REMOVAL OF FERRUM(II) FROM INDUSTRIAL WASTEWATE BY USING DRIED WATER HYACINTH *Eichhornia Crassipes*

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ABSTRACT

Several contamination of industrial wastewater in Hunstman Tioxide (M) Sdn Bhd at Kemaman is Ferum (II). Ferrum (II) is non-biodegrable can be accumulated in living tissues, causing various diseases and disorders. The study is conducted to investigate the effects of biosorbent dosage, orbital shaker speed and contact time on the removal of Ferrum (II) from the industrial wastewater using non-living water hyacinth (*Eichhornia Crassipes)*. The experiment was carried out for six weeks, where one week was spent for collecting water hyacinth (*Eichhornia Crassipes)* and preparing the biosorbent. The experiments for investigating the effects of biosorbent dosage, orbital shaker speed, and contact time were run during the different range. This study of the effect biosorbent dosage was run at the selected range (0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.25, 0.20, 0.25, 0.30, 0.35, 0.40, 0.50, 0.55, 0.60, 0.65, 0.70, and 0.75 grams). Besides, the effect of orbital shaker speed experiment was done by shaking the samples at five different speed of orbital shaker (60, 90, 120, 150, and 175 rpm). Meanwhile, the effect of contact time was studied at the different contact time within three hours (0, 20, 40, 60, 80, 100, 120, 140, 160, and 180 minutes). All the samples were analyzed using the UV-Vis Spectrophotometer. From the result obtained, the optimum conditions for Ferrum (II) ions removal were at 0.75 g of biosorbent dosage, 175 rpm of orbital shaker speed and 180 minutes of contact time. As a conclusion, it is clearly shows that a biomaterial produced from dried water hyacinth can provide a simple, effective and yet cheaper method in removing Ferrum (II) from wastewater.

ABSTRAK

Beberapa sisa pencemaran di kilang Hunstman Tioxide (M) Sdn Bhd, Kemaman adalah ion besi (II). Ion besi (II) adalah ion yang tidak dapat diuraikan dalam rangkaian hidup, dan menyebabkan pelbagai penyakit dan gangguan. Penelitian ini dilakukan untuk mengetahui sukatan bio penyerapan, kelajuan penggoncang dan hubungan masa yang diambil untuk penyerapan ion besi (II) dari sisa kilang dengan menggunakan keladi bunting (*Eichhornia Crassipes)* yang dikeringkan. Penyelidikan dilakukan selama enam minggu, di mana satu minggu dihabiskan untuk mengumpul keladi bunting *(Eichhornia Crassipes)* dan pernyediaan bahan penyerapan. Kajian untuk mengetahui sukatan bahan penyerapan, kelajuan penggoncang dan hubungan masa akan dijalankan dengan menggunakan masa yang berbeza. Kajian keatas sukatan bahan penyerapan dijalankan pada had yang dipilih adalah (0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.1, 0.25, 0.20, 0.25, 0.30, 0.35, 0.40, 0.50, 0.55, 0.60, 0.65, 0.70, dan 0.75 gram). Selain itu, kesan daripada kelajuan penggoncang dilakukan dengan menggoncang sampel pada lima kelajuan yang berbeza iaitu (60, 90, 120 150 dan 175 rpm). Sementara itu, kajian keatas pengaruh masa telah dikaji pada masa yang berbeza selama tiga jam (0, 20, 40, 60, 80, 100, 120, 140, 160, dan 180 minit). Semua sampel dianalisis dengan menggunakan UV-Vis Spektrofotometer. Dari hasil yang diperolehi, nilai optimum untuk mengurangkan kandungan ion besi adalah sebanyak 0.75 g untuk sukatan bahan penyerapan, 175 rpm untuk kelajuan penggoncang dan 180 minit untuk masa yang diambil. Sebagai kesimpulan, itu jelas menunjukkan bahawa bahan yang dihasilkan dari keladi bunting yang kering dapat memberikan kaedah yang sederhana, berkesan dan murah namun dalam mengurangkan kandungan ion besi (II) dari air buangan.

