specific location and whether or not cadmium totals or dissolved cadmium is measured.

As in natural way, cadmium usually is a minor constituent of surface and groundwater. It believe OECD (1994), that cadmium may exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids. Cadmium can also enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition direct discharge from industrial operations, leakage from landfills and contaminated sites, and the dispersive use of sludge and fertilizers in agriculture. Since cadmium is a major compound that usually been used in industry, and so it is highly contributed to problematic environment supported by WHO (1992), also state that much of the cadmium entering fresh waters from industrial sources may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment. Cook and Morrow (1995) also have shown of some data that recent sediments in lakes and streams range from 0.2 to 0.9 ppm in contrast to the levels of generally less than 0. 1 ppm cited above for fresh waters.

The rivers which believe have excess cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, dumping of dredged sediments or

flooding. It has also been demonstrated that rivers can transport cadmium for considerable distances, up to 50 km, from the source (WHO 1992). Nonetheless, studies of cadmium contamination in major river systems over the past twenty to thirty years have conclusively demonstrated that cadmium levels in these rivers have decreased significantly since the 1960s and 1970s (Cook and Morrow 1995, Elgersma *et al.*, 1992, Mukunoki and Fujimoto 1996, Van Assche and Ciarletta 1992). For example, studies on the Rhine River Basin from 1973 through 1987 indicated that the point source cadmium discharges to the Rhine River decreased from 130 to 11 mt per year over that 14-year time span, a reduction of over 90% (Elgersma *et al.*, 1992). Similarly, data on total cadmium and dissolved cadmium at the Dutch/German border over the period from 1971 to 1987 have shown comparable reductions (Van Urk and Marquenie 1989) (Levels of cadmium in environment, <http://www.cadmium.org/>). The distribution of cadmium to waters play big role whether cadmium emitted to waters is able or unable to enter the food chain and affect human health.

2.2 Background Study of Water Hyacinth (*Eichhornia crassipe*)



Figure 2.2: Water Hyacinth in purplish black color.

Water hyacinth with broad, thick and glossy ovate leaves, water hyacinths can be raise till 1 metre in height. The leaves also can rise to 10-20 cm across, supported above

the water surface by long, spongy and bulbous stalks. While the feathery, freely hanging roots are purplish black color. An erect stalk supports a single spike of 8-15 conspicuously attractive flowers, mostly lavender to pinkish in colour with six petals. Water hyacinth grows over a wide variety of wetland types and prefers nutrient-enriched waters. However, it can tolerate considerable variation in nutrients, temperature and pH levels. The optimum pH for growth of water hyacinth is 6–8. It can grow in a wide range of temperature from 1 to 40°C (optimum growth at 25–27.5°C) but it is thought to be cold-sensitive (Wilson *et al.*, 2005). Fruit a 3-celled capsule with many seeds. When not in bloom, water hyacinth may be mistaken for frog's-bit (*Limnobium spongia*). Water Hyacinths are the only large aquatic herb that can float on the water unattached to the bottom. They float on bloated air-filled hollow leaf stalks that give them their Malay name that means "pregnant tuber". Their roots trail underwater in a dense mat.

The Water Hyacinth has special adaptations which are allowing them to grow and spread rapidly in freshwater. They can withstand extremes of nutrient supply, pH level, temperature, and can even grow in toxic water. They grow best in still or slow-moving water. Water hyacinth also known as one of the fastest growing plants, water hyacinth can reproduce primarily by way of runners or stolons, eventually forming daughter plants. They may also reproduce via seeds. The common water hyacinth (*Eichhornia crassipes*) is a vigorous grower known to double its population in two weeks. Water hyacinth grows over a wide variety of wetland types and prefers nutrient-enriched waters.

2.2.1 Environmental Problems by Water Hyacinth

Water hyacinth is listed as one of the most productive and active plants on earth and it are considered as one of the world's worst aquatic plants. It can double its size in 5 days and a mat of medium sized plants may contain 2 million plants per hectare that weigh 270 to 400T (A. Malik, 2007). These dense mats interfere with navigation,

recreation, irrigation, and power generation (Epstein, 1998). Many large hydropower schemes have to devote significant time and money in clearing the weed in order to prevent it from entering the turbine and causing damage and power interruptions. The blockage of canals and rivers can even cause dangerous flooding. On the other hand, increased evapotranspiration due to water hyacinth can have serious implications where water is already scarce. Water hyacinth can also present many problems for the fisherman such as decreased fish population, difficult access to the fishing sites and loss of fishing equipment, resulting in reduction in catch and subsequent loss of livelihood (A. Malik / Environment International 33, 2007).

