REMOVAL EFFICIENCY OF ZINC AND COPPER IN SYNTHETIC WASTEWATER USING CONSTRUCTED WETLAND

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JUDUL **REMOVAL EFFICIENCY OF ZINC AND COPPER IN SYNTHETIC WASTEWATER USING CONSTRUCTED WETLAND**

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A thesis submitted in fulfilment of the requirements for the award of the degree of Bachelor of Chemical Engineering (Biotechnology)

Faculty of Chemical & Natural Resources Engineering
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May 2008

DECLARATION

I declare that this thesis entitled "Removal Efficiency of Zinc and Copper in Synthetic Wastewater using Constructed Wetland" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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DEDICATION

Special Dedication to my family members that always love me,

Especially my father and my mother,

Abd Manap bin Abd Rani and Noormiah binti Omar

My friends, my fellow colleague

And all faculty members

For all your care, support and believe in me.

Sincerely

Abdul Zul Afif

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ABSTRACT

Constructed wetland has been widely used to provide "natural" ecotechnological treatment solutions for industrial wastewater. Heavy metals such as zinc and copper can cause serious health problem to human and wildlife. The objective of this research is to determine the removal efficiency of zinc and copper in constructed wetland. The scopes of these studies are to study the removal efficiency of zinc and copper as the quantities of plant are increased and to study the effect of pH change in constructed wetland. In this research, the batch mode system of constructed wetland was used and the wetland plant use was water lettuce (*pistia stratiotes*). For analysis, atomic absorption spectroscopy was used to determine the concentration of zinc and copper. The research was conducted within 7 days of treatment. Each parameter with varying quantity of plants and pH were setup in four containers including control. The control container containing no water lettuce (*pistia stratiotes*) to compare the effectiveness of constructed wetland using water lettuce (*pistia stratiotes*). The results for varying quantity of plant for zinc removal are 15 plants achieved highest removal efficiency (74.77 %), followed by 10 plants (69.79 %), 5 plants (32.99 %) and the control (6.06 %). For effect of pH experiment for zinc removal, the result is ph 7 achieved highest removal efficiency (80.41 %), followed by pH 5 (72.22 %), pH 9 (76.47 %) and the control (70.41 %). The results for varying quantity of plant for copper removal are 15 plants achieved highest removal efficiency (90.58 %), followed by 10 plants (86.32 %), 5 plants (81.35 %) and the control (47.95 %). For effect of pH experiment for copper removal, the result is ph 7 achieved highest removal efficiency (93.36 %), followed by pH 5 (92.43 %), pH 9 (85.38 %) and the control (63.47 %). The removal of copper is more effective than zinc removal. As a conclusion, constructed wetland using water lettuce show a good result in removal of zinc and copper in wastewater.

ABSTRAK

Tanah bencah buatan secara meluasnya telah digunakan untuk untuk merawat air buangan industri. Logam berat seperti zink dan kuprum boleh menyebabkan masalah kesihatan yang serius kepada manusia dan alam sekitar. Objektif kajian ini ialah menentukan tahap keberkesanan tanah bencah buatan dalam menyingkirkan logam berat zink dan kuprum dalam air tercemar. Skop kajian merangkumi penentuan keberkesanan tanah bencah buatan menggunakan bilangan pokok kiambang yang berbeza dan mengkaji kesan pH. Dalam kajian ini, sistem tanah bencah buatan yang digunakan ialah sistem kelompok. Untuk menganalisis, alat yang digunakan ialah *atomic absorption spectroscopy*. Kajian ini dijalankan selama 7 hari. Untuk setiap eksperimen, empat bekas plastik digunakan termasuk bekas kawalan yang digunakan untuk membandingkan keberkesanan sistem menggunakan pokok kiambang dengan sistem yang tidak menggunakan pokok kiambang. Dalam eksperimen memvariasikan bilangan pokok, merujuk kepada penyingkiran zink, keputusannya ialah 15 bilangan pokok menunjukkan penyingkiran tertinggi (74.77 %), diikuti dengan 10 bilangan pokok (69.79 %), 5 bilangan pokok (32.99 %) dan bekas kawalan (6.06 %). Sementara itu, untuk eksperimen kesan pH, nilai pH yang memberi penyingkiran tertinggi ialah pH 7 (80.41 %), diikuti dengan pH 5 (72.22 %), pH 9 (76.47 %) dan bekas kawalan (70.41 %). Dalam eksperimen memvariasikan bilangan pokok kiambang, merujuk kepada penyingkiran kuprum, keputusannya ialah 15 bilangan pokok menunjukkan penyingkiran tertinggi (90.58 %), diikuti dengan 10 bilangan pokok (86.32 %), 5 bilangan pokok (81.35 %) dan bekas kawalan (47.95 %). Sementara itu, untuk eksperimen kesan pH, nilai pH yang memberi penyingkiran tertinggi ialah pH 7 (93.36 %), diikuti dengan pH 5 (92.43 %), pH 9 (85.38 %) dan bekas kawalan (63.47 %). Penyingkiran kuprum adalah lebik baik daripada penyingkiran zink. Kesimpulannya, tanah bencah buatan menggunakan kiambang menunjukkan keputusan yang baik dalam menyingkirkan zink dan kuprum dalam air tercemar.

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LIST OF SYMBOLS

%	-	Percent
°C	-	Degrees
°F	-	Fahrenheit
BOD	-	Biological Oxygen Demand
Cd	-	Cadmium
$Cd(NO_3)_2$	-	Cadmium nitrate
cm	-	Centimeter
COD	-	Chemical oxygen demand
Cu	-	Copper
CWs	-	Constructed wetlands
FWS	-	Free water surface
HCl	-	Hydrochloric acid
HNO_3	-	Nitric acid
kPa	-	Kilo pascal (Pa)
L	-	Liters
mg	-	miligram
mm	-	milimeter
mM	-	Milimolar
NH_4	-	Ammonia
Ni	-	Nikel
nm	-	Nano meter
NO_3	-	Nitrate
Pb	-	Lead
$Pb(NO_3)_2$	-	Lead nitrate
SF	-	Surface flow
SS	-	Suspended Solid
Zn	-	Zinc

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Natural wetland systems have often been described as the “earth’s kidneys” because they filter pollutants from water that flows through on its way to receiving lakes, streams and oceans. Natural wetland can improve water quality, therefore engineers and scientists construct systems that replicate the functions of natural wetlands. Constructed wetlands are treatment systems that use natural processes involving wetland vegetation, soils, and their associated microbial assemblages to improve water quality. Constructed wetland can be considered as wetlands built to fulfill desired objectives. White (1998) defines a constructed wetland as "purpose built structures, utilizing the predominantly natural materials of soil water and biota, which perform the desired physical, chemical and biological processes and functions of natural wetlands to achieve desired objectives.". Constructing a wetland where one did not exist before avoids many of the environmental concerns and user conflicts associated with natural wetlands and allow design of the wetland for optimum wastewater treatment. Unlike natural wetlands, which are confines by availability and proximity of the wastewater source, constructed wetlands can be built almost everywhere, including lands with limited uses and other system components can be managed as required include vegetation (Reed *et al*., 1988).

Designing and building wetlands to treat wastewater is not a new concept. As many as 5,000 constructed wetlands have been built in Europe and about 1,000 are currently in operation in the United States. Constructed treatment wetlands, in some cases involving the maintenance of important wetland habitat, have become particularly popular in the Southwest, where the arid climate makes the wetland habitat supported by these projects an especially precious resource. Constructed wetland can significantly reduce biological oxygen demand (BOD), suspended solids (SS), and nitrogen, as well as metals like zinc and copper, traces organics and pathogens. The basic treatment mechanisms include sedimentation, chemical precipitation and adsorption, and microbial interactions with BOD, SS and nitrogen, as well as some uptake by the vegetation (U.S. EPA, 1988).

