BIOSORPTION OF FERRUM (II) FROM INDUSTRIAL WASTEWATER BY USING WATER SPINACH (*Ipomoea aquatica*)

MUHAMAD HAFIZ BIN HALIM

Final year project report submitted as a partial fulfillment of the requirement for the award of Bachelor of Chemical Engineering

Faculty of Chemical Engineering and Natural Resources
Universiti Malaysia Pahang

DECEMBER 2010

ABSTRACT

The increasing amount of industrial wastewater discharges to the environment have contibuted to the increasing amount heavy metals in clean water sources such as river, pond and lake. This matter is seems to be a major problem as heavy metals in water source can cause illnesses, diseases and disorders to human and other organism. Thus, industrial wastewaters containing heavy metal should be treated before discharged to the environment. However, treatment methods of removing heavy metals are very costly and due to requirement discovery of new method that is not costly and also efficient. This research is about the capability of a new technique called biosorption in removing ferrum from industrial wastewater. The biological material that is used as the biosorbent is water spinach (*Ipomoea aquatica*) and the sample of wastewater is obtained from Huntsman Tioxide (M) Sdn. Bhd. The analysis of the wastewater shows that the concentration of ferrum is 16 g/L. The parameters analyzed in this research is the amount of biosorbent used to absorb ferrum from the wastewater and the time contact between biosorbents and wastewater. The experiment is done by planting water spinach in 9 liters of wastewater in a plastic container. The amount of biosrbents are varies from 100g to 600g while the contact time is from 1 day to 8 days. After several experiment and analysis of results, it is found that the ferrum removal increased until day 7 before it becomes constant with highest percentage removal of 86.57%. For water spinach amount parameter, ferrum removal is higher with bigger amount of biosorbents with highest percentage removal of 85.32%. As a conclusion, application of water spinach as biosorbent exhibits high potential in wastewater since its capable of removing high percentage of ferrum.

ABSTRAK

Peningkatan jumlah pembuangan air sisa industri ke alam sekitar telah menyumbang kepada peningkatan jumlah logam berat dalam sumber-sumber air bersih seperti sungai, kolam dan tasik. Hal ini merupakan satu masalah utama kerana logam berat dalam sumber air boleh menyebabkan penyakit dan gangguan terhadap kesihatan manusia dan organisma lain. Oleh itu, air sisa industri yang mengandungi logam berat perlu dirawat sebelum dibebaskan ke alam sekitar. Namun, kos proses merawat logam berat adalah sangat tinggi dan disebabkan itu, penemuan kaedah baru yang berkos rendah dan effisien amat diperlukan. Penyelidikan ini adalah tentang kemampuan suatu teknik baru yang disebut “biosorption” dalam menyerap ferrum (II) dari air sisa industri. Bahan biologi yang digunakan sebagai penyerap adalah kangkung (*Ipomoea aquatica*) dan sampel air sisa diperolehi daripada Huntsman Tioxide (M) Sdn. Bhd. Analisis air sisa menunjukkan bahawa kepekatan ferrum (II) adalah 16 g/L. Parameter yang dikaji dalam kajian ini adalah jumlah penyerap digunakan untuk menyerap ferrum (II) dari air sisa dan masa bersentuh antara penyerap dan air sisa. Eksperimen dilakukan dengan menanam kangkung didalam bekas plastic yang mengandungi 9 liter air sisa industri. Jumlah penyerap yang berbeza-beza dari 100 ke 600g dan waktu sentuhan dari 1 hingga 8 hari telah digunakan. Setelah beberapa eksperimen dan analisis data yg diperoleh, didapati bahawa peratus penyerapan ferrum (II) meningkat sehingga hari ketujuh sebelum menjadi malar dengan peratus penyerapan tertinggi 86.57%. Untuk parameter jumlah kangkung pula, pnyerapan ferrum (II) adalah lebih tinggi selaras dengan peningkatan jumlah penyerap. Peratus penyerapan tertinggi ialah 85,32%. Kesimpulannya, aplikasi kangkung sebagai penyerap ferrum (II) dari air sisa mempunyai potensi yang tinggi berdasarkan peratus penyerapannya yang tinggi.

