BIOSORPTION OF LEAD (II) FROM AQUEOUS SOLUTION BY DRIED WATER HYACINTH *(Eichhornia Crassipes)*

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I declare that this dissertation entitled "*Biosorption of Lead (II) from Aqueous Solution by Dried Water Hyacinth (Eichhornia Crassipes)* "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.

Signature : ....

Name : …Siti Aishah Binti Abd Wahid

Date : ....

Special dedication for:

My beloved mother, Zuraidah Binti Mohd.Ali

My beloved father, Abd.Wahid Bin Che Dan

Beloved Siblings

and

My Lovely Friends

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ABSTRACT

The contamination of wastewaters, river sediments and soil with toxic metals is a complex problem. The removal of these contaminations has received much attention in recent year using conventional methods such as chemical reduction, ion exchange and electrochemical treatment. The alternative methods is discovered which is biosorption, refer to the physics-chemical binding of metal ions to biosorbent. It is a relatively new process that has been proven very promising in the removal of contaminants from aqueous effluents. It has been shown to be an economically feasible alternative method for removing heavy metals (Sabriye et al., 2005). Water hyacinth approaches being a scourge in many parts of the world, choking waterways and hindering transport upon them. The usefulness of the biosorbent of water hyacinth roots in removing metal ions from solution was investigated recently and it was shown that the roots have the potential of being used as a cheap source of biosorbent for metal ions (Kaustubha et al., 2005). The purpose of this study is to investigate the ability of dried water hyacinth (*Eichhornia Crassipes*) as biosorbent in biosorption of Lead (II) from aqueous solution. This study is a small scale research that might be practice in wastewater plant. The effect of physic-chemical parameters like biosorbent dosage, initial concentration, pH and contact time were investigated. The analysis was done by using Atomic Absorption Spectroscopy. From the result obtained, the removal of Pb (II) ions was optimum when initial lead concentration was almost 40 mg/ L, biosorbent dosage at 0.225 g, pH 5.5 and at 8 minutes contact time. Other process conditions were optimized. These were volume of sample: 40 mL, temperature: 25°C and agitation speed: 120 rpm. In this study, it is shows that a biomaterial produced from dried water hyacinth can provide a simple, effective and yet cheaper method in removing lead from contaminated water.

ABSTRAK

Pencemaran air sisa, endapan sungai dan tanah oleh logam toksik adalah satu masalah yang rumit. Penyingkiran bahan tercemar ini telah mendapat perhatian sejak kebelakangan ini dengan menggunakan kaedah konvensional seperti tindak balas penurunan kimia, penukaran ion dan rawatan elektrokimia. Kaedah alternatif iaitu penjerapan bio telah digunakan dalam merawat air sisa yang mengandungi logam toksik. Ia terbukti bahawa ia adalah kaedah yang menjimatkan untuk dilaksanakan didalam penyingkiran ion logam (Sabriye et al., 2005). Penggunaan bahan penjerap iaitu keladi bunting di dalam penyingkiran ion logam daripada larutan telah dikaji kebelakangan ini dan ia terbukti bahawa akar mempunyai potensi sebagai bahan penjerap ion logam yang murah (Kaustubha et al., 2005). Kajian ini dilakukan bertujuan mengkaji kemampuan keladi bunting atau dalam bahasa saintifiknya ia dikenali sebagai *Eichhornia Crassipes* yang telah dikeringkan sebagai bahan penjerap di dalam proses penjerapan bio ion plumbum dari larutan akues. Kajian ini adalah sebuah percubaan yang mungkin akan dipraktikkan di tempat rawatan air tercemar. Kesan parameter fizik-kimia seperti dos bahan penjerap, kepekatan awal, pH dan masa tindakbalas telah dikaji. Analisis telah dilakukan dengan menggunakan "Atomic Absorption Spectroscopy". Daripada keputusan yang diperolehi, penyingkiran Pb (II) ion adalah optimum ketika kepekatan plumbum awal adalah 40 mg/ L, dos bahan penjerap pada 0.225g, pH 5.5 dan masa tindakbalas adalah 8 minit. Keadaan proses yang lain adalah tetap iaitu isipadu sampel: 40 mL, suhu: 25°C dan kelajuan goncangan: 120 rpm. Didalam kajian ini, ia membuktikan bahan bio yang dibuat daripada keladi bunting yang telah dikeringkan boleh menjadi proses yang mudah, berkesan dan murah di dalam penyingkiran plumbum daripada air yang tercemar.