Constructed wetland is now widely used to provide "natural" ecotechnological treatment solutions for urban, industrial and agricultural waste-, storm-and drainage-waters (U.S. EPA, 1993, 2000; Kadlec and Knight, 1996; IWA, 2000). Construction and operating costs are low relative to mechanical treatment plants providing suitable land is available, and provision of wildlife habitat and green spaces may provides ancillary benefits. Much of the historical development and application of constructed wetland has occurred in America, Europe and Australia, but interest is now rapidly increasing in Asia.

Phytoremediation is widely viewed as an ecologically acceptable alternative as opposed to the conventional physicochemical techniques of heavy metals in polluted water or wastewater including zinc and copper. During disposal, a large amount of waste can increase the concentration of metals and become toxic. At higher concentration, heavy metals such as zinc and copper are known to cause many illness, damages or illness to human (Gunawardhana *et al.*, 2002; Gurzau *et al.*, 2003). Every industrial will be discharged heavy metals like zinc and copper everyday and it will increase from day to day.

Wetland plants are an important component in constructed wetlands. The roles that they can fulfill or to which they can contribute to are numerous. Wetland plants have adaptations that allow the transportation of oxygen to the roots and rhizomes (Brix, 1997). Plants that thrive and flower in soil that is saturated for a long period can be considered wetland plants (Sainty and Beharrell, 1998). Water lettuce (*pistia stratiotes*) is one of the wetland plants in group of floating plants (Wong, 2004). There are many cases that related to water lettuce and involving the plant in the same family with water lettuce (floating plants) such as water hyacinth and many more.

1.2 Objective of Research

The objective of this study is to determine the removal efficiency of heavy metals (zinc and copper) in synthetic wastewater using constructed wetland.

1.3 Scope of Study

The study will be focused on the percentage of removal of zinc and copper using constructed wetland. The constructed wetland designed with the same plant species, which is water lettuce (*pistia stratiotes*) species. This experiment also focused on the zinc and copper removal from synthetic wastewater using constructed wetland. The scopes for this study were:

a) To study the removal efficiency of heavy metals (zinc and copper) as the quantities of plant were varies.

b) To study the removal efficiency of heavy metals (zinc and copper) as the pH conditions were varies.

The experiment was carried out at Basic Science Laboratory, Faculty of Chemical Engineering and Natural Resources, Universiti Malaysia Pahang (UMP). The study was carried out within 7 days of treatment.

1.4 Problem Statement

Increasing development in industrial area contributes to the increasing of quantity heavy metals in wastewater that release to the environment. Most human activities and needs are closely related to water. First, the need of drinking water, then agriculture and industry, attract people build their homes near riverbanks. Today, the largest cities with highly developed industry are built along the river basins. Large quantities of heavy metal wastes were disposed as a result of industrial production which, when improperly stored, can spread to the environment. In Malaysia, as a developing country the industrial activities are grown rapidly and the quantity of wastewater is increasing.

Various anthropogenic activities in industries bring to the increasing in concentration of heavy metals especially zinc and copper. Heavy metals can cause bad effect to the human safety and health, materials and environment. As an example zinc can cause *zinc shakes* or *zinc chills* that can be induced by the inhalation of freshly formed zinc oxide meanwhile copper can cause *Wilson's* disease and *schizophrenia*.

The role of constructed wetland in such cases is very importance. The constructed wetland is the new technology that already used in others country but it still not localized in Malaysia. It is economic system and it potential to remove heavy metals from wastewater has been discovered recently. The water lettuce (*pistia stratiotes*).is one of free floating plant that on the list of additional species that can be used in constructed wetland (Beharrell, 1996). The ability of floating plant families to remove heavy metals is also well documented by Wang (2002) through their studies and clearly manifested that floating plant families are more efficient in the removal of heavy metals in wastewater compared to other families.

CHAPTER 2

LITERATURE REVIEW

2.1 Wetland

Wetlands are transitional areas between land and water. The boundaries between wetlands and uplands or deep water are therefore not always distinct. The term “wetlands” encompasses a broad range of wet environments, including marshes, bogs, swamps, wet meadows, tidal wetlands, floodplains, and ribbon (riparian) wetlands along stream channels.

All wetlands - natural or constructed, freshwater or salt - have one characteristic in common: the presence of surface or near-surface water, at least periodically. In most wetlands, hydrologic conditions are such that the substrate is saturated long enough during the growing season to create oxygen-poor conditions in the substrate. The lack of oxygen creates reducing (oxygen-poor) conditions within the substrate and limits the vegetation to those species that are adapted to low-oxygen environments. The hydrology of wetlands is generally one of slow flows and either shallow waters or saturated substrates. The slow flows and shallow water depths allow sediments to settle as the water passes through the wetland. The slow flows also provide prolonged contact times between the water and the surfaces within the wetland. The complex mass of organic and inorganic materials and the diverse opportunities for gas or water interchanges foster a diverse community of microorganisms that break down or transform a wide variety of substances. Most wetlands support a dense growth of vascular plants adapted to saturated conditions. This vegetation slows the water, creates microenvironments within the water column, and provides attachment sites for the microbial community. The litter that accumulates as plants die back in the fall creates additional material and exchange sites, and provides a source of carbon, nitrogen, and phosphorous to fuel microbial processes. Wetland can be divided into two types which are natural wetland and constructed wetland.

2.1.1 Natural Wetland

Natural wetland systems have often been described as the “earth’s kidneys” because they filter pollutants from water that flows through on its way to receiving lakes, streams and oceans (Figure 2.1). Because these systems can improve water quality, engineers and scientists construct systems that replicate the functions of natural wetlands.

Natural wetlands perform many functions that are beneficial to both humans and wildlife. One of their most important functions is water filtration. As water flows through a wetland, it slows down and many of the suspended solids become trapped by vegetation and settle out. Other pollutants are transformed to less soluble forms taken up by plants or become inactive. Wetland plants also foster the necessary conditions for microorganisms to live there. Through a series of complex processes, these microorganisms also transform and remove pollutants from the water. Nutrients, such as nitrogen and phosphorous, are deposited into wetlands from storm water runoff, from areas where fertilizers or manure have been applied and from leaking septic fields. These excess nutrients are often absorbed by wetland soils and taken up by plants and microorganisms. For example, wetland microbes can convert organic nitrogen into useable, inorganic forms (NO_3 and NH_4) that are necessary for plant growth and into gasses that escape to the atmosphere.

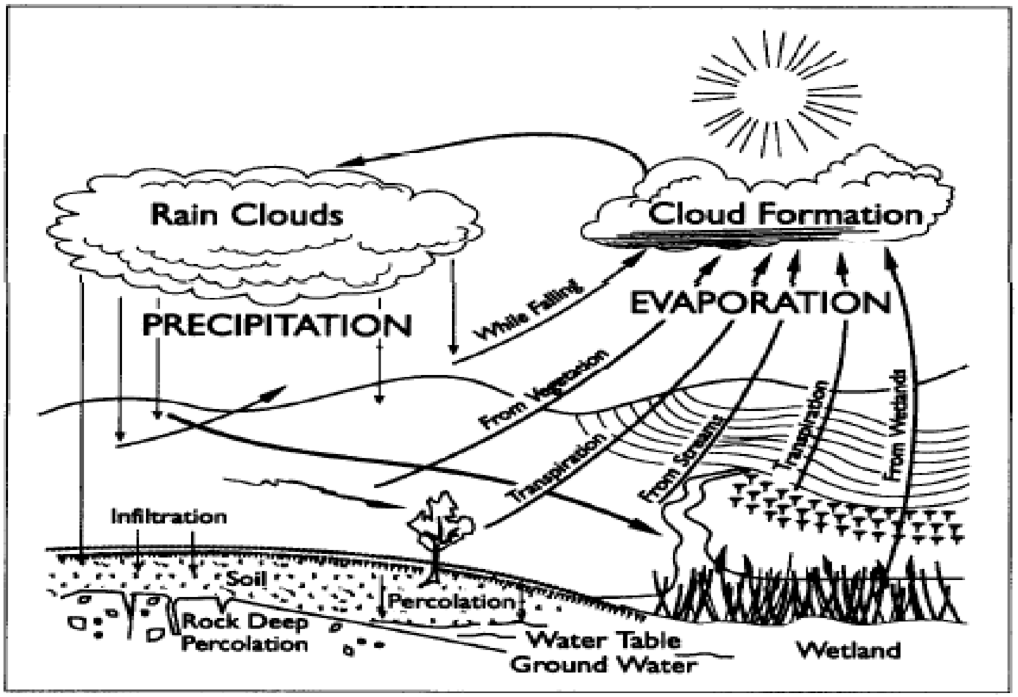

Figure 2.1: Drawing model for natural wetland (Noor, 2006)