Water hyacinth is blamed for the reduction of biodiversity as well. These mats competitively exclude native submerged and floating-leaved plants and its associated fauna, thereby causing an imbalance in the aquatic micro-ecosystem. Diversity of fish stocks is also affected. Low oxygen conditions beneath the mats create good breeding conditions for mosquito vectors of malaria, encephalitis and filariasis. Lately the hyacinth has invaded many tropical lakes including Lake Victoria, East Africa where it caused several of the above described problems such as reduction in fish catch, interference with transportation and water supply and breeding of snails, mosquitoes and snakes (Mailu, 2001, and Mironga, 2004). Plummer (2005) reported that the density of snails *Biomphalaria sudanica* (hosts of the disease organism *Schistosoma mansoni*) was increased in the vicinity of water hyacinth in Lake Victoria, East Africa. Until only a few years ago, Simberloff *et al.*, 1997; Langeland and Burks, 1998 reported that the major problem with water hyacinth in Florida were actually covering as many as 125,000 acres of water with up to 200T of hyacinths per acre.

2.2.2 Water Hyacinth as Metals Removal

In the last few decades, significant progress in bioremediation of metals and radionuclide has been made (Prasad and De Oliveira Freitas, (2003); Malik, 2004). Aquatic plants are known to accumulate metals from their environment and affect metal fluxes through those ecosystems. Water hyacinth has exceptionally high affinity and accumulation capacity for several metals (Zaranyika *et al.*, (1994); Polprasert and Katiwada, 1998; Zhu *et al.*, 1999). Therefore, it is used as a biomarker and is introduced in wetlands for water phytoremediation (Satyakala and Jamil, 1992).

Due to these reasons, investigations on metal sorption capacity of the dried biomass of water hyacinth have gained momentum (Table 2.2). Compared to living systems, dried biomass presents advantages for conservation, transport and handling. Metals are mostly concentrated at the roots of water hyacinth, indicating that the root system could act as an efficient biosorbent for various materials which are soluble in water (Low and Lee, 1990; Hao *et al.*, 1993; Low *et al.*, 1994).

Therefore, the usefulness of the dried biomass of non-living water hyacinth roots in removing metal ions from solution has been actively researched in the last decade (Table 2.2). The efficient sorption of uranium, copper as well as basic dyes by dead water hyacinth roots has been demonstrated (Low *et al.*, 1994; Shawky *et al.*, 2005). Al Rmali *et al.* (2005) have shown that more than 93% of arsenite (As(III)) and 95% of arsenate (As(v)) were removed from a solution containing 200µg As/L within 60min of exposure to a powder produced from dried roots. There has been little direct comparison of the relative heavy metal biosorption by water hyacinth or its parts with biosorption by various other biosorbents. Schneider *et al.* (1995) however, have shown that dried roots and aerial parts of water hyacinth are better biosorbent than yeast (*Candida parapsilosis*), bacterial (*Mycobacterium phlei*) and fungal (*Rhizopus oryzae*) strains. The authors suggested that the dried biomass of the plant might be placed in simple bags and used in a very low-cost metal ion removal system for decontamination of chemical and mining industry wastewaters. Udaya Simha *et al.* (2002) showed that the root of water hyacinth is an effective and attractive proposition compared to activated carbon in removing

fluoride from water bodies. Further, activated carbon prepared from water hyacinth plant has been found to show better adsorption of pollutants like dyes and phenol than commercial activated carbon and the same has been used for the removal of metals like Hg and Pb also (Table 2.2).

Table 2.2: Pollutants biosorption by dried/processed water hyacinth plant part (A. Malik, 2007)

