REDUCTION OF Fe(II) AND Zn(II) USING FRESH EICHHORNIA CRASSIPES

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ABSTRACT

The high content of Iron(Fe) and Zinc(Zn) in the wastewater become one of the major problem to the industry because the they will contaminate the environment and furthermore the ecosystem. The ability of Eichhornia Crassipes as a heavy metal removal is investigated in this research. The objective of this research is to remove Fe(II) and Zn(II) from aqueous solution and to investigate the potential of Eichhornia Crassipes for reduction of Fe(II) and Zn(II). The fresh Eichhornia Crassipes is obtained from local lake in Gambang,Pahang. This research was run based on three parameter. These parameter are contact time, adsorbent dosage and pH. The absorbance of each parameter was analyzing using Ultraviolet-visible Spectroscopy. This research was run at various contact times such as 1 day, 2 day, 3 day, 4 day and 5 day. For effect of adsorbent dosage, different amount of adsorbent was use to absorb the heavy metal. This also applies to the effect of pH. Various value of pH in each aqueous solution was used. It was found out that, increasing the contact time will increase the removal Fe(II) and Zn(II) from aqueous solution. Increasing the number of plant also will increase the reduction of Fe(II)and Zn(II). Based on the data acquire, the Fe(II) and Zn(II) can be totally remove. This research also found out that Eichhornia Crassipes can remove Fe(II) from industrial wastewater up to 80 % removal.

ABSTRAK

Kandungan Fe(II) dan Zn(II) yang tinggi dalam air pembuangan menjadi salah satu masalah besar kepada industri kerana ia akan mencemarkan persekitaran dan seterusnya ekosistem. Kebolehan Eichhornia Crassipes sebagai pembuang logam berat disiasat dalam kajian ini. Objektif kajian ini ialah untuk membuang Fe(II) dan Zn(II) daripada larutan akues dan juga menyiasat kebolehan Eichhornia Crassipes dalam menurunkan Fe(II) dan Zn(II). Eichhornia Crassipes yang segar diambil daripada tasik tempatan di kawasan Gambang, Pahang. Kajian ini dijalankan berdasarkan tiga parameter. Parameter tersebut ialah pH , masa sentuhan, dan dos adsorbent. Absorban untuk setiap parameter dianalisis menggunakan Ultraviolet-visible spectroscopy. Kajian ini dijalankan pada pelbagai masa sentuhan seperti 1 hari, 2 hari, 3 hari, 4 hari dan 5 hari. Untuk efek dos adsorban, jumlah adsorban yang berbeza digunakan untuk menyerap logam berat. Hal ini juga diaplikasi untuk efek pH. Nilai pH yang pelbagai digunakan untuk larutan akues. Ini dapat diketahui dengan meningkatkan masa sentuhan akan meningkatkan perbuangan Fe(II) dan Zn(II) dari larutan akues. Menambah bilangan pokok juga meningkatkan penurunan Fe(II) dan Zn(II). Berdasarkan data yang diperolehi, Fe(II) dan Zn(II) boleh dibuang seluruhnya. Kajian ini juga mendapati Eichhornia Crassipes boleh membunag Fe(II) daripada air pembuangan industry sehingga ke 80 peratus.

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LIST OF ABBREVIATION

$Ca(OH)_2$	Calcium hydroxide
$CaSO_4$	Calcium sulphate
CO_2	Carbon dioxide
Cr	Chromium
Cu	Copper
DNA	Deoxyribonucleic acid
Fe	Ferum
$FeSO_4$	Ferum sulphate
H_2O_2	Hidrogen peroxide
HCl	Hydrocloric acid
Hg	Mercury
K	Sodium
Mg	Magnesium
Na	Natrium
NaOH	Natrium hydroxide
Ni	Nickel
$Ni(OH)_2$	Nickel hydroxide
$NiSO_4$	Nickel sulphate
NPDES	National Pollution Discharge Elimination System
Pb	Lead
UV	Ultra violet
WTP	Wastewater treatment plants
Zn	Zinc
$ZnSO_4$	Zind sulphate