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LIST OF SYMBOLS

PbS	-	Plumbum Sulfide
$PbSO_4$	-	Plumbum Sulfate
$PbCO_3$	-	Plumbum Carbonate
Pb (II)	-	Lead ion
Fe^{2+}	-	Ferum ion
Zn^{2+}	-	Zinc Ion
NaOH	-	Natrium Hydroxide
H^+	-	Hydrogen ion
Ppm	-	part per million
mg/L	-	milligrams per liter
TEL	-	tetra ethyl lead
$Pb(NO_3)_2$	-	Plumbum Nitrate
SEM	-	Scanning electron microscopy
FTIR	-	Fourier Transform Infrared
mL	-	mililitre
rpm	-	revolution per minute
µm	-	micro metre
Ci	-	initial concentration
Ce	-	equilibrium concentration
Qe	-	uptake capacity
AAS	-	Atomic Absorption Spectrophotometer

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CHAPTER 1

INTRODUCTION

1.1 Background

The natural environment often suffers from dentrimental effects of industrial pollution with progress in technology (Lalitagauri et al., 2005). Industrial wastewater, which have heavy metals are an important source of environmental pollution (Sabriye et al., 2005). According to the S. Senthilkumaar research, these metals are widely distributed in materials which make up the earth's surface. One of the elements that classified in this metal is lead.

According to the David Tin, lead occurs naturally in the earth's crust, in ores such as galena, Lead (II) sulfide and PbS. However, human activity has resulted in atmospheric Lead, mainly as $PbSO_4$ and $PbCO_3$. Industries such as coating, paint, lead smelting and mining generate large quantities of wastewater containing various concentrations of lead (Lalitagauri et al., 2005; Gardea et al., 2004; Sabriye et al., 2005; Wallace et al., 2003). Lead poisoning in humans causes severe damage to the kidneys, nervous system, reproductive system, liver and brain, and can cause sickness or death (Vinoj et al., 2006; Lalitagauri et al., 2005; Wallace et al., 2003). Severe exposure to lead has been associated with sterility, abortion, stillbirth, and neonatal deaths (Lalitagauri et al., 2005).

J. L.Gardea-Torresdey found that current methodologies used in the removal of Lead found in both water and wastewater include procedures such as chemical precipitation, membrane filtration, ion exchange, carbon adsorption, and coprecipitation or adsorption. These aforementioned techniques are all generally expensive and might possibly generate by-products dangerous to human health, such as in the case of leachates, which originate from ion-exchange resins.

Biosorption is presented as an alternative to traditional physicochemical means for removing toxic metals from ground-waters and wastewater (Lalitagauri et.al). It is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. It has been shown to be an economically feasible alternative method for removing heavy metals (Sabriye et al., 2005). Mechanisms involved in the biosorption process include chemisorptions, complexation, ion exchange, microprecipitation, hydroxide condensation onto the biosurface and surface adsorption (Gardea et al., 2004). The phenomenon of biosorption has been described in a wide range of non-living biomass like nile rose plant powder and ceramics (Abdel-Halim et al., 2002).

In this study, the adsorption of heavy metals onto biomaterial derived from the water hyacinth was investigated. Water hyacinth has been listed as most troublesome weed in aquatic systems. It is a severe environmental and economical problem in many tropical and subtropical parts of the world. Water hyacinth is a submerged aquatic plant, found abundantly throughout the year in very large and drainage channel systems in and around the fields of irrigation. Previous studies have reported that water hyacinth has successfully resisted chemical, physical, biological or hybrid means used to eradicate it. The only accepted use of water hyacinth is in treating the biodegradable wastewaters. The final disposal of water hyacinth used in wastewater treatment is still an unsolved problem. Therefore, a novel technology with ecological sound and economically viable is urgently required to solve the problem of aquatic weed disposal and management. The usefulness of the biomass of water hyacinth roots in removing metal ions from solution was investigated recently and it was shown that the roots have the potential of being used as a cheap source of biosorbent for metal ions (Kaustubha et al., 2005).