Pollutant	Water hyacinth part	Maximum sorption capacity/removal	Reference	Comments
Basic dyes (methylene blue and Victoria blue)	Dried roots	Methylene blue (128.9mg g ⁻¹) and Victoria blue (145.4 mg g ⁻¹)	Low et al. (1995)	Sorption depends on pH, sorbent dose and dye conc.
Pb, Cd, Cu, Zn	Dried roots and aerial parts	Pb (47 mg g ⁻¹), Cd (27), Cu (23), Zn(20)	Schneider et al. (1995)	WH found to be better biosorbent than yeast, bacterial and fungal strains
Pb, Cu, Zn, Cd, Cr, Mn, Ni, Co, Au, Ag (5 mg l ⁻¹)	Treated roots	Acidic and basic treatments increased the metal uptake	Yao and Ramelow (1997)	
Lead (15-25 mg l ⁻¹)	Activated carbon prepared from water hyacinth	16.61 mg g ⁻¹ at pH 5, particle size (125-180µm)	Shekinah et al. (2002)	Pb removal increased with increase in pH from 2 to 4
Mercury (10-40 mg l ⁻¹)	Activated carbon prepared from water hyacinth	28.4 mg g ⁻¹ at pH 5, particle size (125-180µm)	Kadirvelu et al. (2004)	Sorption dependent on contact time, pH, Hg(II) and carbon conc. Data fitted both Freundlich and Langmuir isotherm models
Organic pollutants viz methylene blue (MB), Congo red (CR), p-	Activated carbon prepared from water hyacinth	MB (139 mg g ⁻¹), CR (154), PNP (149), P (59)	Al Rmalli et al. (2005)	Activated carbon prepared from WH showed better adsorption than commercial activated carbon

nitrophenol (PNP), phenol (P)				
Arsenic	Powdered dried root	93% of As(III) and 95% of As(v) removal from 200µg As I ⁻¹ within 60 min	Shawky et al. (2005)	As conc. In treated solution < 10 µg I ⁻¹ (WHO guideline limit value)
Uranium (20-100µgml ⁻¹)	Dried roots	64000U ⁶⁺ µg g ⁻¹		Rapid sorption depends on pH, sorbent dose and U conc.; follows Langmuir isotherm

2.3 Biosorption

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992). Algae, bacteria and fungi and yeasts have proved to be potential metal biosorbents (Volesky, 1986). The major advantages of biosorption over conventional treatment methods include (Kratochvil and Volesky, 1998 a):

- 1) Low cost;
- 2) High efficiency;
- 3) Minimisation of chemical and/or biological sludge;
- 4) No additional nutrient requirement;
- 5) Regeneration of biosorbent; and
- 6) Possibility of metal recovery.

The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate

species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases. (Biosorption of heavy metals, N. Ahalya, T.V. Ramachandra* 1 and R.D. Kanamadi 2., <http://www.ces.iisc.ernet.in/energy/water/paper/biosorption/biosorption.htm#6>)

2.3.1 Mechanism of Metal Biosorption

Adsorption and desorption studies invariably yield information on the mechanism of metal biosorption: how is the metal bound within the biosorbent. This knowledge is essential for understanding of the biosorption process and it serves as a basis for quantitative stoichiometric considerations which constitute the foundation for mathematical modeling of the process.

A number of different metal-binding mechanisms have been postulated to be active in biosorption such as:

- 1) Chemisorptions by ion exchange, complexation, coordination, chelation
- 2) Physical adsorption, microprecipitation.

Boya Volesky, 1999, said that there are also a possibility oxidation/reduction reactions taking place in the biosorbent. Due to the complexity of the biomaterials used it is quite possible that at least some of these mechanisms are acting simultaneously to varying degrees depending on the biosorbent and the solution environment.

2.3.1.1 Ion Exchange

Cell walls of microorganisms contain polysaccharides and bivalent metals ions exchange with the counter ions of the polysaccharides. For example, the alginates of

marine algae occur as salts of K^+ , Na^+ , Ca^{2+} , and Mg^{2+} . These ions can exchange with counter ions such as CO_3^{2-} , Cu^{2+} , and Zn^{2+} resulting in the biosorptive uptake of heavy metals (Kucuyak and Volesky, 1988). The biosorption of copper by fungi *Gaboderma lucidum* (Muraleedharan and Venkobachr, 1990) and *Aspergillus niger* was also up taken by ion exchange mechanism. Ion exchange reactions are stoichiometric and reversible, and in that way they are similar to other solution phase reactions.

For example:



2.3.1.2 Complexation

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

2.3.1.3 Chelation

Chelation(from Greek, chele. Meaning claw) is the binding - or complexation – of a bi – or multidentate ligand. These ligands which are often organic compounds are called chelant, chelator, chelating agent, sequestering agent form a chelate complex. The

term is reserved for complexes in which the metal ion is bound to two or more atoms of the chelating agent, although the bonds may be any combination of coordination or ionic bonds. Figure 2.3 shows the example of chelation.

