HEAVY METALS REMOVAL FROM INDUSTRIES WASTEWATER BY USING SEAWEED THROUGH BIOSORPTION PROCESS

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A thesis submitted in partial fulfillment of

the requirements for the award of the degree of

Bachelor of Civil Engineering

Faculty of Civil Engineering & Earth Resources

University Malaysia Pahang

28 NOVEMBER, 2010

ABSTRACT

One of the systems in treatment the heavy metals in industrial waste is by using the seaweed through the biosorption process. Biosorption using brown seaweed is most applicable method. In this study, biosorption of Cooper, Ferum and zinc were investigated. The industrial wastewater samples chosen are from industry of KNM, ASTURI and PPSC. All these industries are contributed in Metal manufacturing ang cleaning process. Comparing on those three industries, KNM showed the impressive absorption of heavy metals because of their high concentration of heavy metals in wastewater. These heavy metals have been effectively removed from very dilute solutions by the dried biomass of some brown marine seaweed Ecklonia maxima, which is 77 % of ferum, 51 % of Zinc, 29 % of Copper in industrial wastewater form industry of KNM was removed successfully. Besides, metals removal efficiency of the adsorbent was investigated as a function of different absorption parameters. From the Atomic Absorption Spectrometer (AAS) indicated the optimum of biosorption process was 180 minute of contact time, pH 5, 1.5 % of adsorbent dose, and 600 μm of adsorbent particle size used for biosorption process. The analysis of biosequestering capacity of different seaweed to different metals and their suitability for bioremediation under the influence of effluent is discussed. Definitely, this dilute solution used as a control solution for guiding the real sample of industrial wastewater which applicable in environmental remediation.

ABSTRAK

Salah satu sistem dalam rawatan logam berat dalam sisa industri adalah dengan menggunakan rumput laut melalui proses biosorpsi. Biosorpsi menggunakan rumput laut dari jenis coklat adalah yang paling banayak digunakan. Dalam kajian ini, Biosorpsi Cooper, Ferrum dan Zinc diselidiki. Sampel air sisa industri yang dipilih adalah dari industri KNM, ASTURI dan PPSC. Semua industi ini terlibat di dalm process ppembuatan dan mencuci besi. Perbandingan pada tiga industri, KNM menunjukkan penyerapan logam berat yang berkesan di sebabkan oleh kepekatan sisa logam berat yang paling tinggi. Melalui hasilnya, logam-lagam berat ini ini telah berjaya dibuang dengan sangat berkesan dari cecair tiruan sisa industtri oleh Biojisim kering dari jenis rumput laut coklat iaitu maxima Ecklonia, sebanyak Logam berat ini telah dibuang dari berkesan sangat cair penyelesaian oleh Biojisim kering dari beberapa maxima Ecklonia coklat laut rumput laut, 77% daripada ion besi, 51% dari Zinc, 29% dari Tembaga dalam bentuk sisa industri industri KNM telah dihapuskan dengan berkesan. Selain itu, kecekapan penyisihan logam diselidiki sebagai fungsi dari beberapa parameter penyerapan yang berbeza. Hasil Atomic Absorption Spektrometer (AAS) menunjukkan optimum masa untuk proses biosorpsi adalah pada 180 minit pertama, pH 5, 1.5% dari dos adsorben, dan 600 μm saiz zarah adsorben digunakan untuk proses biosorpsi. Analisis kapasiti biosequestering rumput laut yang berbeza untuk logam yang berbeza dan kesesuaian mereka untuk bioremediasi bawah pengaruh efluent yang berbeza dikaji. Semestinya, cecair tiruan yang digunakan adalah sebagai larutan kawalan untuk mengawal proses rawatan sisa industry dimana proses ini boleh di adaptasi kepada pemulihan alam sekitar.