2.1.2 Constructed Wetland

A constructed wetland is a shallow basin filled with some sort of substrate, usually soil or gravel, and planted with vegetation tolerant of saturated conditions. Water is introduced at one end and flows over the surface or through the substrate, and is discharged at the other end through a weir or other structure which controls the depth of the water in the wetland. A constructed wetland consists of a properly designed basin that contains water, a substrate, and, most commonly, vascular plants. These components can be manipulated in constructing a wetland. Other important components of wetlands, such as the communities of microbes and aquatic invertebrates, develop naturally. Constructed can be considered as wetland built to fulfill desired objectives. White (1998) defines a constructed wetland as “purpose built structures, utilizing the predominantly natural materials of soil water and biota, which perform the desired physical, chemical and biological process and functions of natural wetlands to achieve desired objectives” .

Constructing a wetland where one did not exist before avoids many of the environmental concern and user conflicts associated with natural wetland and allow design of the wetland for optimum wastewater treatment. Unlike natural wetlands, which are confined by availability and proximity of the wastewater source, constructed wetland can built most anywhere, including land with limited uses. Typically, a constructed wetland should perform better than a natural wetland of equal area since the bottom is usually graded and the hydraulic regime in the system is controlled. Process reliability is also improved because the vegetation and other systems component can be managed as required (Reed *et al*., 1988).

Constructed wetland is classified into two types: free water surface (FWS) with shallow water depth and subsurface flow (SF) or vegetated submerged bed (VSB) systems with water flowing laterally through the sand or gravel. The types are as follows:

2.1.2.1 Free Water Surface Systems (FWS)

These systems typically consists a basins or channels, with a natural or constructed subsurface barrier of clay or impervious geotechnical material to prevent seepage, soil or another suitable medium to support the emergent vegetation, and water at a relatively shallow depth flowing over the soil surface (Figure 2.2). The shallow water depth, low flow velocity and presence of the plant stalks and litter regulate water flow and, especially in long, narrow channels, ensure plug-flow conditions to minimize short circuiting (U.S. EPA, 1988).

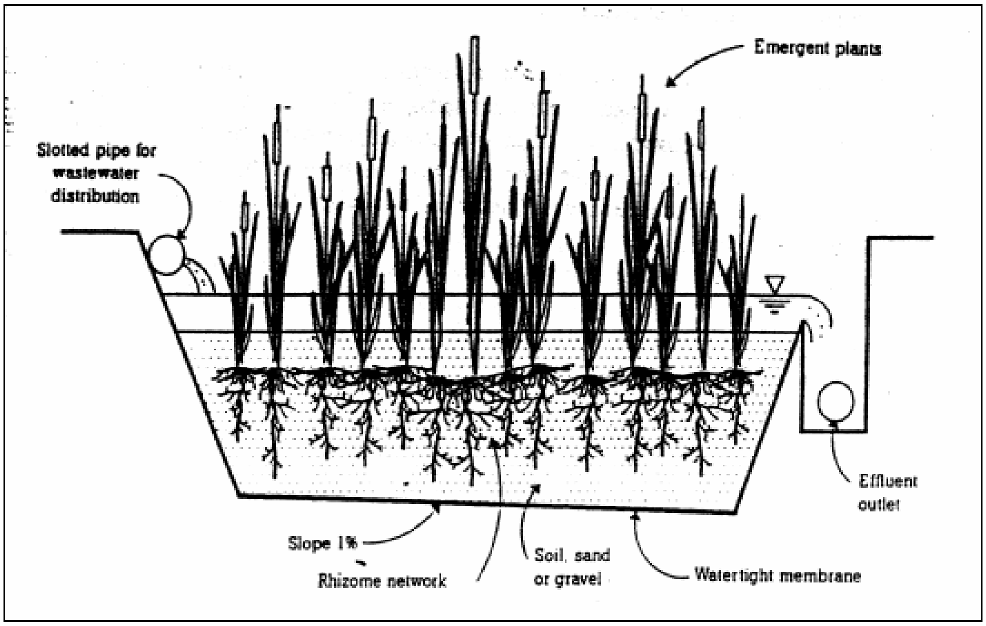

Figure 2.2: Free water surface systems (FWS) (Noor, 2006)

2.1.2.2 Subsurface Flow Systems (SF)

A subsurface flow system typically consists of a trench or a bed underlain by impermeable material to prevent seepage and containing a medium that supports the growth of emergent vegetation. The media used have included rock or crushed stone (10 to15 cm diameter), gravel, and different soils, either alone or in various combinations (Reed *et al.*, 1988). The wastewater flows laterally through the medium and is purified during the contact with the surfaces of the medium and the root zone of the vegetation. This subsurface zone is continuously saturated and therefore is generally anaerobic. However, the plants can convey an excess of oxygen to the root system, so there are anaerobic micro sites adjacent to the roots and rhizomes (Figure 2.3).

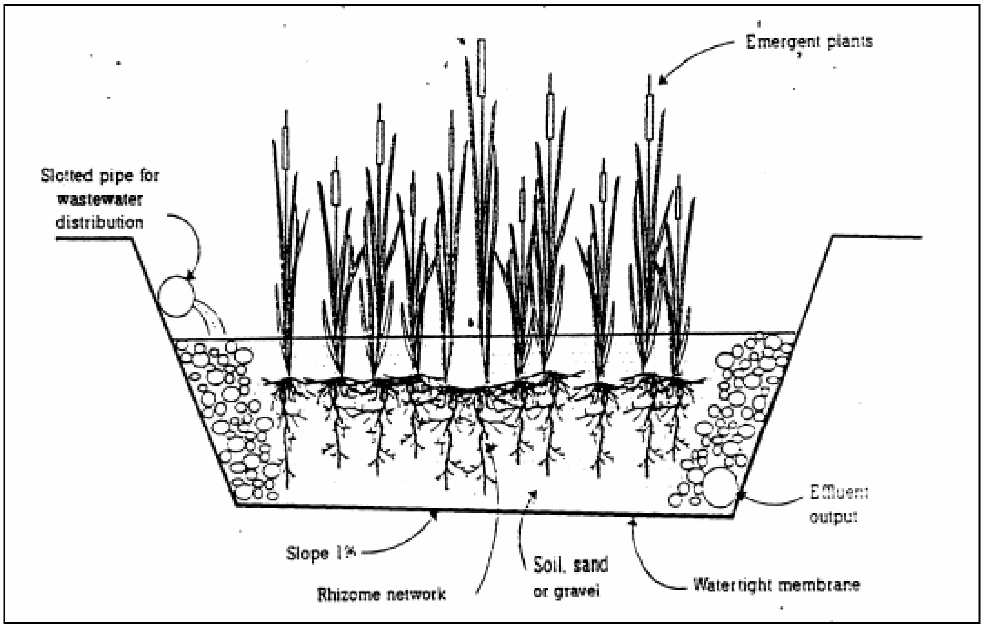

Figure 2.3: Subsurface flow systems (SF) (Noor, 2006)

Constructed wetland offer several potential advantages as a wastewater treatment process. These potential advantages include site location flexibility, less rigorous pre-application treatment, no alteration of natural wetlands, simple operation and maintenance, process stability under varying environmental conditions, lower construction and operating cost, and in the case of free water surface systems, the possibility to create a wildlife habitat. The potential problems with free water surface systems constructed wetland include mosquitoes. Start-up problems in establishing the desired aquatic plant species can be problem with free water surface systems and subsurface flow systems alike (U.S. EPA, 1988; Bastian *et al*., 1989). More advantages and disadvantages were illustrated in the Table 2.1.