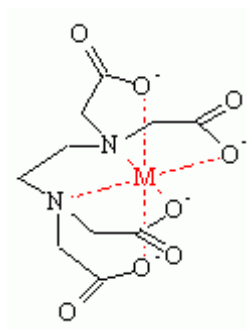


Figure 2.3: Metal-EDTA chelate

Virtually all biochemicals exhibit the ability to dissolve metals cations. Thus proteins, polysaccharides, and polynucleic acids are excellent polydentate ligands for many of the metal ions. In addition to these adventitious chelators, several are produced to specifically bind certain metals. Such chelating agents include the porphyrin rings in hemoglobin or chlorophyll and the Fe^{3+} -chelating siderophores secreted by microorganisms.

2.3.2 Factors Affecting Biosorption

The investigation of the efficacy of the metal uptake by the microbial biomass is essential for the industrial application of biosorption, as it gives information about the equilibrium of the process which is necessary for the design of the equipment.

The metal uptake is usually measured by the parameter 'q' which indicates the milligrams of metal accumulated per gram of biosorbent material and 'qH' is reported as a function of metal accumulated, sorbent material used and operating conditions.

The following factors affect the biosorption process:

1. Temperature seems not to influence the biosorption performances in the range of 20-35 °C (Aksu *et al.* 1992)
2. pH seems to be the most important parameter in the biosorptive process: it affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Friis and Myers-Keith., 1986, Galun *et al.*, 1987)
3. Biomass concentration in solution seems to influence the specific uptake: for lower values of biomass concentrations there is an increase in the specific uptake (Fourest and Roux., 1992; Gadd *et al.*, 1988). (Gadd *et al.*, 1988) suggested that an increase in biomass concentration leads to interference between the binding sites. (Fourest and Roux., 1992) invalidated this hypothesis attributing the responsibility of the specific uptake decrease to metal concentration shortage in solution. Hence this factor needs to be taken into consideration in any application of microbial biomass as biosorbent.
4. Biosorption is mainly used to treat wastewater where more than one type of metal ions would be present; the removal of one metal ion may be influenced by the presence of other metal ions. For example: Uranium uptake by biomass of bacteria, fungi and yeasts was not affected by the presence of manganese, cobalt, copper, cadmium, mercury and lead in solution (Sakaguchi and Nakajima., 1991). In contrast, the presence of Fe²⁺ and Zn²⁺ was found to influence uranium uptake by *Rhizopus arrhizus* (Tsezos and Volesky, 1982) and cobalt uptake by different microorganisms seemed to be completely inhibited by the presence of uranium, lead, mercury and copper (Sakaguchi and Nakajima, 1991).

2.4 Atomic Adsorption Spectroscopy (AAS)

Atomic absorption (AA) is the standard method for the analysis of specific metals. It is widely practiced in environmental analysis. The general aspects of the techniques are:

- a) mg/L to µg/L detection is routine

- b) analysis is generally very specific to a given element (although interferences are common)
- c) some techniques offer multiple compound analysis for one injection
- d) the techniques are fast and relatively inexpensive

(Refer to appendix D for further explanation on AAS method and applications)

2.5 Current Studies of Biosorption of Cadmium

2.5.1 Sorption of Cadmium and Zinc from Aqueous Solutions by Water Hyacinth (S.H. Hasan *et al.*, 2007)

The water hyacinth (*Eichhornia crassipes*) has been successfully utilized for the removal of Cd(II) as well as their admixture from samples of aqueous solutions. The growth of the plant after 16 days of exposure to the metal ions showed an increasing trend up to 2.5 ppm of Cd(II) concentrations, however, the growth became nondetectable or inhibited above these concentrations. The overall metal uptake by the plant was dependent upon the concentration of the metal and the duration of the exposure time. The metal uptake from a mixture of Cd(II) was reflected by a rate constant quite different from those solutions containing only one metal ion. A water hyacinth based system can be used to remove Cd(II) and Zn(II) from water/wastewater.