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LIST OF SYMBOLS / ABBREVIATIONS

AAS	-	Atomic Absorb Spectrometer
SEM	-	Scanning Electron Microscopy
ppm	-	Part per Million
%	-	Percentage
mg	-	Milligram
g	-	Gram
ml	-	Milliliter
m	-	Mass
mol	-	Molecular
µm	-	Micrometer
L	-	Liter
rpm	-	Revolutions per minute
pA	-	Pascal
pH	-	Measure of the acidity or basicity of a solution
°C	-	Celsius
v	-	Volume
q	-	Capacity

C_i	-	Initial concentration
C_f	-	Final Concentration
Pb	-	Plumbum
Cd	-	Cadmium
Cu	-	Cuprum
Fe	-	Ferrum
Zn	-	Zinc
Ni	-	Nickel
Co	-	Copper
Cr	-	Chromium
NaOH	-	Sodium Hydroxide
H_2SO_4	-	Sulfuric Acid
BOD	-	Biochemical Oxygen Demand
COD	-	Chemical Oxygen Demand
EQA	-	Environmental Quality Act
WQA	-	Water Quality Act

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CHAPTER 1

INTRODUCTION

1.1 Background of study

An Industrial waste is generated directly by industries. Untreated industrial waste usually contains the metals and a large number of potentially harmful compounds. It is can case to environmental pollution and can affect the ecosystem. One of the systems in treatment the hazard in industrial waste is by using the seaweed through the Biosorption Process.

Therefore, various Seaweeds are found throughout the world's oceans and come in three basic colours such as Brown (Phaeophyta), Red (Rhodophyta), and Green (Chlorophyta). Brown and red seaweeds are almost exclusively aquatic life, but the vast majority of green-coloured seaweeds are freshwater and terrestrial. The brown colour of the Phaeophyta results from the dominance of the xanthophyll pigment fucoxanthin which masks the other pigments while the red colour of the Rhodophyta is due to the presence of the pigment phycoerythrin which reflects red light and absorbs blue light.

The green colour of the Chlorophyta comes from chlorophyll *a* and *b*. (M.A. Hashim., K.H. Chu., 2003)

Many of the studies on metal biosorption by seaweeds have largely been restricted to various species of brown seaweeds. On the other hand, green and red seaweed species have not been evaluated to any great extent. Thus, this study was aimed at screening the abilities of brown seaweed as biosorbent of heavy metals in industrial waste water.

1.2 Case Study

Biosorption processes are relatively easy to operate and possess several inherent advantages, including low cost, operation over a wide range of conditions and the possible reuse of biosorbents. Biosorption can be defined as the uptake of contaminants, via various physico-chemical mechanisms, including ion-exchange, adsorption, complexation, chelation and microprecipitation etc., by inactive/dead biological materials. *(Volesky B, Schiewer S., 1999)*

In treatment the hazard waste of industrial, biosorption using brown seaweed is most applicable. Based on the results from the reported of studies in biosorption, the best-performing species was selected to further studies in treatment the industrial waste.

1.3 Objective of Study

The objective of this study is:

- To propose a system of wastewater treatment for seaweed application in removal the heavy metals

1.4 Scope of Study

The scope of this study is to treatment the heavy metals in industrial waste water using seaweed through the Biosorption water treatment system from waste sample of industrial in Pahang. We found that many industrial factories have to remove the contaminants of heavy metals before discharge into river. Biosorption is the process which a common treatment and low cost process. The inherent advantages and applications of biosorption have been extensively reviewed by several investigators. Seaweeds have proved to be the most efficient and practical biomass for the removal of heavy metal ions from aqueous solutions

1.5 Problem Statement

The presence of heavy metals in the environment is major concern because of their toxicity and threat to plant and animal life. Many industries are responsible for the release of heavy metals into the environment through their wastewaters. These include pigment manufacturing, iron and steel production, mining and mineral processing, the non-ferrous metal industry, battery manufacture, the printing and photographic industries and metal-working and finishing processes (electroplating). In addition, considerable quantities of heavy metals can be released into the environment through routes other than in aqueous form in wastewaters. *(Brauckmann, B. M., 1990).*

This environmental problem has lead to extensive research into developing effective alternative technologies for the removal of these potentially damaging substances from effluents and industrial wastewaters. Furthermore moreover, recovery of heavy metals from industrial waste streams is becoming increasingly important to neutralize the hazard from the industrial waste and not harmful to plant and animal life.

1.6 Significance of the Study

From this research, we realize about the significant of industrial wastewater treatment. There have many types of treatment process but the selecting of economical and effective method must do many resources to pay the higher prevention to pollution.

The time-tested proverbs,'Prevention is better than cure' and 'Prevention pays' has enormous economic and ecological significance. There is great economic and

ecological wisdom in resorting to preventive measure rather than corrective measure for industrial waste management.