Table 2.1: Advantages and disadvantages of constructed wetland (Wong, 2004)

Advantages	**Disadvantages**
▪ wetlands can be less expensive to build than other treatment options ▪ operation and maintenance expenses (energy and supplies) are low ▪ operation and maintenance require only periodic, rather than continuous, on-site labor ▪ wetlands are able to tolerate fluctuations in flow ▪ they facilitate water reuse and recycling ▪ they provide habitat for many wetland organisms ▪ can be built to fit harmoniously into the landscape they provide numerous benefits in addition to water quality improvement, such as wildlife habitat and the aesthetic enhancement of open spaces ▪ they are an environmentally-sensitive approach that is viewed with favor by the general public.	▪ they generally require larger land areas than do conventional wastewater treatment systems. Wetland treatment may be economical relative to other options only where land is available and affordable. ▪ performance may be less consistent than in conventional treatment. Wetland treatment efficiencies may vary seasonally in response to changing environmental conditions, including rainfall and drought. While the average performance over the year may be acceptable, wetland treatment cannot be relied upon if effluent quality must meet stringent discharge standards at all times. ▪ the biological components are sensitive to toxic chemicals, such as ammonia and pesticides ▪ flushes of pollutants or surges in water flow may temporarily reduce treatment effectiveness ▪ they require a minimum amount of water if there are to survive. While wetland can tolerate

	temporary drawdown, they cannot withstand complete drying ▪ the use of constructed wetlands for wastewater treatment and storm water control is a fairly recent development. There is yet no consensus on the optimal design of wetland systems nor is there much information on their long-term performance.

2.1.3 Wetland plants

Wetland plants have adaptations that allow the transportation of oxygen to the roots and rhizomes (Brix, 1997). This oxygen is needed not only for respiration in saturated soils by rot or rhizome, but also for the leakage of oxygen which prevents toxins from accumulating in the root zone under saturated conditions.

Although there are numerous definitions of a wetland plant, none are satisfactory as there are always exceptions that fall outside the definitions. However, plants that thrive and flower in soil that is saturated for long periods can be consider as wetland plants (Sainty and Beharrell, 1998). There are notable exceptions such as *Phragmites australis* (common reed), which grow in damp pasture land where soil is not saturated.

Generally, wetland plants can be divided into four groups as follows:

a) Littoral plants

These species thrive in periodically flooded land and usually grow among species that are not strictly wetland plants. Notable species in this group are some *juncus* spp. (rushes) and *cyperus* spp. (sedges).

b) Emergent plants

Emergent plants contain most of the wetland plant species; these species grow through the water column, examples include *eleocharis* spp. (spikerushs) and *scirpus* spp.

c) Submerged plants

Submerged plants are rooted or free-floating plants with their foliage entirely below the water surface. Examples include *potamogeton* spp. (pondweeds) and *vallasenairia* spp.

d) Floating plants

These float at the water surface. This type includes the duckweeds (*lemna* spp)., *pirodela* spp., water lettuce (*pistia stratiotes*) and *azolla* spp. and the introduced noxious weeds (*salvinia molesta*) and water hyacinth (*eichhornia crassipes*). It also includes the floating attached plants such as. marshworts (*nymphoides* spp) and. water lilies (*ymphaea* spp).

Wetland plants are an important component in constructed wetlands. The roles that they can fulfill or to which they can contribute to are numerous (Gersberg *et al*., 1986; Mitsch and Gosselink, 1993; Chambers *et al*., 1995). In surface water constructed wetland the roles of wetland plants can include:

a) Biochemical process, reduce nutrient and other pollutant concentrations

b) Influencing sediment deposition and physically filtering the sediment particles from the water column

c) Influencing hydrology and hydraulics in constructed wetlands by increasing flow roughness and transpiration

d) Providing shade, thus decreasing light availability for algal photosynthesis

e) Decreasing erosion by reducing wave energy and flow velocities while binding soil particles with their root systems

f) Providing a basis for wetland food chains and supplying shelter for invertebrates, amphibians, reptiles, bird and mammals

g) Improving visual amenity by adding color, texture, contrast and variety of patterns in landscape

In this research, the plant used is water lettuce (*pistia stratiotes*). Water lettuce belongs to the family *Araceae*. It is a monocotyledonous, free floating aquatic plant. The plant reproduces vegetatively and sexually. It is widely distributed in tropical and subtropical countries in lakes, rivers, ponds and ditches (Schmitz *et al*., 1993). Water lettuce floats on the water surface and will also grow on mud around the water's edge. It spreads by stolons; white root-like structures which link plants together at their bases. Each plant forms a rosette with the leaves held erect, rather like a mignonette lettuce. Leaves are pale yellow-green and fan-shaped, with 6 or more prominent veins on the underside. They are densely covered with short white hairs which trap air and provide buoyancy. Flowers are inconspicuous and are followed by small berry-like fruits, in the range of 5 till 8mm across. There are some characteristic will be shown in Table 2.2.

Water lettuce is preferred still or slows flowing fresh water, such as farm dams, lagoons on river floodplains, rivers and creeks (Figure 2.4). Water lettuce is frost tender and unlikely to thrive on the south coast. It may be native to the Northern Territory (having a pan-tropical distribution including Asia, Africa and equatorial America), where there are fewer natural controls on its spread. Water lettuce could blanket the water surface reducing light levels, temperature and oxygen in the water below. This has profound effects on communities of native plants and animals in the water. It may interfere with animal access for drinking water, human access for swimming and boating, reduce water quality and block pumps.

Lettuce is such a vigorous grower it sometimes uses up one or more nutrients in the pond. Lettuce and other floating plants also usually respond well to any of the micro nutrient solutions specially made for pond plants. There are a couple different varieties of water lettuce. The two most common are the Ruffled Water Lettuce and Jurassic Water Lettuce. ‘Ruffles’ has more wavy leaves and doesn’t grow as large as the other varieties. It is perfect for small container ponds. Jurassic Lettuce is a large form that can grow to be the size of a dinner plate. It doesn’t seem to grow as fast as the common variety.

Table 2.2: Characteristic of water lettuce

Common name	Water lettuce
Latin name	*Pistia stratiotes*
Hardiness	Zone 10
Size	Individual rosettes can range from 2” to 18” across.
Light	Does best with shade during the hottest part of the day, but can adapt to full sun.

Figure 2.4: Water lettuce

2.1.4 Treatment Process Mechanism

Constructed wetland can significantly reduce biological oxygen demand (BOD_5), suspended solids (SS), and nitrogen, as well as metals like zinc and copper, traces organics and pathogens. The basic treatment mechanisms include sedimentation, chemical precipitation and absorption, microbial interactions with BOD_5, SS, and nitrogen, as well as some uptake by the vegetation (U.S.EPA, 1998). In this topic, it will be focus in the heavy metals removals as the objectives. When dissolved metals entered a wetland ecosystem, possible removal mechanisms include: phytoextraction, hyperaccumulation, rhizofiltration, and phytostabilization.