LIST OF SYMBOL

°C	celcius
g	gram
$g.cm^{-3}$	gram per centimeter cubic
g/L	gram per litre
$g.mol^{-1}$	gram per mole
h	hour
$kJ.mol^{-1}$	kilojoule per mole
km^2	kilometer square
µ	micro
mg/L	milligram per litre
min	minute
nm	nanometer
%	percent
$	price
t	time
y	year

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Pollution of air, soil, and water with heavy metals is a major environmental problem. This is because metals cannot be easily degraded and the cleanup usually requires their removal (Soltan et al., 2003). Heavy metals are generally considered to be those whose density exceeds 5 g per cubic centimeter. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death (Barakat et al., 2010).

Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults (Tangjuank et al., 2008). Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater.

Different kinds of heavy metals exist in the different forms, so their treatment methods are also different. As for the treatment of heavy metal wastewater, many methods have been put forward at home and abroad, including chemical-treatment method, ion-exchange method, electrolytic method, adsorption method, reverse-osmosis method, electrodialytic method, physico-chemical method, evaporating concentration and biological treatment, etc. However, limited by economic and technical reasons, the method mostly adopted at home and abroad for the treatment of heavy metal currently is the chemical method of neutral precipitation (Ying et al. 2006).

The physico-chemical processes can be expensive when metals are found in relatively moderate concentrations. Biological methods may provide an attractive alternative to existing technologies. A review of lowcost sorbents showed high adsorption capacities some metals (Ismail et al., 2009). These sorbents included bark, chitosan, xanthate, zeolite, clay, peat moss, seaweed, dead biomass, and others. The practical limitation of the application has been examined. Heavy metals have been removed from industrial wastewaters by adsorption onto activated carbon. Adsorption of cadmium by activated carbon had been modelled by using the Langmuir and Freundlich isotherm expressions (Mahamadi et al.,2010).

Among plants that have been studied for their uptake of heavy metals from aquatic systems, Eichhornia crassipes has been shown to possess the ability for the sorption of several heavy metals (Jianbo et al., 2008). Previous researchers used a tracer technique and spectroscopy to study the distribution and chemical states of iron and cobalt in living E. crassipes cultivated with a nutrient solution containing isotopes of the metals. Their results showed that both metals tended to accumulate mainly in the roots of the weed. On studying the contribution of E. crassipes grown under different conditions to Fe-removal mechanisms in constructed wetlands (Mahesh et al., 2008).

1.2 Problem Statement

Mobilization of heavy metals in the wastewater due to industrial activities is become a major problem. This is because of the toxicity of these metals to human and other forms of life. Removal of toxic heavy metals from industrial wastewater is essential from the standpoint of environmental pollution control. One of the most rich heavy metal components in the wastewater is Iron and Zinc. The conventional wastewater treatment cost a lot of money because it consist many treatment stage such as precipitation, ion exchange, adsorption, solvent-extraction, liquid membrane and electrochemical process. Due to the problem, an alternative method for low cost adsorbent has been searching to replace the conventional method. Besides that, an unoptimalized used of biological adsorbent such as Eichhornia Crassipes inspired the industry to try this adsorbent.

1.3 Objective

i) To remove Fe(II) and Zn(II) from aqueous solution.

ii) To investigate the potential of Eichhornia Crassipes for reduction of Fe(II) and Zn(II).

iii) To observe the effect of pH, contact time and adsorbent dosage on reduction of Fe(II) and Zn(II).