1.2 Problem Statement

Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated wastewaters. A high degree of industrialization and urbanization has substantially enhanced the degradation of our aquatic environment through the discharge of industrial wastewaters and domestic wastes (S. Senthilkumaar et al., 2000). The presence of this heavy metal in water, even at very low concentrations, is highly visible and undesirable. Lead particles can be inhaled posing serious threats to human health (Krishnakumar et al., 2006). High amount of lead in water attract use to do this study as a way to control water pollution.

A range of different methods can be used for the removal of Lead (II) from water that contains this hazardous element. However, these high-end processes have significant disadvantages, including incomplete metal removal, requirement of expensive equipment, high energy requirements and generation of toxic sludge or other waste products that require disposal.Some factors such as cost effective and simple technology must be considered to settle this problem (Shaban et al., 2005).

Biosorption is one of the most effective processes of advanced wastewater treatment, which reduces trace hazardous organic and inorganic wastes left in effluents after the conventional treatment. It is also used to remove toxic inorganic and organic compounds from contaminated groundwater (Kaustubha et al., 2005). We can use different type of biosorbent in this process such as bacteria and aquatic plant. Currently, the most widely used and effective adsorbent in industry is activated carbon, although running costs are expensive. In recent years, agricultural by-products have been widely studied for lead (II) removal from wastewater (Srinivasa et al, 2007). Water hyacinth is chosen as biosorbent in this study because it can be a good uptake of Lead (II) and the abundant supply of it that easy to get in low cost compare to other chemical biosorbent such as activated carbon. Because of its fast-growth and the robustness of its seeds, water hyacinth has become a major cause of water irrigation especially in rivers and drainage.

Some studies have been reported on the use of dried plant material as a potential biosorbent in industrial to remove Lead (II) in the waste water. Shao-Wei Liao in 2004 found that water hyacinth plants had a high bioconcentration of these trace elements when grown in water environments with low concentrations of the Lead elements. The use of biomaterial derived from dried water hyacinth roots may be a more convenient and effective method for the removal of toxic metals (Shaban et al., 2005). In this study, preferred to use dried water hyacinth because the growth of water hyacinth is very fast and need a large place to growth it. Moreover, this condition resulted in massive growth of mosquitos' pest which will Lead to serious health problems to the environment. Furthermore, we can reduce the usage of transportation and the cost to transport itself.

1.3 Objective

The proposed research was studied to achieve the following objectives:

1. To study the biosorption of Lead (II) using dried water hyacinth.
2. To investigate the ability of water hyacinth as biosorbent.
3. To identify the optimum condition in the removal Lead (II) by using dried water hyacinth.

1.4 Scope of Study

In order to achieve the objectives, the following scopes have been identified:

1) Effect of pH
2) Effect of dried water hyacinth dosage.
3) Effect of time.
4) Effect of initial concentration.

1.5 Rationale and Significance

This study is to remove Lead (II) which causes environmental problem because Lead cannot be degraded or destroyed. It can cause dangerous because it tend to bioaccumulation and it can enter our bodies via food, drinking water and air (Maryam et al, 2007). This study practice biosorption process, a biological method of environmental control as an alternative to replace conventional method that are ineffective or extremely expensive (B. Preetha et al, 2005).

In this study, we only use dried water hyacinth that is a noxious weed that has attracted worldwide attention due to its fast spread and congested growth, which lead to serious problems in navigation, irrigation, and power generation (Anushree Malik, 2006). By doing this study we can also settle problems that caused by water hyacinth to the environment such as the blockage of canals and rivers that can even cause dangerous flooding. Besides that, water hyacinth is a low-cost, high efficiency of metal removal from dilute solutions and easily available material for biosorbent (Kaustubha Mohanty et al., 2005).