2.1.4.1 Phytoextraction

Phytoextraction involves the removal of toxins, especially heavy metals and met- alloids, by the roots of the plants with subsequent transport to aerial plant organs (Figure 2.5). Pollutants accumulated in stems and leaves are harvested with accumulating plants and removed from the site. Phytoextraction can be divided into two categories: continuous and induced. Continuous phytoextraction requires the use of plants that accumulate particularly high levels of the toxic contaminants throughout their lifetime (hyperaccumulators), while induced phytoextraction approaches enhance toxin accumulation at a single time point by addition of accelerants or chelators to the soil. In the case of heavy metals, chelators like EDTA assist in mobilization and subsequent accumulation of soil contaminants. The ability of other metal chelators such to enhance metal accumulation has also been assessed in various plant species (Huang *et al*., 1997; Lombi *et al*., 2001). However, there may be risks associated with using certain chelators considering the high water solubility of some chelator toxin complexes which could result in movement of the complexes to deeper soil layers (Wu *et al*., 1999; Lombi *et al*., 2001) and potential ground water and estuarine contamination.

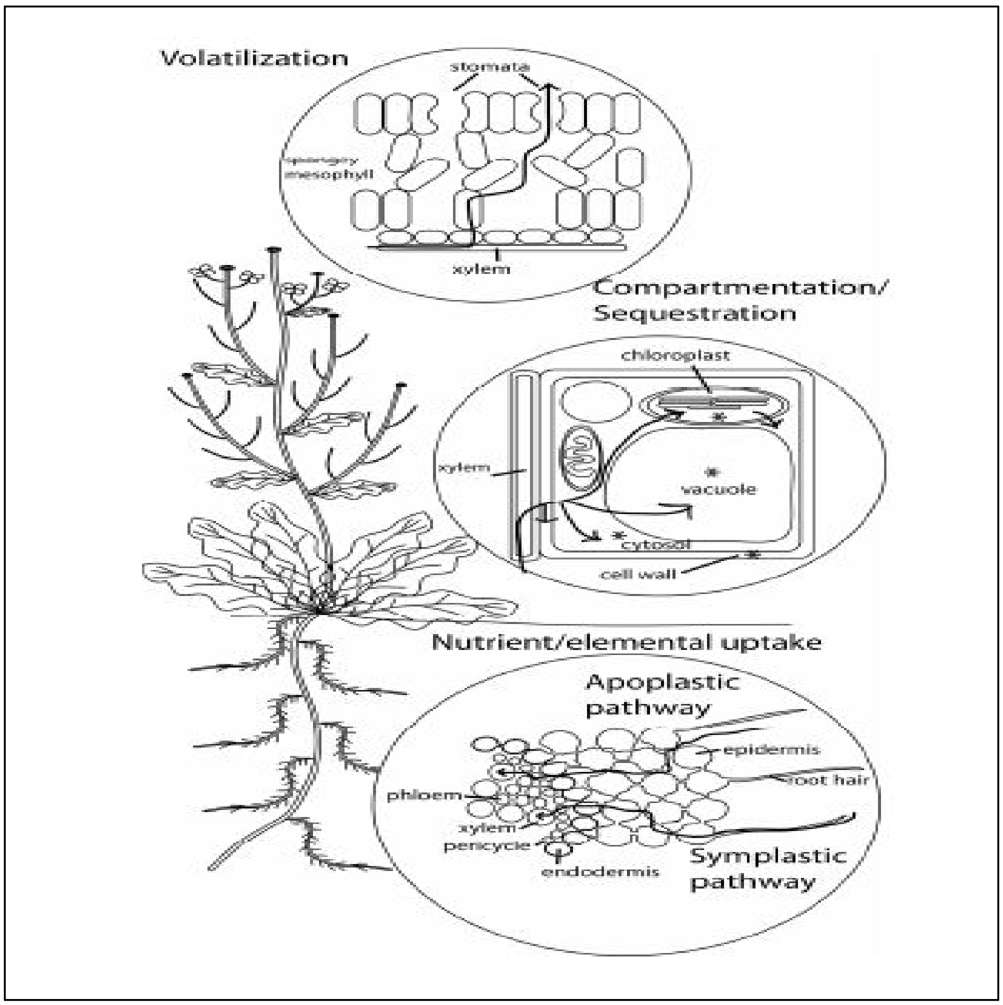

Figure 2.5: Pathway of nutrient or metal uptake in plants. (Noor, 2006)

2.1.4.2 Hyperaccumulation

Hyperaccumulators take up particularly high amounts of a toxic substance, usu- ally a metal or metalloid, in their shoots during normal growth and reproduction (Reeves 1992; Baker and Whiting 2002). Hyperaccumulation reported in senescing plants generally represents a breakdown of homeostatic mechanisms and is clearly not a function of normal growth processes, although such accumulations could be technologically useful. The metal or metalloid concentration that must be accumulated by the plant before it is designated a “hyperaccumulator” depends upon the particular metal or metalloid in question. In early hyperaccumulator studies, Brooks and coworkers (1977) defined nickel hyperaccumulators as those accumulating greater than 1000 micrograms nickel per gram dry weight in their leaves. The defined levels of these elements are typically at a concentration of one order of magnitude greater that those found in non-accumulator species (Salt and Kramer 2000). Hyperaccumulators are found in 45 different families, with the highest occurrence among the *Brassicaceae* (Reeves and Baker 2000). These plants are quite varied, from perennial shrubs and trees to small annual herbs. While tolerance is necessary for accumulation, evidence suggests that tolerance and accumulation are independent traits. Changes in the levels of these compounds and enzymes appear to be associated with Ni tolerance required for hyperaccumulation. It is noteworthy that this demonstration of Ni tolerance without accumulation represents an example of the distinction between metal tolerance mechanisms and metal hyperaccumulation mechanisms and supports previous findings showing partial independent genetic control of hyperaccumulation and tolerance.

2.1.4.3 Rhizofiltration

Rhizofiltration removes contaminants from water and aqueous waste streams, such as agricultural run off, industrial discharges, and nuclear material processing wastes. Absorption and adsorption by plant roots play a key role in this technique, and consequently large root surface areas are usually required. In closed systems with recirculating nutrients have exhibited the benefits of rhizofiltration and biofiltration using a variety of species (such as mosses and scented geraniums).

2.1.4.4 Phytostabilization

Erosion and leaching can mobilize soil contaminants resulting in aerial or water- borne pollution of additional sites. In phytostabilization, accumulation by plant roots or precipitation in the soil by root exudates immobilizes and reduces the availability of soil contaminants. Plants growing on polluted sites also stabilize the soil and can serve as a groundcover thereby reducing wind and water erosion and direct contact of the contaminants with animals. Plants with high transpiration rates, such as grasses, sedges, forage plants, and reeds are useful for phytostabilization by decreasing the amount of ground water migrating away from the site carrying contaminants (Suresh and Ravishankar ,2004). Combining these plants with hardy, perennial, dense rooted or deep rooting trees (poplar, cottonwoods) can be an effective combination.

2.2 Heavy Metals

Heavy or toxic metals are harmful to humans in small quantities. Toxic metals that may be dissolved in water include zinc, copper, arsenic, barium, cadmium, lead, mercury, and silver. These metals are concentrated by the food chain, thereby posing the greatest danger to organisms near the top of the chain (Peavy *et al.,* 1985).

2.2.1 Zinc

Zinc is a metallic chemical element with the symbol Zn and atomic number 30. Zinc is a moderately reactive, blue gray metal that tarnishes in moist air and burns in air with a bright bluish-green flame, giving off fumes of zinc oxide. It reacts with acids, alkalis and other non-metals. If not completely pure, zinc reacts with dilute acids to release hydrogen. The one common oxidation state of zinc is positive 2. From 100 °C to 210 °C (212 °F to 410 °F) zinc metal is malleable and can easily be beaten into various shapes. Above 210 °C (410 °F), the metal becomes brittle and will be pulverized by beating. Zinc is nonmagnetic.

Zinc is the fourth most common metal in use, trailing only iron, aluminium, and copper in annual production. Zinc is used to galvanize steel to prevent corrosion, parkerize steel to prevent rust and corrosion, used in alloys, die casting notably in the automobile industry and many more.