1.4 Scope of Study

i) Reduction of Fe(II)and Zn(II) using Eichhornia Crassipes

ii) Investigate the effect process parameter on the reduction of Fe(II)and Zn(II)

iii) Use UV Visible Spectroscopy to analyze Fe(II) and Zn(II) initial and final concentration

1.5 Research Advantges

i) The main raw material fresh Eichhornia Crassipes can be easily be found in any river, lake or pond in Malaysia and do not require special treatment for their growth.

ii) The cost of this research is lower because the materials are easily to find and the equipment also common one that is used.

iii) The aqueous solution that used is ferum and zinc sulfate which is easily to prepare.

iv) The processes are environmental friendly.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of Iron and Zinc

Figure 2.1: Zinc

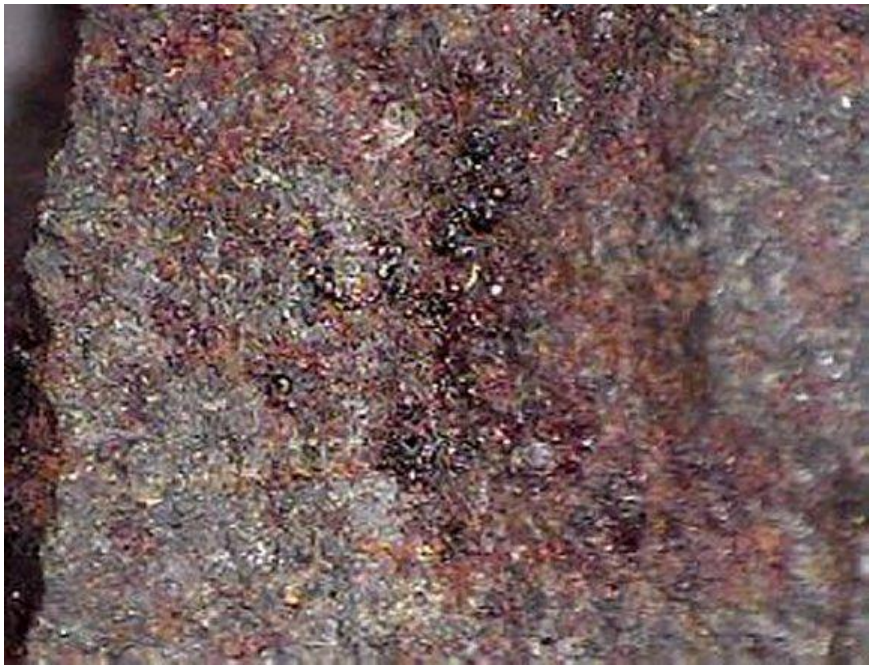

Figure 2.2: Iron

Iron is a chemical element with the symbol Fe and atomic number 26. It is a metal in the first transition series. It is the most common element in the whole planet Earth, forming much of Earth's outer and inner core, and it is the fourth most common element in the Earth's crust. It is produced in abundance as a result of fusion in high-mass stars, where the production of nickel-56 (which decays to iron) is the last nuclear fusion reaction that is exothermic, becoming the last element to be produced before collapse of a supernova leads to events that scatter the precursor radionuclides of iron into space.

Iron (Fe) is one of the vital elements for humans and for other forms of life. Nevertheless, high doses of Fe 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. 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. Since Fe is toxic and is a pollutant at higher concentrations developed countries such as the USA under the National Pollution Discharge Elimination System (NPDES) has enacted a permissible limit of 1.6 mg/L for inland surface waters. However, developing countries such as Sri Lanka are yet to enact a permissible limit to the discharging of Fe-rich wastewaters into inland surface waters and land despite the fact that high contamination of freshwater resources and groundwaters with heavy metals such as Fe due to various anthropogenic activities such as blue-print paper, paints and pigments manufacturing facilities, laundry bluing facilities and disposal of sludges from water treatment plants has been a major environmental problem in the industrial areas over the past decades (Mahesh et al., 2008).

Zinc metal is produced in all continents of the world and location of production is more closely in tune with zinc consumption than is the mining of zinc and the production of zinc concentrates – in other words zinc metal tends to be produced close to the market, not close to the original zinc mining source. Whilst it could be argued that production of zinc metal would be, for reasons of transport or for the easier disposal of waste, more appropriately carried out close to the mine, there are usually stronger reasons for locating smelters close to the metal market (Chakravarty et al 1997). A mine has a limited lifespan and is usually remotely located, and sourcing raw material for a smelter located at a (later closed) mine is difficult. In addition, smelters generally produce large quantities of sulphuric acid, which is costly to transport large distances, and a location close to other industries is desirable. Furthermore, large economic sources of energy are required for zinc production and these are less likely to be available in the more remote mining locations than where there is a developed infrastructure (Martin et al., 2002).