2.5.2 Removal of Cadmium and Zinc by Water Hyacinth, *Eichhornia crassipes* (ScienceAsia 30, 2004)

Toxic heavy metal pollution of water and soil is a major environmental problem, and most conventional remediation approaches do not provide acceptable solutions. Wetland plants are being used successfully for the phytoremediation of trace elements in natural and constructed wetlands. This study demonstrates the phytoremediation

potential of water hyacinth *Eichhornia crassipes*, for the removal of cadmium (Cd) and zinc (Zn). The phytoaccumulation of heavy metals, Cd and Zn, by water hyacinth *E. crassipes*, was studied. Water hyacinths were cultured in tap water, which was supplemented with 0.5, 1, 2 and 4 mg/L of Cd and 5, 10, 20, and 40 mg/L of Zn, and were separately harvested after 0, 4, 8 and 12 days. The experiment showed that both Cd and Zn had effects on plant relative growth. Removal of metals from solution was fast especially in the first four days. The accumulation of Cd and Zn in shoots and roots increased with the initial concentration and also with the passage of time. Plants treated with 4 mg/L of Cd accumulated the highest concentration of metal in roots (2044 mg/kg) and shoots (113.2 mg/kg) after 8 days; while those treated with 40 mg/L of Zn accumulated the highest concentration of metal in roots (9652.1 mg/kg) and shoots (1926.7 mg/kg) after 4 days. The maximum values of bioconcentration factor (BCF) for Cd and Zn were 622.3 and 788.9, respectively, suggesting that water hyacinth was a moderate accumulator of Cd and Zn and could be used to treat water contaminated with low Cd and Zn concentrations.

2.5.3 Sorption of Cd ions onto akagan'ite-type nanocrystals (Deliyanni, Matis, 2005)

The aim of this paper is to remove cadmium ions from aqueous solutions by sorption onto synthetic akagan'ite-type nanocrystals. This material was shown to be a promising inorganic adsorbent due to its favourite characteristics. Synthetic akagan'ite was prepared in the laboratory according to a new method. In this paper, the effects of adsorbent amount, initial cadmium concentration, pH value of solution, concentration of background electrolyte ions and temperature variation on the treatment process of cadmium removal by akagan'ite were investigated. Typical adsorption isotherms (Freundlich and Langmuir) were determined for the mechanism of sorption process. From the aforementioned results, the following can be concluded: Sorption depended greatly on the solution pH value, increasing as pH increased; for a change of around 2.5

pH units, cadmium removal varied between 0 and 100%. Cadmium removal was shown to decrease with the increase of the electrolyte ions in solution.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The experiment was conducted start from the preparation of biosorbent of dried water hyacinth, where the water hyacinth was dried, cut, grind and stored. Then, 100 mg/L cadmium solution as stock solution was prepared. The parameters that have been studied are; dosage of biosorbent, contact time, pH and temperature. Lastly, the experiment was analyzed using AAS to measure the percent removal of biosorbent water hyacinth as a removal of cadmium solution. Figure 3.1 show the overall process for this experiment.

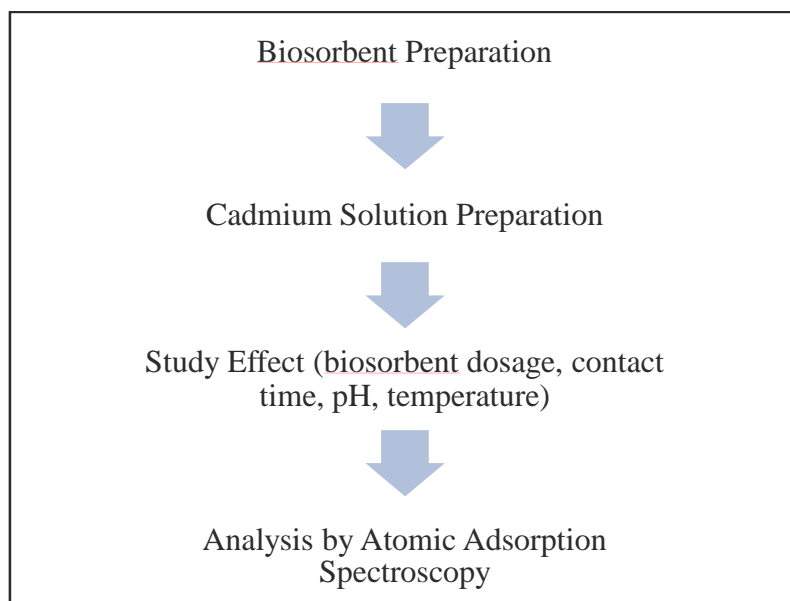


Figure 3.1: Overall process diagram of experiment.