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NOMENCLATURE

Al (III)	=	Aluminium ion
°C	=	Celcius
Cd	=	Cadmium
Ce	=	Final Concentration
Ci	=	Initial Concentration
Cr	=	Chromium
Cu	=	Cuprum
DNA	=	Deoxyribonucleic acid
Etc	=	Et cetera @ and other thing
Fe (II)	=	Ferrous ion
Fe(III)	=	Ferric ion
G	=	Gram
H_2O_2	=	Hydrogen peroxide
Kg	=	Kilogram
LD	=	Lethal Dose
mg	=	Milligram
min	=	Minute
mL	=	Milliliter
Ni	=	Nickel ion
Pb	=	Plumbum ion
RPM	=	Revolution Per Minute
Si (IV)	=	Silica ion
Zn	=	Zinc ion
%	=	

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CHAPTER 1

INTRODUCTION

Nowadays, heavy metals are among the most important pollutants in source and treated water, and are becoming a severe public health problem. Industrial and municipal wastewaters frequently contain metal ions. Industrial waste constitutes the major source of various kinds of metal pollution in natural water. Heavy metal ions are reported as priority pollutants, due to their mobility in natural water ecosystems and due to their toxicity. The heavy metal ions are stable and persistent environmental contaminants since they cannot be degraded and destroyed. These metal ions can be harmful to aquatic life and water contaminated by toxic metal ions remains a serious public health problem for human health. Heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation (Ayhan *et al.,* 2008).

The presence of copper, zinc, cadmium, lead, mercury, iron, nickel and others metals, have a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded. Many methods of treatment for industrial wastewater have been reported in literature. Amongst these methods are neutralization, precipitation, ion exchange and adsorption (Ayhan *et al.,* 2008). For low concentrations of metal ions in wastewater, the adsorption process is recommended for their removal. The process of adsorption implies the presence of an "adsorbent" solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap (Ayhan *et al.*, 2008).

Wastewater is the flow of used water from a community. The wastewater discharges will vary from one location to another location depending upon of population and industrial sector served, land uses, groundwater levels, and degree of separation between storm water, and sanitary wastes. The wastewater includes typical waste from kitchens, bathrooms, laundries and factories. Wastewater contains heavy metals such as Cadmium (II), Arsenic (III), Chromium (III), Lead (II), Nickel (II), Ferrum (II) and other metals.

Ferrum (II) is one of the vital elements for humans and nature. Nevertheless, high doses of Ferrum(II) 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).

Water hyacinth (*Eichhornia crassipes*) is a noxious freshwater weed with flourishing roots and is listed as one of the world's worst aquatic plants. Its high productivity and toleration of considerable variation in nutrients, temperature and pH levels have led to many environmental and economic problems, such as reduction of biodiversity, interference with navigation, irrigation and power generation. In the scenario of reusing wastes for wastewater treatment, roots of water hyacinth were employed as a biosorbent material to decontaminate wastewater that contains Ferrum (II).

Biosorption of heavy metals from wastewater is a relatively new process that has proven very promising in removal of contaminants from wastewater effluents. Biosorption is essentially a passive or physico-chemical binding of chemical species to biopolymers and the existence of this phenomenon has been reported for a broad range of biomass type. Biosorbent materials are available in abundance, low in cost and found to be more efficient for the removal of heavy metals. In this study, the potential of non-living water hyacinth in removing ferrous iron from industrial wastewater is investigated.

1.1 Problem Statement

Nowadays, many people and industries are aware about environmental problem. The amount of Ferrum (II) in industrial wastewater is increase and it can cause a serious problem to environment and human health. Ferrum (II) is non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders. Therefore, they must be removed before discharge and one of the methods of removal is through biosorption.

Biosorption is very effective in reducing the concentration of heavy metal ions to very low levels and use very inexpensive biosorbent materials. The biosorption has conventional treatment method include: low-cost, high efficiency and low chemical consumption. The purpose of this research is to use the water hyacinth *(Eichhornia Crassipes)* as biosorbent in removing Ferrum (II) because the water hyacinth is low cost and easily available material. This is due to water hyacinth fast-growth and the robustness of its seeds. Therefore water hyacinth can be a good uptake of Ferrum (II) compare to other chemical biosorbent such as activated carbon. Additionally, the metal sorption capacity of the dried biomass of aquatic plants has been recently investigated (Scheinder *et al.,* 1994). Dried biomass presents advantages for conservation, transport and handling, being able to be applied in waste water treatment plants as a simple sorbent material as compared to living systems.

1.2 Objective of the study

The main objective of this research is to study the ability of non-living Water Hyacinth (*Eichhornia Crassipes*) in removing Ferrum (II) from wastewater.