Zinc is a trace element that is essential for human health. When people absorb too little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc-shortages can even cause birth defects. Although humans can handle proportionally large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia (Liu et at., 2005) . Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc chloride can cau serespiratorydisorders In the work place environment zinc contagion can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity Zinc can be a danger to unborn and newborn children. When their mothers have absorbed large concentrations of zinc the children may be exposed to it through blood or milk of their mothers

The world's zinc production is still rising. This basically means that more and more zinc ends up in the environment. Water is polluted with zinc, due to the presence of large quantities of zinc in the wastewater of industrial plants. This wastewater is not purified satisfactory. One of the consequences is that rivers are depositing zinc-polluted sludge on their banks. Zinc may also increase the acidity of waters (Bi et al., 2006). Some fish can accumulate zinc in their bodies, when they live in zinc-contaminated waterways. When zinc enters the bodies of these fish it is able to bio magnify up the food chain. Large quantities of zinc can be found in soils. When the soils of farmland are polluted with zinc, animals will absorb concentrations that are damaging to their health. Water-soluble zinc that is located in soils can contaminate groundwater (Utgikar et at., 2004). Zinc cannot only be a threat to cattle, but also to plant species.

Plants often have a zinc uptake that their systems cannot handle, due to the accumulation of zinc in soils. On zinc-rich soils only a limited number of plants has a chance of survival. That is why there is not much plant diversity near zinc-disposing factories. Due to the effects upon plants zinc is a serious threat to the productions of farmlands. Despite of this zinc-containing manures are still applied. Finally, zinc can interrupt the activity in soils, as it negatively influences the activity of microrganisms and earthworms. The breakdown of organic matter may seriously slow down because of this.

Table 2.1: Properties of Iron

Atomic number	26
Atomic mass	55.85 $g.mol^{-1}$
Electronegativity according to Pauling	1.8
Density	7.8 $g.cm^{-3}$ at 20°C
Melting point	1536 °C
Boiling point	2861 °C
Vanderwaals radius	0.126 nm
Ionic radius	0.076 nm (+2) ; 0.064 nm (+3)
Isotopes	8
Electronic shell	[Ar] $3d^6$ $4s^2$
Energy of first ionisation	761 $kJ.mol^{-1}$
Energy of second ionisation	1556.5 $kJ.mol^{-}$
Energy of third ionisation	2951 $kJ.mol^{-1}$
Standard potential	- 0.44 V (Fe^{2+}/ Fe) ; 0.77 V (Fe^{3+}/ Fe^{2+})
Discovered by	The ancients

Table 2.2: Properties of Zinc

Atomic number	30
Atomic mass	65.37 $g.mol^{-1}$
Electronegativity according to Pauling	1.6
Density	7.11 $g.cm^{-3}$ at 20°C
Melting point	420 °C
Boiling point	907 °C
Vanderwaals radius	0.138 nm
Ionic radius	0.074 nm (+2)
Isotopes	10
Electronic shell	[Ar] $3d^{10}$ $4s^2$
Energy of first ionisation	904.5 $kJ.mol^{-1}$
Energy of second ionisation	1723 $kJ.mol^{-1}$
Standard potential	- 0.763 V
Discovered by	Andreas Marggraf in 1746

2.2 Heavy Metal in Wastewater

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries (Wan et at.2007).

Many heavy metals and their compounds have been found that are toxic, while some are also subjected to biomagnification. Environmental impact by heavy metals was earlier mostly connected to industrial sources. In recent years, metal production emissions have decreased in many countries due to legislation, improved cleaning technology and altered industrial activities (Michalis et al 2003). Today and in the future, dissipate losses from consumption of various metal containing goods are of most concern.

Therefore, regulations for heavy metal containing waste disposal have been tightened. A significant part of the anthropogenic emissions of heavy metals ends up in wastewater. Major industrial sources include surface treatment processes with elements such as Cu, Zn, Ni and Cr, as well as industrial products that, at the end of their life, are discharged in wastes (Sun and Shi, 1998).