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LIST OF SYMBOLS/ABBREVIATIONS

mg	-	Miligram
g	-	Gram
L	-	Liter
ppm	-	part per million
hr	-	Hour
^{o}C	-	Degree Celcius
%	-	Percentage
e.g	-	Example
Fe^{2+}	-	Ferrous Iron
Fe^{3+}	-	Ferric Iron
Cu^{2+}	-	Copper Ion
Zn^{2+}	-	Zink Ion
K^{+}	-	Potassium Ion
Na^{+}	-	Natrium Ion
Ca^{2+}	-	Calcium Ion
Mg^{2+}	-	Magnesium Ion
Cd^{2+}	-	Cadmium Ion
Abs	-	Absorbance
MRI	-	Magnetic Resonance Imaging
H_2SO_4	-	Sulphuric Acid
$FeSO_4$	-	Ferrum Sulphate

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The amount of heavy metals released to environment by the industry have seems to be a major problem. Heavy metals such as Cadmium, Nickel, Ferrum, Lead are often detected in industrial wastewaters. Heavy metals in water source can be very harmless to human as they can cause illnesses, diseases and disorders. Furthermore, heavy metals are non-biodegradable; therefore they must be separated and removed before discharged to the environment.

Rising cost in treating wastewater resulting the discovery of new technique in removing heavy metals. The new technique is called biosorption which 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). This method proved to be a good alternative for ion removal process and it has a good potential to replace high cost treatment system such as chemical precipitation and ion exchange according to many researches. Water hyacinths (*Eichhorria crasspies*) are able to remove Cd and Ni rapidly from the aqueous system by root absorption and concentration (Low and Lee, 1981). This is one of the research that shows the ability of aquatic plant in removing heavy metals from water. Biosorption is presented as an alternative to traditional physicochemical means for removing toxic metals from ground-waters and wastewater (Lalitagauri et.al., 2003). Doyorum et al., (2006) reported that biosorption is an economically feasible alternative method for removing heavy metals. Discovery on the unique ability of aquatic plant in absorbing heavy metals from wastewater are very useful for wastewater treatment. Microprecipitation, ion exchange, chemisorptions, complexation, hydroxide condensation onto the biosurface, surface adsorption are the known mechanisms that involved in the biosorption process.

In this research, Water Spinach (*Ipomoea aquatica*) is used for the same purpose which is removing heavy metals from wastewater. Water spinach is an herbaceous trailing vine that dwells in muddy stream banks, freshwater ponds, and marshes. This perennial aquatic vine is confined to the tropics and subtropics zones because it is susceptible to frosts and does not grow well when temperatures are below 23.9 C, meaning that this aquatic plant can be found easily in Malaysia.

Water spinach populations reported to have caused environmental damage by creating impenetrable masses of tangled vegetation obstructing water flow in drainage and flood control canals. They have infested lakes, ponds, and river shorelines, displacing native plants that are important for fish and wildlife. The veins of the plant create dense impenetrable canopies over small ponds and retention basins creating stagnant water conditions that are ideal breeding environments for mosquitoes.

The heavy metal focused in this research is Ferrum (Fe) which is one of the vital elements for humans and for other forms of life. Nevertheless, high dosage of Ferrum are known to cause hemorrhagic necrosis, sloughing of mucosa areas in the stomach, tissue damage to a variety of organs by catalyzing the conversion of H_2O_2 to free radical ions that attack cell membranes, proteins and break the DNA double strands and cause oncogene activation (Mahesh et al., 2008). With pathological conditions it is known that Fe metabolism and superoxide metabolism can exacerbate the toxicity of each other. Further Fe toxicity leads to diabetes mellitus, atherosclerosis and related cardiovascular diseases, hormonal abnormalities, and a dysfunctional immune system. Moreover, oxidative stress induced by excess Fe may also cause brain damage (Gurzau et al., 2003).

1.2 Problem Statement

Nowadays, Ferrum which is considered as pollutants and hazardous to human and also ecosystems can be easily found in sources of clean water. The main reason is the discharges of industrial wastewater that contain high concentration of Ferrum by the industry. Ferrum can lead to diabetes mellitus, atherosclerosis and related cardiovascular diseases, hormonal abnormalities, and a dysfunctional immune system. Thus, Ferrum in industrial wastewater need to be treated before discharges into the environment.