1.3 Scope of study

i. To determine the effect of biosorbent dosage towards the removal of Ferrum (II) from wastewater.
ii. To study the effect of rotary shaker speed in removing Ferrum (II) from wastewater.
iii. To investigate the effect of contact time towards the removal of Ferrum (II) from wastewater.

1.4 Rationale and Significance

The purpose of this study is to remove Ferrum(II) from industrial wastewater because Ferrum(II) may cause conjunctivitis, choroiditis, and if it contacts and remains in the tissues in our bodies. In this study, the dried water hyacinth has been used due to it is a noxious freshwater weed with flourishing roots and listed as one of the world's worst aquatic plants. Its high productivity and toleration of considerable variation in nutrients, temperature and pH levels have led to many environmental and economic problems, such as reduction of biodiversity, interference with navigation, irrigation and power generation (Zheng *et al.*, 2009). The plant has attracted worldwide attention due to its fast spread and congested growth. By conducting this research, the problems that caused by water hyacinth to the environment such as the blockage of canals and rivers can be solved. Besides that, the water hyacinth can be considered as a low-cost, high efficiency of metal removal from dilute solutions and easily available material for biosorbent (Kaustubha *et al.*, 2005).

CHAPTER 2

LITERATURE REVIEW

2.1 Water Hyacinth

Water Hyacinth (*Eichlornia Crassipes)* is an aquatic plant which can reproduce floating freely on the surface of fresh waters or can be anchored in mud. Figure 2.1 is shown the water hyacinth (*Eichlornia Crassipes)* plant. Plant size ranges from a few inches to metres in height. Its rate of proliferation under certain circumstances is extremely rapid and it can spread to cause infestations over large areas of water causing a variety of problems. It grows in mats up to 2 metres thick which can reduce light and oxygen, change water chemistry, affect flora and fauna and cause significant increase in water loss due to evapotranspiration (Intermediate Technology Development Group Website, 2010). It also causes practical problems for marine transportation, fishing and at intakes for hydro power and irrigation schemes. It is now considered a serious threat to biodiversity.

Figure 2.1: Water Hyacinth

Water hyacinth (*Eichhornia Crassipes)* is highly effectiv,e in removing excess nutrients, heavy metals, toxic metals, minerals and organic chemicals, and herbicides from polluted water (Soltan *et al.*, 2001). The plant has variable chemical contents which have been related to differences in study site, season, plant parts, and the chemical nature of the habitat (Soltan *et al*., 2001). In addition, water hyacinth *(Eichhornia Crassipes)* has been shown its effectiveness in removing a number of pollutants, including heavy metals from aqueous solution such as removal of cadmium, lead and mercury.

The water hyacinth is able to cross a freshwater body through salt water from another freshwater body while retaining its viability. It is also to cut pieces of the weed to re-colonize areas that previously cleared. Hence, the ability of the weed to reduce in size to enable it tides over unfavorable conditions.

2.2 Biosorbent

Absorption is a much preferable technique for the removal of heavy metals from polluted waters compared to others due to ease of operation and cost effective process (Hao *et al.*, 2009). Even though the most promising absorbent for absorption is activated carbon, it involves high operation costs and there is a need for regeneration after each absorption cycle (Marsh *et al.*, 2006). Hence, it is imperative to find an alternative with low-cost sorbent material to replace the high cost of activated carbon for water and wastewater treatment (Babel *et al.*, 2003). Figure 2.2 shows the example of biosorbent.

Figure 2.2: Dried water hyacinth is use as a biosorbent

Over the past two decades, numerous low-cost materials have been tested for their heavy metal sorption potential. Of these materials, plants waste materials, such as peat, rice husk, sugar beet pulp, banana pith, saw dust, plant leaves, bark, coir, etc., are causing scientist's interest in wastewater treatment due to broad availability and relative cheapness (Hao *et al.*, 2009).

Adsorption at a solid solution interface is an important means for controlling the extent of pollution due to metallic species of industrial effluents. Cost is an important parameter for comparing the sorbent materials. Hence, the usage of indigenous biodegradable resources for treating hazardous waste would be less expensive. The biodegradable resources such as sunflower stalks, rice husk, almond husk, sawdust, spent grain, etc. have been used as biosorbent in treating wastewater. Most of these materials contain functional groups associated with proteins, polysaccharides and cellulose as major constituents. Metal uptake is believed to occur through a sorption process involving the functional groups mentioned above. The cost of these biomaterials is negligible compared with the cost of activated carbon or ion-exchange resins which are in the range of approximately \$2.0–4.0 kg $^{-1}$ (Yasemin *et al.,* 2006). Tables 2.1 summaries a different types of biosorbent as a removal heavy metal from aqueous solution and wastewater.