Wastewater treatment plants (WTPs) are expected to control the discharge of heavy metals to the environment. Conventional processes in the field of wastewater treatment can be divided into two main phases: (1) generation of suspended solids from colloidal and dissolved solids by physical, chemical and biological means in addition to the already existing suspended solids; (2) separation of suspended solids by chemical and mechanical methods including sedimentation, flotation and filtration (Michalis et al 2003). As a result, effluents from municipal WTPs may contain metals at concentrations above background levels since heavy metals present in the influent wastewater concentrate in sludge, disposal of heavy metal-loaded sludge also represents an environmental hazard when used for agriculture or landfilling (Lazzari et al., 2000; Scancar et al., 2000).

In advanced countries, removal of heavy metals in wastewater is normally achieved by advanced technologies such as precipitation–filtration, ion exchange and membrane separation (Katsumata et al., 2003). However, in developing countries, these treatments cannot be applied because of technical levels and insufficient funds. Therefore, it is desired that the simple and economical removal method which can utilize in developing countries is established. Although the treatment cost for precipitation–filtration method is comparatively cheap, the treatment procedure is complicated. On the other hand, adsorption method such as ion exchange and membrane separation is simple one for the removal of heavy metals.

The increasing levels of these metals in the environment, their entry into food chain and the overall health effects are of major concern to researchers in the field of environmental biology. Cleanup (remediation) technologies available for reducing the harmful effects of heavy metal-contaminated sites include

i. excavation (physical removal),
ii. stabilization of the metals in situ, and
iii. the use of plants to extract the metals from the polluted site.

Each of these methods however has its advantages depending on the nature and size of the site being remediated. Excavation could be ideal when the site is small, dry land or wetland (not aquatic). Stabilization could be considered to be a more practical remediation approach especially when the site being remediated is an agricultural land. Phytoremediation is relatively cost effective and is of wide public acceptance. It can remediate a site without dramatically disturbing the landscape. It is an emerging technology that could be used to remediate wastewaters, wetlands, natural water bodies and agricultural soils polluted with heavy metals. It is potentially effective and applicable to a number of different contaminants and sites conditions (Lasat 2002).

Wastewater treatment plant (WTP) treats water from many sources. The two end products in the WTP are sludge and effluent. Sludge contains nutrients, mainly phosphorous and nitrogen. In Sweden the goal is that by 2010 at least 75% of the phosphorus recovered from waste and sewage sludge be recycled and used in agricultural or other productive lands without risk to health or the environment (Sorme et al., 2002). If sludge (with the nutrient phosphorous) is to be used, its pollutant content—some heavy metals, for example—must be minimized.

Historically, the sources of heavy metals to sludge have been industrial activities such as surface treatment with elements such as Cu, Zn, Ni and Cr. In recent years, industries have to a large degree moved out of the cities and the release of heavy metals and other compounds has decreased due to various pre-treatments of the effluent. This is reflected in the total amount of heavy metals in sludge. Generally, most of the metals in incoming water will end up in the sludge (except Ni); only a small amount is released via outgoing water (Sorme et at., 2002).

2.3 Background of Eichhornia Crassipes

Eichhornia Crassipes is an aquatic plant which can flourish and reproduce floating freely on the surface of water or it can also be anchored in mud. Eichhornia Crassipes is an important aquatic weed plant of sub-tropical regions of the world. Dense populations of this plant can render water ways navigable, reduce water flow and restrict commercial fishing (Ruben et al., 2004). On the positive side, they have been shown to absorb and accumulate toxic elements such as Cd, Hg, Zn, Cu, Pb and rare earth elements. The absorption by water hyacinth is depending on pH, volume, stirring, salinity of the solution, concentration of the element, exposure time, complexing agent, competing ions, and its root mass/number

Eichhornia crassipes also an aggressive aquatic weed throughout its range in virtually all tropical and subtropical areas of the world. This species usually has high