Existing heavy metals treatments such as chemical precipitation and ion exchange using zeolite catalyst and resins are very costly. In this research, a method of biosorption using aquatic plant is used because of some advantages. The major advantages of biosorption over conventional treatment methods include (Kratochvil and Volesky, 1998).

a) No additional nutrient requirement
b) High efficiency in removing heavy metals
c) Renewable biosorbent (lower cost)
d) Minimisation of chemical used
e) Possibility of metal recovery

The chosen aquatic plant is water spinach (*Ipomoea aquatica*) which is considered to have high potential in removing heavy metals from wastewater. This aquatic plant is easy to find because of its high growth rate in swamps, lake, canal and drainage systems. Its high growth has caused environmental problems such as blockage of canals and rivers that can even cause dangerous flooding. By using water spinach (*Ipomoea aquatica*) as biosorbent in heavy metal treatment, these environmental problem can also be reduced because huge amount of it is needed for the biosorption process.

1.3 Objective

The objective of this experiment is to study the capability of water spinach (*Ipomoea aquatica*) in removing Ferrum from industrial wastewater.

1.4 Scope of Study

In order to achieve the objective of this research, the scope of study has been determined to based on two parameters which are the contact time between the water spinach and the industrial wastewater and amount of water spinach (*Ipomoea aquatica*) used in the biosorption of ferrum.

1.5 Rational and Significance

Ferrum is one of the most hazardous metals that can be easily found in our environment and can lead to many disorders, diseases and sickness. Majorly, this problem is caused by the industrial wastewater containing high concentration of ferrum discharged by the industry. Thus, the ferrum contained in industrial wastewater needed to be treated before discharged into the environment. In this study, the wastewater that contains high concentration of ferrum is obtained from Huntsman Tioxide (M) Sdn. Bhd. The biosorption method is chose which can reduce the cost in removing heavy metals from wastewater compared to other process such as chemical precipitation and ion exchange.

Water spinach (*Ipomoea aquatica*) is used in this study as the biosorbent for the biosorption of ferrum. This aquatic plant is easy to find because of its high growth rate in swamps, lake, canal and drainage systems. Furthermore, the cost of wastewater treatment can be reduced. By doing this study we can also settle problems that caused by water spinach to the environment such as the blockage of canals and rivers that can even cause dangerous flooding.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and agriculture and can encompass a wide range of potential contaminants and concentrations. It consists of many substances that can be classified to organic and inorganic compound. Some of these substances might be toxic to human and even to the ecosystem. Inorganic compound consisted in water are hazardous and not biodegradable.

Rising cost of effluent treatment and stringent environmental regulations have encourage widespread water conservation efforts. The lack of clean water has always be an issue of environmental concern all over the world. Kris Min (2000) in his article has reported that wastewater pollution has always been a major problem throughout the world. 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 (Prigione et al., 2008). 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.

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. Sewage is correctly the subset of wastewater that is contaminated with faeces or urine, but is often used to mean any waste water. Wastewater is not just sewage. All the water used in the home that goes down the drains or into the sewage collection system is wastewater. This includes water from baths, showers, sinks, dishwashers, washing machines, and toilets. Small businesses and industries often contribute large amounts of wastewater to sewage collection systems; others operate their own wastewater treatment systems. In combined municipal sewage systems, water from storm drains is also added to the municipal wastewater stream.

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, 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 include many commonly found industrial, agricultural and domestic chemicals. Examples of some hazardous materials include paints, drugs, cosmetics, cleaning chemicals and detergents. Hazardous materials can cause adverse health effects such as asthma, skin rashes, allergic, cancer, and other long term diseases from exposure to substances.

To deal with the wastewaters, many types of treatment systems are used to treat their wastewater such as sedimentation, coagulation, lagoon & pond, activated sludge, ion exchange, chemical precipitation, land treatment system, reverse osmosis, electro dialysis, ozonation, filtration, flocculation etc. The treatment systems used are based on the type of contaminant detected in the wastewater. The treatment systems that are usually used for heavy metals contaminants are land treatment system, chemical precipitation and ion exchange.