Zinc is an essential element, necessary for sustaining all life. It is estimated that 3,000 of the hundreds of thousands of proteins in the human body contain zinc prosthetic groups, one type of which is the so-called zinc finger. In addition, there are over a dozen types of cells in the human body that secrete zinc ions, and the roles of these secreted zinc signals in medicine and health are now being actively studied. Zinc is an activator of certain enzymes, such as carbonic anhydrase. Carbonic anhydrase is important in the transport of carbon dioxide in vertebrate blood. It is also required in plants for leaf formation, the synthesis of indole acetic acid (auxin) and anaerobic respiration (alcoholic fermentation).

Even though zinc is an essential requirement for a healthy body, too much zinc can be harmful. Excessive absorption of zinc can also suppress copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish. A recent example showed 6 micromolar killing 93 % of all daphnia in water. The free zinc ion is also a powerful Lewis acid up to the point of being corrosive. Stomach acid contains hydrochloric acid, in which metallic zinc dissolves readily to give corrosive zinc chloride. Swallowing a post 1982 American one cent piece (97.5 % zinc) can cause damage to the stomach lining due to the high solubility of the zinc ion in the acidic stomach. Zinc toxicity, mostly in the form of the ingestion of US pennies minted after 1982, is commonly fatal in dogs where it causes a severe hemolytic anemia. In pet parrots zinc is highly toxic and poisoning can often be fatal.

2.2.2 Copper

Copper is a chemical element with the symbol Cu and atomic number 29. It is a ductile metal with excellent electrical conductivity, and finds extensive use as an electrical conductor, heat conductor, as a building material, and as a component of various alloys. Copper is an essential trace nutrient to all high plants and animals. In animals, including humans, it is found primarily in the bloodstream, as a co-factor in various enzymes, and in copper-based pigments. However, in sufficient amounts, copper can be poisonous and even fatal to organisms.

Copper has played a significant part in the history of humankind, which has used the easily accessible uncompounded metal for thousands of years. Several early civilizations have early evidence of using copper. During the Roman Empire, copper was principally mined on Cyprus, hence the origin of the name of the metal as Cyprium, "metal of Cyprus", later shortened to Cuprum.

Copper has a high electrical and thermal conductivity, second only to silver among pure metals at room temperature. Copper is a reddish-colored metal and it has its characteristic color because of its band structure. In its liquefied state, a pure copper surface without ambient light appears somewhat greenish, a characteristic shared with gold. When liquid copper is in bright ambient light, it retains some of its pinkish luster.

Copper occupies the same family of the periodic table as silver and gold, since they each have one s-orbital electron on top of a filled electron shell. This similarity in electron structure makes them similar in many characteristics. All have very high thermal and electrical conductivity, and all are malleable metals. Copper is malleable and ductile, a good conductor of heat and, when very pure, a good conductor of electricity . Some application of copper is in piping, electronics industries, architectures, household products, coinage, biomedical application and chemical application.

Copper is essential in all plants and animals. Copper is carried mostly in the bloodstream on a plasma protein called ceruloplasmin. When copper is first absorbed in the gut it is transported to the liver bound to albumin. Copper is found in a variety of enzymes, including the copper centers of cytochrome oxidase and the enzyme superoxide dismutase (containing copper and zinc). In addition to its enzymatic roles, copper is used for biological electron transport. The blue copper proteins that participate in electron transport include azurin and plastocyanin.

It is believed that zinc and copper compete for absorption in the digestive tract so that a diet that is excessive in one of these minerals may result in a deficiency in the other. Thirty grams of copper sulfate is potentially lethal in humans. A significant portion of the toxicity of copper comes from its ability to accept and donate single electrons as it changes oxidation state.

An inherited condition called Wilson's disease causes the body to retain copper, since it is not excreted by the liver into the bile. This disease, if untreated, can lead to brain and liver damage. In addition, studies have found that people with mental illnesses such as schizophrenia had heightened levels of copper in their systems

Too much copper in water has also been found to damage marine life. The observed effect of these higher concentrations on fish and other creatures is damage to gills, liver, kidneys, and the nervous system. It also interferes with the sense of smell in fish, thus preventing them from choosing good mates or finding their way to mating areas.

2.3 Metal Analysis

For this research, the equipment that will be used is atomic absorption spectroscopy. The advantage of these equipment is that atomic spectra, and do not include broad absorption and emission bands. This makes it easier to select individual elements from a complex mixture, with much less chance of interfere. Atomic absorption is used for analysis of metals in air, water and solid samples (Kebbekus and Mitra, 1998).

2.3.1 Atomic Absorption Spectroscopy (AAS)

The atomic absorption spectrometer requires that the sample be atomized, broken down into individual atoms, before it is passed into the radiation beam for absorbance measurement. In flame atomic absorption, a liquid solution containing the sample is aspirated into a flame. This is achieved using a nebulizer, which mixes the sample with gaseous fuel and oxidant to form a uniformly mixed aerosol of the solution. Several different phenomena take place in the flame while the measurement is occurring. Each drop first dries to a small salt particle, then evaporates completely. The ion clusters heat further until they absorb enough energy to dissociate into free atoms in vapor state. The beam is passed through the flame and absorbance by the atomized species in the flame is measured. It should be noted that the absorbance is proportional to the concentration of ground state atoms in the flame (Kebbekus and Mitra, 1998).

Because the atomic absorption measurements in the flame are done in a dynamic system, it is especially important to be sure that the samples and standards are in similar matrix. The viscosity of the solutions, the behavior of the mist in the flame, its drying and evaporation characteristic, and even the droplet size, can all have an effect on the rate of formation atoms in the flame. In usual work, all standards and samples are made up in dilute acidic aqueous solutions. Where the characteristics of the sample are such that the standards may not be made in a similar matrix, the method of standards may not be made in a similar matrix, the method of standard addition is often used (Kebbekus and Mitra, 1998).

2.4 Synthetic Wastewater

The artificial wastewater or known as synthetic wastewater is defined as wastewater that made and not natural from industries or other sources. The references in making the artificial wastewater will be shown in Table 2.3.

Table 2.3: Parameter limitation for zinc and copper for standard A and standard B (Akta Kualiti Alam Sekeliling 1974 (Kumbahan dan Effluen-Effluen Perindustrian) 1979).

Metal	Unit	Standard A	Standard B
Zinc (Iron)	mg/L	2.0	2.0
Copper	mg/L	0.2	1.0

Standard A means that the factories or industrial activities use water sources from the river after the location of the factory meanwhile the standard B means that the factories or industrial activities use water sources from the river before the location of the factories (Figure 2.6).

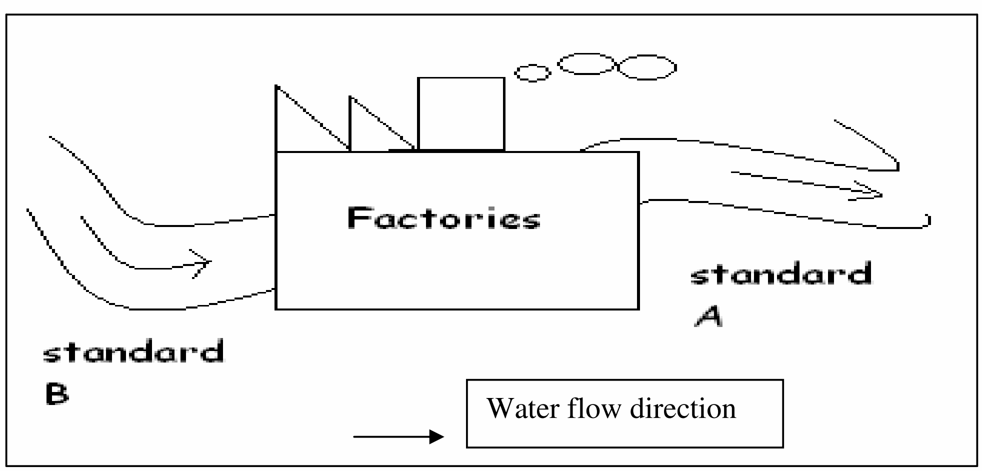

Figure 2.6: Definition model for standard A and standard B

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this research the methodology part was divided into 4 parts as shown in Figure 3.1. The experiment was carried out at open area near the Faculty of Chemical Engineering and Natural Resources (FKSSA) lab, Universiti Malaysia Pahang (UMP).