Table 2.1: Types of biosorbent as a removal of heavy metal

Biosorbent	**Heavy Metal**	**References**
Tea Waste	Cu and Pb	Amarasinghe *et al*., 2007
Wheat Bran	Pb (II)	Yasemin *et al.,* 2005
Water Hyacinth	Nickel	Norhaslin 2008
Water Hyacinth	Cadmium	Puteri, 2008
Water Hyacinth	Cadmium and Zinc	Mei Lu *et al.*, 2004
Water Hyacinth	Chromium (VI)	Sujana *et al.*, 2008
Water Hyacinth	Lead	Tin Win *et al.*, 2003
Water Hyacinth	Pb(II), Cu(II), Zn(II), Cd(II)	Schneider *et al.*, 1995
Tamarink Bark and Potato Peel Waste	Fe(II)	Devi Prasad *et al.*, 2009
Papaya Wood	Copper (II), Cadmium (II), Zinc (II)	Asma *et al.*, 2005
Rice Husk Ash	Al(III), Si(IV), Fe(III)	Abo *et al.*, 2009
Cinnamomum camphora	Copper (II)	Chen *et al.*, 2009

leaves powder		
Tartaric Acid modified Rice Husk	Cuprum and Plumbum	Wong *et al.,* 2003
Dried Sunflower Leaves	Copper Ion	Benaissa *et al.,* 2006
Non living Ulva Seaweed	Cd, Zn, Cu, Cr and Ni	Suzuki *et al.,* 2005
Maize (*Zea mays*) wrapper	Zinc (II)	Adesola *et al.,* 2008

2.3 Ferrum (II)

Ferrum (II) is considered as an aesthetic contaminant. Ferrous Ion (Fe (II)) gives water a disagreeable taste and produces an inky, black appearance when it combines with tea and coffee. It causes staining on laundries, fixtures and tableware. Ferrum (II) is usually discharged to the environment through the effluent of many industries such as basic steel, inorganic chemicals, alkalis, chlorine, fertilizers and petroleum refining (Devi Prasad *et al.,* 2009). Ferrum (II) is one of the vital elements for humans and for other forms of life. Nevertheless, high doses of Ferrum (II) 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.,* 2006). With pathological conditions it is known that Ferrum (II) metabolism and superoxide metabolism can exacerbate the toxicity of each other. Further Ferrum (II) toxicity leads to diabetes mellitus, atherosclerosis and related cardiovascular diseases, hormonal abnormalities, and a dysfunctional immune system. Moreover, oxidative stress induced by excess Ferrum (II) may also cause brain damage (Mahesh W. *et al.,* 2006).

2.3.1 Characteristic of Ferrum (II)

Ferrum(II) is a lustrous, ductile, malleable, silver-gray metal (group VIII of the periodic table). It is known to exist in four distinct crystalline forms. Ferrum(II) rusts in dump air, but not in dry air. It dissolves readily in dilute acids. Ferrum(II) is chemically active and forms two major series of chemical compounds, the bivalent Ferrum (II), or ferrous, compounds (Jayaweera et al., 2007.

2.3.2 Applications of Ferrum(II)

Ferrum(II) is the most used of all the metals, including 95 % of all the metal tonnage produced worldwide. Thanks to the combination of low cost and high strength it is indispensable. Its applications go from food containers to family cars, from screwdrivers to washing machines, from cargo ships to paper staples. Steel is the best known alloy of iron, and some of the forms that iron takes include: pig iron, cast iron, and carbon steel, and wrought iron, alloy steels, iron oxides.

2.3.3 Ferrum(II) in the environment

Ferrum(II) is believed to be the tenth most abundant element in the universe. Ferrum(II) is also the most abundant (by mass, 34.6%) element making up the Earth; the concentration of Ferrum(II) in the various layers of the Earth ranges from high at the inner core to about 5% in the outer crust. Most of this Ferrum(II) is found in various Ferrum(II) oxides, such as the minerals hematite, magnetite, and taconite.

The earth's core is believed to consist largely of a metallic iron-nickel alloy. Ferrum(II) is essential to almost living things, from micro-organisms to humans.