2.2 Heavy Metal

One of the inorganic compounds contain in wastewater is heavy metal which can be defined as a member of an ill-defined subset of elements that exhibit metallic properties, which would mainly include the transition metals, some metalloids, lanthanides, and actinides. Heavy metals are ubiquitous in the environment, as a result of both natural and anthropogenic activities, and humans are exposed to them through various pathways (Wilson and Pyatt, 2007). Heavy metals can be classified as pollutant which is foreign material or substance that is introduced into a biosphere. They can be easily found in our surrounding as a result of excessive release into the environment due to rapid industrialization. They can enter human body through respiration, drinking, eating and adsorption through the skin. Heavy metals are classified toxic as they can cause illnesses, diseases and disorders. In the body, they may undergo biotransformation, metabolism and excreted without the risk of toxicity depending on the chemical characteristics of the compound and the dose. However, some of the pollutants resist chemical and biological transformation and accumulate in the tissues, including the nerves, to cause toxicity. The adverse effects of these pollutants on the nerves give rise to neurotoxicity and some of the heavy metals are neurotoxic. For instance lead, mercury, nickel, zinc, cadmium, chromium and manganese (Gabriel Oze et.al, 2006)

Heavy metal is also hazardous to the environment, and therefore it is necessary that they are appropriately removed from waste stream before being discharged into the environment. In fact, a total recycle of heavy metals is an ultimate goal that all industries should be aiming at. Nowadays, natural waters are contaminated high with concentration of heavy metals caused by the uncontrollable discharges of wastewater by the industry and mining waste. Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated wastewaters (Parvathi et al., 2007). This of course a primary importance that the contaminated wastewater must be properly treated before discharged. However, this might not be achieved in the near future due primarily to the limitation in available recovery technologies.

Wallace et al., 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. Additionally, mining, mineral processing and extractive metallurgical operations generate huge volumes of toxic liquid waste.

Industrial effluents contribute enormously to water deterioration and their treatment is the subject of discussion and regulation in many countries. Effluent from textile, leather, tannery, electroplating, galvanizing, pigment and dyes, metallurgical and paint industries and other metal processing and refining operations at small and large scale sector contains considerable amounts of toxic metal ions (Ahluwiya and Goyal, 2007). Textile and tanning effluents are ones of the most difficult to treat wastewaters on account of their considerable amount of weakly biodegradable and often toxic substances such as dyes and heavy metals that including lead, copper, lead, silver, mercury, copper, nickel, chromium, zinc, cadmium and tinnickel. Others are detergents, surfactants and other additives. When released into the environment, these effluents exhibit toxic effects on many organisms and can also be very harmful for human health even at low concentrations. Toxic substances contained in industrial wastewaters should therefore be completely removed before being released into the environment (Gabriel Oze *et.al.*, 2006).

2.2.1 Ferrum (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. Ferrum is one of the most prevalent metals among various metal ions present in wastewater that are detected in the waste streams from industries.

Ferrum, is a metallic chemical element with the symbol Fe and atomic number 26. Iron is a group 8 and period 4 element in the periodic table and is therefore classified as a transition metal (Raghavan, 2004). Pure ferrum is a metal but is rarely found in this form on the surface of the earth because it oxidizes readily in the presence of oxygen and moisture. Iron are mostly occurs as Fe^{2+} (ferrous iron) and Fe^{3+} (ferric iron).

In the aspect of health, Fe can be useful and can also be hazardous based on the amount of it. Heavy metal ions such as Cu^{2+}, Zn^{2+}, Fe^{2+} are essential micronutrient for plant mechanism but when it present in excess it can become extremely toxic(Williams LE et al., 2000). Further Fe toxicity leads to diabetes mellitus, hemochromatosis, atherosclerosis and related cardiovascular diseases, hormonal abnormalities, and a dysfunctional immune system. Moreover, oxidative stress induced by excess ferrum may also cause brain damage (Gurzau et al., 2003).

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 also known as phytoextraction 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 no additional nutrient requirement, high efficiency in removing heavy metals, renewable biosorbent (lower cost), minimisation of chemical and biological sludge. In addition, it is also has possibility of metal recovery and low affinity with competing cations such as magnessium and calcium (Kratochvil and Volesky, 1998).

The biosorption process involves a solid phase which is sorbent or biosorbent; biological material and a liquid phase which is 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 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).