In this experiment, the focus of study was to evaluate the efficiency heavy metal removal in constructed wetland. The mode system used in constructed wetland was batch mode system. The wetland constructed using plastic basin without soil. The control or blank is setup without water lettuce (*pistia stratiotes*).

Experimental Set Up

- setup of experimental scale of constructed wetland
- making an artificial wastewater
- preparation of wetland plant water lettuce (*pistia stratiotes*)

Experimental Works
Scope of study:

- Varying number of plant used
- Varying pH condition

Sampling and preservation

- Samples are analyze using atomic absorption spectroscopy

Metal Analysis

- Based on parameters studied
- Removal efficiency of pollutants

Figure 3.1: Work flow

3.2 Experimental Setup

The purpose of experimental setup was to prepare the experiment before the experiment can be conducted.

3.2.1 Setup of Experimental Scale of Constructed Wetland

The model wetlands were setup in plastics basin or containers (0.43 m long, 0.315 m wide and 0.29 m high) each with volume used 15 litres. The experimental systems were operated in an open area with top cover and the temperature is about 29ºC which is surrounding temperature. The top cover allowed plants to receive sunlight about 8 hours daily and prevented rain water from altering the concentrations of the heavy metals in containers. This experiment was carried out as a batch study for a period of 7 days, where no effluent in or out of the tank in order to study the removal efficiency of zinc and copper respectively. The experiment started on 29th January 2008 till 28th February 2008.

3.2.2 Synthetic Wastewater Preparation

In the experiment, a synthetic wastewater was created to stimulate the typical concentration of heavy metals from the industrial wastewater. Both metals zinc and copper are prepared in stock solution zinc (II) sulphate and copper (II) sulphate and it will be mixed together to create synthetic wastewater. The stock solutions will be added until it achieves the required concentration. For 15 litres, 0.05 gram of zinc(II) sulphate and 0.3 gram of copper (II) sulphate is measured and then mix with deionized water until it reach 15 litres in the container. First of all, the containers were filled with 3 litres plant habitat water as nutrients and the remaining 12 litres were mixed with 0.05 gram $ZnSO_4$ and 0.3 gram $CuSO_4$. Besides that, zinc and copper mix solution added with other metals such as lead and cadmium to create the synthetic wastewater. Lead and cadmium are not interfering element for both zinc and copper. Lastly, the artificial wastewater was adjusted to the required pH values by adding sulfuric acid and hydrochloric acid.

3.2.3 Preparation of Wetland Plant

Water lettuces (pistia stratiotes) were collected from natural ponds at Perkampungan Batu Hitam, Beserah, Kuantan. The plants with approximately same size, height and weight will be chosen for this experiment. The plants were washed thoroughly in a running tap water and were grown and propagated hydrophonically with plant habitat water as nutrient in a container.

3.3 Experimental Work

In this research, the experimental works were divided into two parts based on the scope of this research. The experimental works for this research were varying quantity of plants used and varying pH conditions.

3.3.1 Varying the Quantity of Plants

The removal efficiency of zinc and copper were determined with the different quantity of plants used in constructed wetland. There were 4 plastic containers will be setup including control. The control was without plant used to compare the effectiveness between constructed wetland with *pistia stratiotes* and without *pistia stratiotes*. The quantities of plants that studied were 5, 10, and 15 plants. The constant variables in this study are the concentrations of zinc, concentration of copper, and pH values in solution. Therefore for each container (except control), 3.33 mg/L zinc, 20 mg/L copper, and pH 7 will be used.

3.3.2 Varying the pH Conditions

The removal efficiency of zinc and copper were determined with the different pH conditions used in constructed wetland. There were 4 plastic containers was setup includes control. The control without plant used to compare the effectiveness between constructed wetland with *pistia stratiotes* and without *pistia stratiotes*. The pH conditions that studied are 5, 7, and 9. The adding of sulfuric acid is needed to gives difference in pH of solution in each set of experiment. Alternatively, the pH of the solution can be adjusted by titration with diluted hydrochloric acid or sodium hydroxide prior to required conditions (Odjegba and Fasidi, 2004). The constant variables in this study are the number or quantity of plants and concentrations of zinc and copper. Therefore for each container (except control), 15 *pistia stratiotes* plants, 3.33 mg/L zinc, and 20 mg/L copper will be used.

3.4 Sampling and Preservation

The samples will be taken once in a day continuously until 7 days (1 week) using sample bottles. The bottles stored in the lab refrigerator under condition 4°C. 15 ml sample were collected using micropipette 5000 microlitres at 3 different places for one bottle sample at one container. The sample bottles are wrapped with an aluminum foil to ensure the sample cannot be exposing to the sunlight (degradation due to the expose). After that, the sample was taken to the Analytical Lab for analysis.

3.5 Metal Analysis

Zinc and copper concentration in wastewater will be determined using quantitative analysis using a flame atomic absorption spectrophotometer at a specific wavelength (Table 3.1). This metal was analyzed in the atomic absorption spectrophotometer using an air acetylene flame. If there any suspended solid present, the sample need to be digest with mixture of hydrochloric acid or nitric acid or using filter (Henna Obarska and Katarzyna, 1999)

Table 3.1: Analytical condition for zinc and copper (Henna Obarska and Katarzyna, 1999)

Zinc	**Copper**
Lamp current: 15 mA Wavelength : 248.3 nm Slit : 0.2 nm Burner head: standard type Burner height : 7.5 mm Flame : air- acetylene Oxidant gas pressure : 160 kPa Fuel gas flowrate: 2.0 L, min	Lamp current: 9 mA Wavelength : 279.6 nm Slit : 0.4 nm Burner head: standard type Burner height : 7.5 mm Flame : air- acetylene Oxidant gas pressure : 160 kPa Fuel gas flowrate: 2.2 L, min

The analytical conditions are constant during the experiment. Different analytical conditions will be used for measurement of different metals.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The result for this experiment was focus on the successful of removal efficiency of heavy metals in constructed wetland in several aspects based on scope of studies.

4.2 Result and Discussion

4.2.1 Varying the Quantity of Plants

The higher quantity of *Pistia stratiotes* plants used in batch mode system of constructed wetland, the higher removal efficiency of zinc and copper. The highest removal efficiency of heavy metal in this experiment is 15 plants followed by 10 plants, 5 plants and control.

According to the result showed in Figure 4.1, the system with 15 plants of water lettuce achieved highest removal efficiency of zinc which is 74.77 % and the efficiency decreased when the quantity of plants decreased. It is because the 15 plant system was able to take more zinc from the system compared to others. For 10 plants studies, the removal efficiency is 69.79 % followed by 5 plants which achieved 33 % for removal of zinc. The blank only achieved 6 % for 7 days. Previous study by Prayad (2004), the result is 79 % for zinc removal from industrial wastewater which is approximately to 74.77 %.