2.3.4 Health Effects of Ferrum(II)

Ferrum(II) can be found in meat, whole meal products, potatoes and vegetables. The human body absorbs Ferrum(II) in animal products faster than Ferrum(II) in plant products. Ferrum(II) is an essential part of hemoglobin; the red coluring agent of the blood that transports oxygen through our bodies.

Ferrum(II) may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in the tissues. Chronic inhalation of excessive concentrations of Ferrum(II) oxide fumes or dusts may result in development of a benign pneumoconiosis, called siderosis, which is observable as an x-ray change. No physical impairment of lung function has been associated with siderosis. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens. LD50 (oral, rat) =30 gm/kg. (LD50: Lethal dose 50. Single dose of a substance that causes the death of 50% of an animal population from exposure to the substance by any route other than inhalation. Usually expressed as milligrams or grams of material per kilogram of animal weight (mg/kg or g/kg) (Jayaweera et al., 2007).)

A more common problem for humans is iron deficiency, which leads to anaemia. A man needs an average daily intake pf 7 mg of iron and a woman 11 mg; a normal diet will generally provided all that is needed.

2.3.5 Environment Effects of Ferrum(III)

Ferrum (III)-O-arsenite, pentahydrate may be hazardous to the environment; special attention should be given to plants, air and water. It is strongly advised not to let the chemical enter into the environment because it persists in the environment.

2.4 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. The domestic water used for normal activity in homes, businesses and institutions. The domestic wastewater is readily treatable industrial. The character of industrial wastewater depends on the type of industry using the water. Some industrial wastewaters can be treated the same as domestic wastes without difficulty.

There's may contain toxic substances or high percentages of organic materials or solids which make treatment difficult. In such cases, the industrial plant may have to pretreatment its wastewater to remove these pollutants or reduce them to treatable levels before they are accepted into a general treatment facility. Storm: usually low in pollutants. Great amounts of storm water can interfere with treatment efficiency in two ways: Storm water may cause too much dilution of the wastewater. At the same time, it may cause hydraulic overloading of the plant. In most cases, wastewater systems now call for separate storm sewers.

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 is one of the most serious environmental problems. The major source of water pollution in the country is domestic wastewater discharge. The need for the provision of wastewater collection and treatment facilities has long been identified by Central Government as a part of its efforts to protect the environment and well being of the population. Implementation of wastewater treatment projects over the past decades was driven by Central Government because of its technical knowhow and capacity to provide funding. However, when these facilities were handed over to local government authorities to operate and maintain, the concerned government agency had difficulty to manage the facilities in a sustainable manner due to inadequate planning, budgeting and ownership (Simachaya *et al.*, 2009).

2.4.1 Characteristics of Wastewater

2.4.1.1 Physical Characteristics

Characteristics of wastewater are detected through the physical senses: temperature, odor, color, and feel of solid material. Fresh wastewater is turbid, grayish-white in color, and has a musty odor. Small particles of feces and paper are visible in the waste stream, but these will rapidly settle if the wastewater is quiescent. Fresh wastewater becomes stale in 2 to 6 hours, depending upon temperature, nature of materials present, and the addition of oxygen through turbulent flow (Susan *et al.*, 2004). Warm wastewater becomes stale more rapidly than cold wastewater. The addition of oxygen helps extend the time that wastewater will remain fresh. Stale wastewater is dark brown to black and has a pronounced hydrogen sulfide (rotten egg) odor. Table 2.2 shows the significant colors of wastewater. Frequently, gas bubbles will evolve from the surface. Carbon dioxide (a product of aerobic decomposition and necessary for the support of algae growth) and sometimes methane (a product of anaerobic decomposition which occurs during wastewater digestion) are found in wastewater.

Table 2.2: Significant colors in Wastewater

COLOR	PROBLEM INDICATED
Gray	None
Green, Yellow, or other	Industrial wastes not pretreated (paints, etc.)
Red	Blood, other industrial wastes, or TNT complex
Red or other soil color	Surface runoff into influent, also industrial flows
Dark brown to black	Hydrogen sulfide
Black	Septic conditions or industrial flows

(Source: Tin Win, 2003)

2.4.1.2 Chemical Characteristics

Wastewater is composed of organic and inorganic compounds as well as various gases. Organic components may consist of carbohydrates, proteins, fats and greases, surfactants, oils, pesticides, phenols, etc. Inorganic components may consist of heavy metals, nitrogen, phosphorus, pH, sulfur, chlorides, alkalinity, toxic compounds, etc.