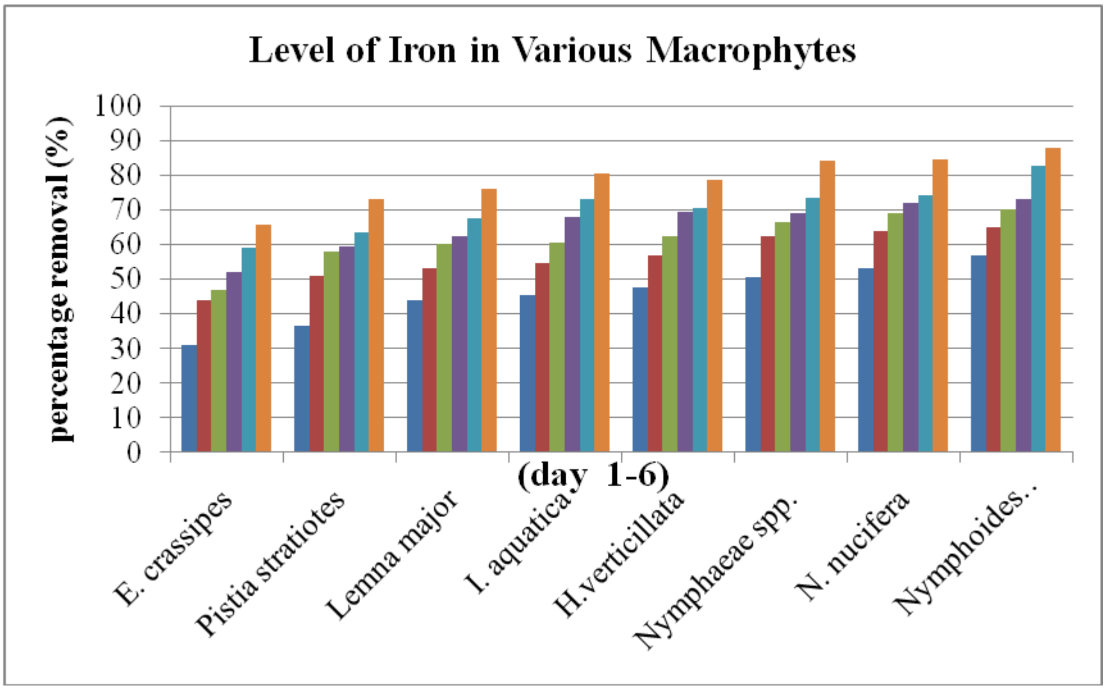

Figure 2.1: Level of Iron in Various Macrophytes (Begum et al., 2009)

Figure 2.1 is one from previous research which shows the potential of various aquatic plants in biosorption of ferrum. The percentage biosorption of the elements in the plants increase according to this sequence: Eicchornia crassipes (65%) > Pistia stratiotes (73%)> Lemna major (76%)> H.verticillata (78.5%)>Ipomoea aquatic(80.5%)> Nymphaeae spp (84 %) > Nelumbo nucifera(84.5) > Nymphoides indica (88%) in 6 days (Begum *et. al.*, 2009).

2.3.1 Biosorption Mechanism

Transport of the metal across the cell membrane yields intracellular accumulation, which is dependent on the cell's metabolism. This means that this kind of biosorption may take place only with viable cells. During non-metabolism dependent biosorption, metal uptake is by physico-chemical interaction between the metal and the functional groups present on the microbial cell surface. This is based on physical adsorption, ion exchange and chemical sorption, which is not dependent on the cells' metabolism. Cell walls of microbial biomass, mainly composed of polysaccharides, proteins and lipids have abundant metal binding groups such as carboxyl, sulphate, phosphate and amino groups. This type of biosorption, i.e., non-metabolism dependent is relatively rapid and can be reversible (Kuyucak and Volesky, 1988).

In the case of precipitation, the metal uptake may take place both in the solution and on the cell surface (Ercole et al., 1994). Precipitation may not be dependent on the cells' metabolism, if it occurs after a chemical interaction between the metal and cell surface.

2.3.1.1 Transport Across Cell Membrane

Heavy metal transport across microbial cell membranes may be mediated by the same mechanism used to convey metabolically important ions such as potassium, magnesium and sodium. Figure 2.2 shows the biosorption of Lead from soil using plants (Ilya Raskin, 2003).