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

Water is a rare and precious commodity and only an infinitesimal part of the earth's water reserves that is approximately 0.03% constitutes the water resource which is available for human activities (Tigini et al., 2004). The lack of clean water has always be an issue of environmental concern all over the world. Kris Min in his article has reported that wastewater pollution has always been a major problem throughout the world. The lack of suitable water used for drinking, agriculture, farming and others activities have declined through the years. This environmental issue is mainly stressed in developing countries today. The main sources of water pollution are from industrial such as chemical, organic, and thermal wastes, municipal such as largely sewage consisting of human wastes, other organic wastes, and detergents, and lastly from agricultural such as animal wastes, pesticides, and fertilizers. With a shortage of water throughout the world, proper methods of treating and recycling water are the key goal in sustaining our limited water resource supply.

2.1.1 Definition

Wastewater can be defined as any water that has been adversely affected in quality by anthropogenic influence. In the most common usage, wastewater refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources. All the water used in the home that goes down the drains or into the sewage collection system is wastewater (Howard S.Peavy, 1985. McGraw-Hill)

Wastewater contains pathogens, nutrients such as nitrogen and phosphorus, solids, chemicals from cleaners and disinfectants and even hazardous substances. According to the statement from Department of Employment and Industrial Relations of The State of Queensland 2006, hazardous substances, lead hazardous substances, stated dangerous goods and combustible liquids are examples of hazardous materials classified according to their relevance to workplace health and safety. Hazardous materials can cause adverse health effects such as asthma, skin rashes, allergic, cancer, and other long term diseases from exposure to substances.

2.1.2 Heavy Metal

Pollution describes the introduction of foreign substances into the biosphere. As xenobiotics, some of these pollutants sometimes find their way into the human system through the food chain. However, some of the pollutants resist chemical and biological transformation and accumulate in the tissues, including the nerves, to cause toxicity. Some heavy metals are neurotoxic. For instance lead, mercury, nickel, zinc, cadmium, chromium and manganese (Gabriel Oze et.al, 2006, Wallace et.al, 2003, Viriya et.al, 2006, Vinoj et.al, 2006).

Natural waters have been found to be contaminated with several heavy metals arising mostly from mining wastes and industrial discharges (T.H. Baig et al., 1999, Sarabjeet et.al., 2007). Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated wastewaters (Martins et al. 2006). Wallace, Aderval, Cristiane and Antonio have reported that the increasing use of metals and chemicals in the process industries has resulted in the generation of large quantities of aqueous effluents that contain high levels of heavy metals, creating serious environmental disposal problems. Heavy metal is hazardous to the environment, and therefore it is necessary that they are appropriately removed from waste stream before being discharged into the environment (Viriya et al., 2006, Tigini et al., 2004).

2.2 Lead (II)

According to the previous study, the presence of certain heavy metals in the environment specifically in various water resources is of major concern because of their toxicity, non-biodegradable nature and threat to human, animal and plant life. Among various metal ions present in wastewater that are detected in the waste streams from mining operations, electroplating and petrochemical industries, Lead is one of the most prevalent metal (Maryam et al., 2007).

Lead is widely used in many industrial applications such as storage battery manufacturing, printing, pigments, fuels and explosive manufacturing (Jalali et al. 2002). Lead is highly toxic as its presence in drinking water above the permissible limit (5 ng/mL) causes adverse health effects such as anemia, encephalopathy, hepatitis and nephritic syndrome (Lo et al. 1999). Lead does, in general, not bioaccumulate and there is no increase in concentration of the metal in food chains. Lead is not essential for plant or animal life. Severe exposure to Lead has been associated with abortion, stillbirth and neonatal deaths. It is therefore, essential to remove Pb (II) from wastewater before disposal (Lalitagauri et al., 2005).