Beside we know the alternative to treatment the wastewater from the industries by using seaweed through absorption method. Although, in global, there have already some researcher found that this impressive alternative but it is not yet deployed in Malaysia. It is such of technologies in physicochemical treatment in remediation system.

According to Sinha (2000), "it takes resources to treat industrial wastewater and remove pollution, and pollution removal generates toxic residues. It takes more resources to dispose of this residue and, in the process, create more pollution". In remediation, it pays to prevent pollution at the 'beginning of the pipe' (BOP) by resorting to cleaner production technologies. With this technology, we found the pollution prevention and the environmental will safe from harmful of heavy metals.

1.7 Expected Result

Expected result from this project is the efficiency of seaweed to remove heavy metals from the industrial waste water is recognized. The parameter from synthetic analysis will be conducting the industrial wastewater treatment.

From the analysis then the waste water treatment system for industrial will be proposed. The analysis will be comparing with the *Water Quality Act (WQA),* 1972

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

In this chapter discussed about the literature review on the industrial wastewater and devoted in treatment process. Besides, it also discussed on related information about this research such as wastewater heavy metal characteristic, type of seaweed and Biosorption process. Besides that, it also discuss on parameter of wastewater treatment and the effect of industrial wastewater pollution to aquatic and human life.

2.1 Wastewater

Wastewater may be defined as the combination of the liquid or water carried wastes removed from residences, institutions, commercial and industrial establishments, after they have been used for various cultural, physiological and technological purposes. Untreated wastewater contains organic matter, pathogenic microorganism, and a large number of potentially compounds. Usually the contaminants of wastewater is large different in different type of wastewater such as domestic, municipal and industrial wastewater.

There is an inherent difference between industrial and municipal wastewater. The number of contaminants in industrial wastewater can run from zero to about 100,000 ppm (parts per million), while those of municipal wastewater (sewage) occur within the rather narrow limits of 100 to 1,000 ppm. Industrial wastewater effluents carry more than 'twice as much degradable organic matter' as the municipal councils combined. Industrial wastewater deoxygenates at rates which vary from negative values to about 5 times the rates at which normal domestic sewage deoxygenates.

2.1.1 Domestic Wastewater

Domestic wastewater contains organic and inorganic matter in suspended, colloidal and dissolved form. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources. Wastewater or sewage can come from Human waste backwater from lavatories, Cesspit leakage, and Septic tank discharge

2.1.2 Industrial Wastewater

Industrial wastewater may contain several types of organic and inorganic matter in dissolved, suspended and colloidal states; may contain hazardous material and toxic compound like phenols, cyanides and compound that are potentially 'carcinogenic' or 'mutagenic' or it may contain acids and alkalis, heavy metals, flammable and even radioactive materials. Some industrial wastewater, such as that emanating from tanneries, vegetable and fruit canneries and slaughterhouses, sometimes discharge wastes containing microbes. Industrial wastewater may be heated, colored (often red, green, blue, black and brown) and give out pungent odors. (*Rajiv, K. S., Sunil H., 2004, p. 5*)

Rajiv, K. S., Sunil H., (2004, p. 6) stated that there are several sources of wastewater resulting from industrial operations. Most industrial processes generate polluted wastewater resulting from the contact of water with gases, liquids or solids. Major water using and wastewater generating industries are steel plants, paper mills,

chemical industries and petroleum refineries. Industries discharges wastewater from the following sources:

i. Wastewater from the production and manufacturing processes in the primary, manufacturing and services industries
   - There are highly polluted and contain most of the organic and inorganic contaminants. Some of which may be highly toxic. They need intensive treatment.

ii. Blow down wastewater from the cooling and boiler systems
   - The basic principle of cooling tower operation is that of 'evaporative condensation'. Water exposed to the atmosphere evaporates. As water is evaporated to reject the heat removed from the process to the atmosphere, the majority of contaminants in the water replenishing the system, both dissolved and suspended, become concentrated in the circulating cooling water.
   - The blow down wastewater from industries which is highly saline. It contains a relatively high level of dissolved and suspended solids, as well as dissolved water treatment chemicals.