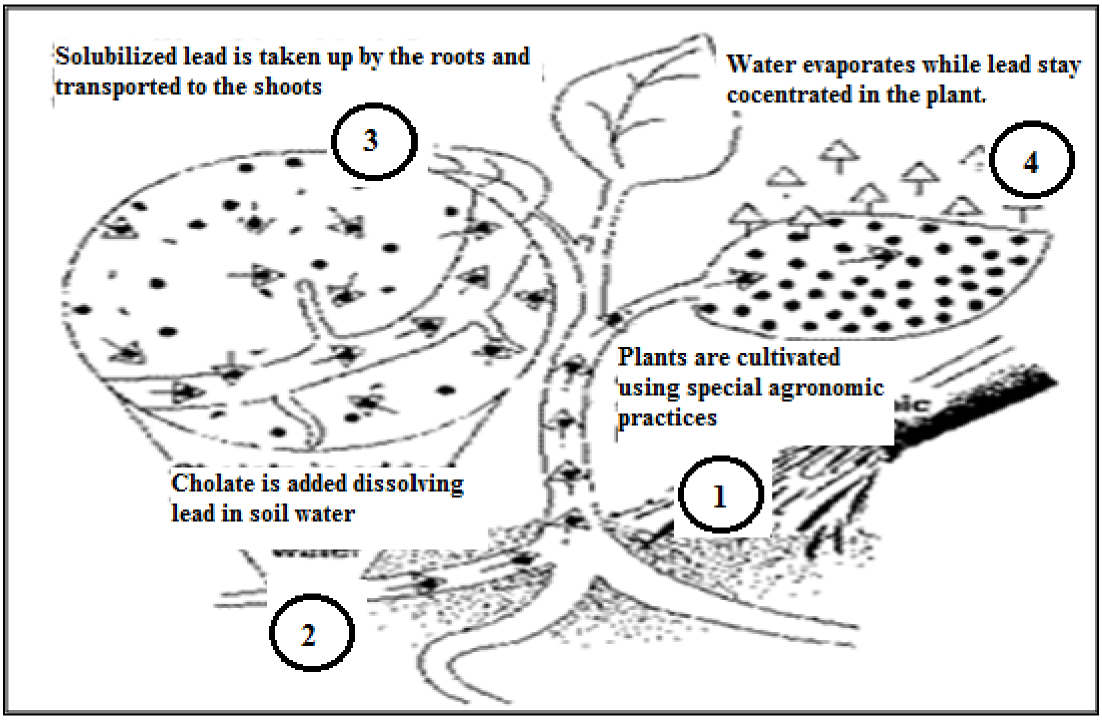

Figure 2.2 : Biosorption of Lead from Soil (Ilya Raskin, 2003)

The concept of transport across cell membrane mechanism is actually the same whether the plant grow on soil or on water. The roots of the plant will absorb water and heavy metals and transport them through the cell membranes to the shoots where the water will evaporate to the surrounding while the heavy metals will stay concentrated in the plant.

The metal transport systems may become confused by the presence of heavy metal ions of the same charge and ionic radius associated with essential ions. This kind of mechanism is not associated with metabolic activity. Basically biosorption by living organisms comprises of two steps. First, a metabolism independent binding where the metals are bound to the cell walls and second, metabolism dependent intracellular uptake, whereby metal ions are transported across the cell membrane. (Costa, et.al., 1990, Gadd et.al., 1988, Ghourdon et.al., 1990, Huang et.al., 1990., Nourbaksh et.al., 1994).

2.3.1.2 Physical Adsorption

In this category, physical adsorption takes place with the help of van der Waals' forces. Kuyucak and Volesky 1988, hypothesized that uranium, cadmium, zinc, copper and cobalt biosorption by dead biomasses of algae, fungi and yeasts takes place through electrostatic interactions between the metal ions in solutions and cell walls of microbial cells. Electrostatic interactions have been demonstrated to be responsible for copper biosorption by bacterium Zoogloea ramigera and alga Chiarella vulgaris (Aksu et al. 1992).

2.3.1.3 Ion Exchange

Cell walls of microorganisms contain polysaccharides and bivalent metal 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 $CO2^{+}$, Cu^{2+}, Cd^{2+} and Zn^{2+} resulting in the biosorptive uptake of heavy metals (Kuyucak and Volesky 1988). The biosorption of copper by fungi Ganoderma lucidium (Muraleedharan and Venkobachr, 1990) and Aspergillus niger was also up taken by ion exchange mechanism.

2.3.1.4 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.