3.2 Equipments Requirement

Equipments used in this experiment;

1. Jar Test
2. Z-5000 Polarized Zeeman Atomic Absorption Spectrophotometer
3. Hybridization Incubator Shaker
4. pH meter (HM 30P)
5. Erlenmeyer Flask
6. Micro pipette (range 100 μ L)
7. Electric balance Shimadzu (AW220)
8. Oven
9. Octagon siever (OCT-DIGITAL 4527-01)

3.3 Chemicals Requirement

Chemicals used in this experiment;

1. Cadmium Nitrate Tetrahydrate (solid)
2. Cadmium Standard Solution
3. Distilled Water
4. NaOH
5. HCL
6. Dried Water Hyacinth (solid)

3.4 Experimental Procedure

3.4.1 Biosorbent Preparation

The *Eichhornia crassipes* used in the experimentation was obtained from wild specimens growing in Pekan, Pahang. The roots, the aerial parts (stems plus leaves) or the whole plant were washed, dried at 60°C and ground in a bladed mixer to less than 0.59 mm (Tyler 28 mesh). The biomass preparation scheme is shown schematically in Figure 3.2. No pretreatment is used in this experimental.

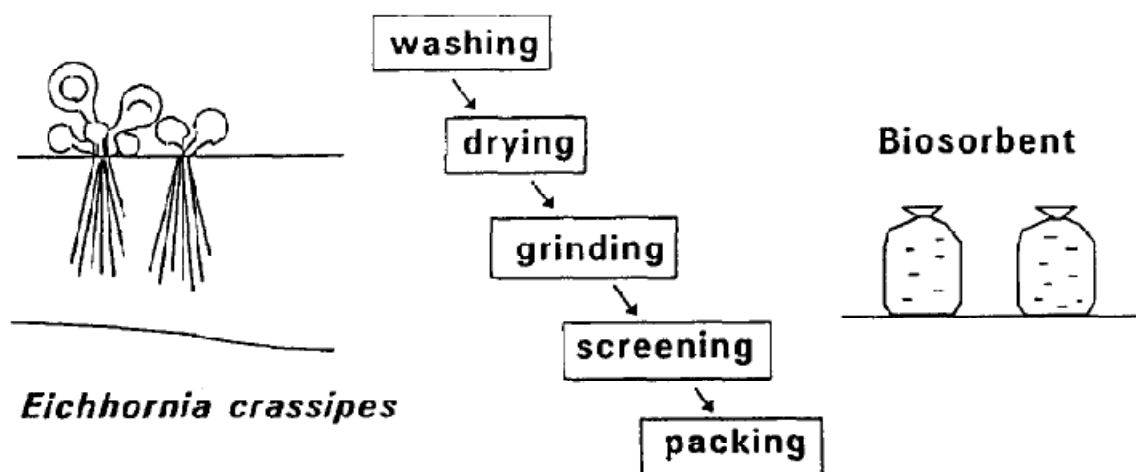


Figure 3.2: Procedure for preparation of *Eichhornia crassipes* biomass.

3.4.2 Cd solutions preparation

A stock solution of cadmium was prepared by dissolving AR grade of Cadmium Nitrate Tetrahydrate, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in distilled water, respectively at an initial concentration of 1000 mg/mL. For the experimental initial concentration used is at 20 mg/L.

The concentration is measured as below:

$$\text{Concentration} = \frac{m}{V}$$

(3.1)

Where;

m = mass

V = volume

For dilution to determined initial concentration, this equation is used:

$$M_i V_i = M_f V_f \quad (3.2)$$

Where M is molarity, V is volume, and the subscripts i and f refer to the initial and final values.

3.4.3 Effect of Water Hyacinth Dosage

To determine the effect of the cadmium ions from solution by the biosorbents, 500 ml of a cadmium solution was stirred using Jar test for 30 min at room temperature, 25°C with different range (0.4 g/L, 0.8 g/L, 1.2 g/L, 1.6 g/L, 2.0 g/L, 2.4 g/L, 2.8 g/L, 3.2 g/L, 3.6 g/L and 4.0 g/L) of water hyacinth biosorbent. The concentration of heavy metal ions in solution was determined both before the introduction of the biosorbent and after the reaction of the biosorbent with the metal containing solution. The amount of heavy metal ions abstracted from solution was determined, using atomic adsorption spectroscopy, by the difference in metal ion concentration from the two analyses performed before and after introduction of the biomass.

3.4.4 Effect of Contact Time