2.1.2.1 Characteristic of Industrial Wastewater

Industrial wastewater contains several organic and inorganic matters, in dissolved, suspended and colloidal states. Industrial wastewater may contain toxic compounds and compounds that are potentially 'carcinogenic' or 'mutagenic'; it may contain acids, alkalis and even radioactive materials. Industrial wastewater may be heated, colored, and emit pungent odor. Besides, it may contain several hazardous materials, harmful ingredients and toxic chemicals like phenols, and cyanides, acids and

alkalis, flammables, heavy metals, radioactive substances, rags and feathers in addition to polluting loads. These wastes can cause as malfunctioning of treatment plants and sewer systems. As technological changes continue to occur in the manufacturing process, changes also occur in the compounds discharged and in the physical, chemical and biological characteristics of resulting wastewater. *(Rajiv, K. S., Sunil H., 2004, p. 10)*

2.2 Heavy Metals

Over the past two decades, the term "heavy metals" has been used increasingly in various publications and in legislation related to chemical hazards and the safe use of chemicals. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity. At the same time, legal regulations often specify a list of "heavy metals" to which they apply. Such lists may differ from one set of regulations to the other, or the term may be used without specifying which "heavy metals" are covered. In other words, the term "heavy metals" has been used inconsistently. This has led to general confusion regarding the significance of the term. There is also a tendency to assume that all so-called "heavy metals" have highly toxic or ecotoxic properties. This immediately prejudices any discussion of the use of such metals, often without any real foundation. (J. H. Dufus., 2002)

Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products. The heavy metals are transported by runoff water and contaminate water sources downstream from the industrial site.

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc. Most heavy metals are well-known toxic and carcinogenic agents and when discharged into the wastewater represent a serious threat to the human population and the fauna and flora of the receiving water bodies (*N.K. Srivastava., C.B. Majumder., 2007)*

Heavy metals of concern include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel (Ahalya et al., 2003). Heavy metal pollution in the aquatic system has become a serious threat today and of great environmental concern as they are non-biodegradable and thus persistent. Metals are mobilized and carried into food web as a result of leaching from waste dumps, polluted soils and water. The metals increase in concentration at every level of food chain and are passed onto the next higher level–a phenomenon called bio-magnification (Paknikar et al., 2003). Heavy metals even at low concentrations can cause toxicity to humans and other forms of life. The toxicity of metal ion is owing to their ability to bind with protein molecules and prevent replication of DNA and thus subsequent cell division (Kar et al., 1992). To avoid health hazards it is essential to remove these toxic heavy metals from waste water before its disposal. The effects on human health are quite evident from Table 2.1 below. (Alluri et al., 2007)

Table 2.1: Type of heavy metals and their effect on human health

Pollutants	Major sources	Effect on human Health	Permissible level (ppm)
Arsenic	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis	0.02
Cadmium	Welding, electroplating, pesticide fertilizer CdNi batteries, nuclear fission plant	Kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer	0.06
Lead	Paint, pesticide, smoking, automobil emission, mining, burning of coal	Liver, kidney, gastrointestinal damage, mental retardation in children	0.1
Manganese	Welding, fuel addition, ferromanganese production	Inhalation or contact causes damage to central nervous system	0.26
Mercury	Pesticides, batteries, paper industry,	Damage to nervous system, protoplasm poisoning	0.01
Zinc	Refineries, brass manufacture, metal Plating, plumbing	Zinc fumes have corrosive effect on skin, cause damage to nervous membrane	15

2.2.1 Heavy Metals in Industrial wastewater

Most of the point sources of heavy metal pollutants are industrial wastewater from mining; metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber andwood products, etc. The heavy metals are transported by runoff water and contaminate water sources downstream from the industrial site. All living things including microorganisms, plants and animals depend on water for life. Heavy metals can bind to the surface of microorganisms and may even penetrate inside the cell. Inside the microorganism, the heavy metals can be chemically changed as the microorganism uses chemical reactions to digest food. *(N.K. Srivastava., C.B. Majumder., 2008)*

The potential sources of copper in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production, and the fertilizer industry, etc. Since copper is a widely used material, there are many actual or potential sources of copper pollution. It is toxic to aquatic organisms even at very small concentrations in natural water. It is also a micronutrient in agriculture and can, therefore, accumulate in surface waters. Copper may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product such as food, water or drink. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well. For example, the excessive intake of copper results in its accumulation in the liver and produces gastrointestinal problems, and continued inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers.*(Y. Nuhoglu., E. Oguz.,2003)*