2.2.1 Characterictics of Lead

Lead is a main group element with symbol Pb and atomic number 82. Lead is a soft, malleable poor metal, also considered to be one of the heavy metals. Its common ore is galena where it occurs in the form of sulphide (Jyotikusum Acharya et al., 2008). Lead is also present at 50 parts per million (ppm) in the earths crust. In sea water 5 parts per billion (ppb) lead is present. It is found in all living organism. Those it is distributed in food and in environment. A human body contains about 121 ppb, 96% in the bone. Lead is used in building construction, lead-acid batteries, bullets and shot, weights and radiation shields. Other anthropogenic sources of lead include the combustion of coal, processing and manufacturing of lead products and manufacturing of Lead additives such as tetra ethyl lead (TEL) for gasoline.

2.2.2 Effects of Lead

Like mercury, another heavy metal, Lead is a potent neurotoxin that accumulates in soft tissues and bone over time. Lead is systemic poison causing anemia, kidney malfunction, tissue damage of brain and even death in extreme poison. Lead is deposited mostly in bones and in some soft tissues. Lead is also retaining by mammals in lever, kidney, muscles and others. The presence of lead in waste water is dangerous to aquatic flora and fauna even in relatively low concentration and stringent environmental regulation attracts the attention of chemists and environmental engineers for its control. Various chemical and physico-chemical methods for the treatment of wastewaters containing lead wastes are known, such as chemical precipitation, electrochemical reduction, ion exchange, biosorption and adsorption. The choice of treatment depends on effluent characteristics such as concentration of lead, pH, temperature, flow volume, biological oxygen demand, and the economics involved and the social factor like standard set by government agencies.

2.3 Biosorption

A number of methods exist for the removal of heavy metal pollutants from liquid wastes when they are present in high concentrations that include methods such as precipitation, evaporation, electroplating, ion-exchange and membrane processes (T.H.Baig et al., 1999; Gardea et al., 2004; Wallace et al., 2003; Y. Prasanna et al., 2006; Yi-Ling et al., 2008). The major disadvantage with conventional treatment technologies is the production of toxic chemical sludge and its treatment becomes a costly affair and is not eco-friendly. Therefore, removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner assumes great importance (Sarabjeet et al., 2006). Biosorption of heavy metals from aqueous solution can be considered as an alternative technology in industrial wastewaters treatment (T.H.Baig et al., 1999; Gardea et al., 2004; Wallace et al., 2003; Viriya et al, 2006).

2.3.1 Definition

Biosorption is defined as a process in which solids of natural origin, such as microorganisms or their derivatives are employed for sequestration of heavy metals from an aqueous environment. It is a property of certain types of inactive, non-living microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solution (Sarabjeet et al., 2005). Biomass exhibits this property, acting just as chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria, which was found responsible for this phenomenon. The transfer of metal ions from aqueous to solid biosorbent phase can be due to passive, facilitated or active transport.

N. Ahalya, T.V. Ramachandra and R.D. Kanamadi reported that 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. Algae, bacteria and fungi and yeasts have proved to be potential metal biosorbents.

The biosorption process involves a solid phase and a liquid phase containing a dissolved species to be sorbed. 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. In others, biosorption is defined as a process in which solids of natural origin, such as microorganisms or their derivatives are employed for sequestration of heavy metals from an aqueous environment (B. Preetha et al, 2005). Many studies have already been done on the biosorption ability of a diverse variety of agricultural waste materials such as water hyacinth (S.H. Hasan et al., 2006; Schneider et al., 1995), orange peel (Yi-Ling et al., 2008) and Apricot stones (Demirbas et al., 2007).

Biosorption is a rapid phenomenon of passive metal uptake sequestration by non-growing biomass. Further, sorption capacity is evaluated by sorption isotherms described by Langmuir and Freundlich models. The uptake of metal by two biosorbents must be compared at the same equilibrium concentration. The adsorption is easy to understand when it refers to a single metal situation; however in a multi-ion situation, which is generally encountered in effluent, the assessment of sorption becomes complicated. Most of the work exists with single metal solution and realistic approach would be inferring results in mixed metal solution at extreme pH and variable metal concentration. Biosorption efficiency depends upon many factors, including the capacity, affinity and specificity of the biosorbents and their physical and chemical conditions in effluents.