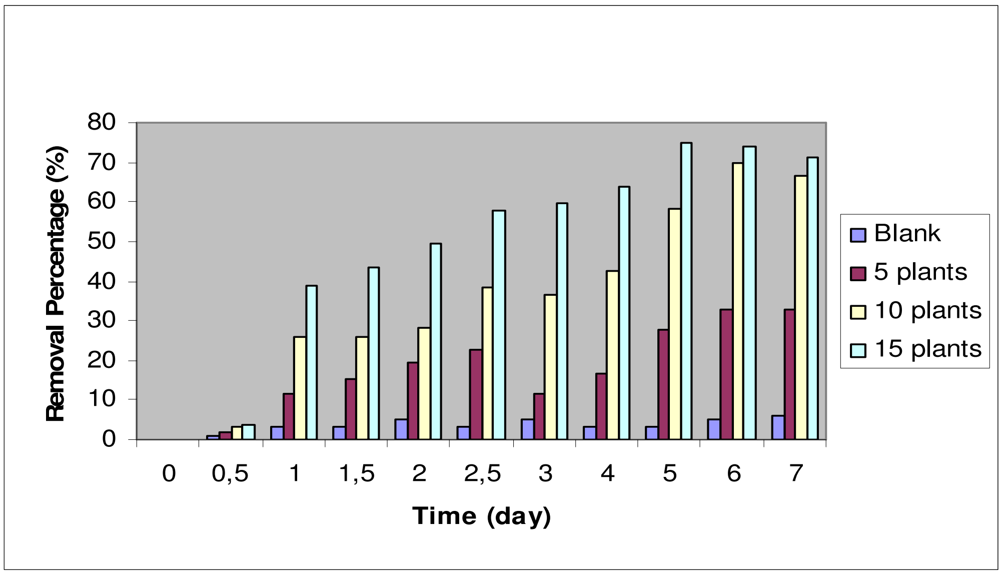

Figure 4.1: Graph of removal efficiency of zinc (varying quantity)

A few hours after the experiment start, there was no removal for blank, 5 plants, 10 plants and 15 plants but after 1 day the concentration of heavy metal in the constructed wetland were reduced. There are huge differences between 15 plants with the others.

For 15 plants, the removal is increase until day 5 and it start to fall in day 6 and 7 about 2 % per day. Same as 10 plants, the removal is increase until day 6 and in the day 7, the removal decrease about 3 %. For 5 plants, the removal is increase until day 2 and decreasing in day 3 about 10 % but from day 4 it increasing until day 7. There were horizontal line pattern for removal in blank studies. When the optimum value is achieved by the plant, the pattern is always decrease and constant after optimum value. The main reason for this pattern is the plant has enough heavy metal as nutrient for their growth and decrease until constant value (Prayad et al., 2004).

Figure 4.2 showed the result for copper removal and as expected, the pattern is same with the zinc. The 15 plants achieved the highest removal efficiency. Compared to the result of zinc removal, copper removal is more efficient because the highest removal is 92 % compared to zinc removal only 75 %. Jain (1989) stated that floating plants species such as water lettuce can accumulate copper to higher level. For 10 plants studies, the removal percentage is 90.38 % followed by 5 plants which achieved 82 % for highest removal. The blank only achieved about 48 %.

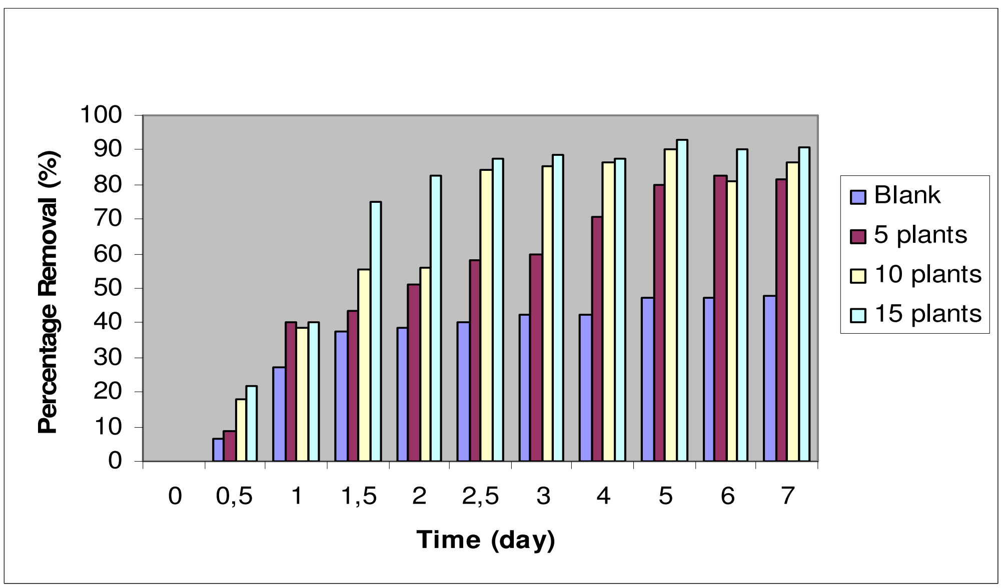

Figure 4.2: Graph of removal efficiency of copper (varying quantity)

For 15 plants, the removal is increase until day 3 and it begin to constant until day 7. Same as 10 plants, the removal is increase until day 2 and until the day 7, the pattern is constant. For 5 plants, the removal is increase until day 5 and constant until day 7. For the blank, the removal increasing until day 1 and start to constant till the end.

4.2.2 Varying the pH Conditions

Value of pH 5 is acidic meanwhile pH 9 is alkaline. Both of the value of pH is not suitable for growth of *pistia stratiotes*. Therefore both values of pH in the synthetic wastewater results in a lower number of plants survive. The pH 7 is suitable for growth of *pistia stratiotes* and the result should be approximately as 15 plants used in constant concentration of zinc and copper, and pH 7. Maine (2006) stated that pH toxicity threshold below 5 and over 9 so the condition between the values is consider safe for water lettuce growth.

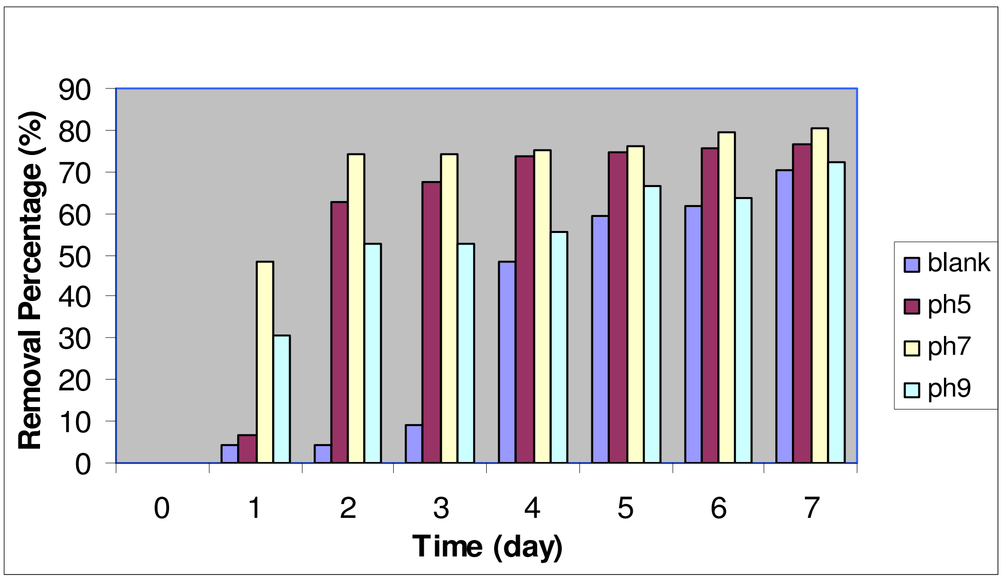

Figure 4.3: Graph of removal efficiency of zinc (pH effect)

According to the result showed in Figure 4.3, it stated that the pH 7 achieved highest removal efficiency of zinc compared to others. It can be conclude that pH 7 is the suitable condition in zinc removal. By using 15 plants of water lettuce in a week, system can remove the heavy metal to 80% removal efficiency. Meanwhile the pH 5 and pH 9 conditions can remove the heavy metal to 76 % and 72 % removal efficiency. For the blank, it only can remove the heavy metal up to 30 %. Previous study by Prayad (2004), the result is 82 % for zinc removal from industrial wastewater which is approximately to 80 %.

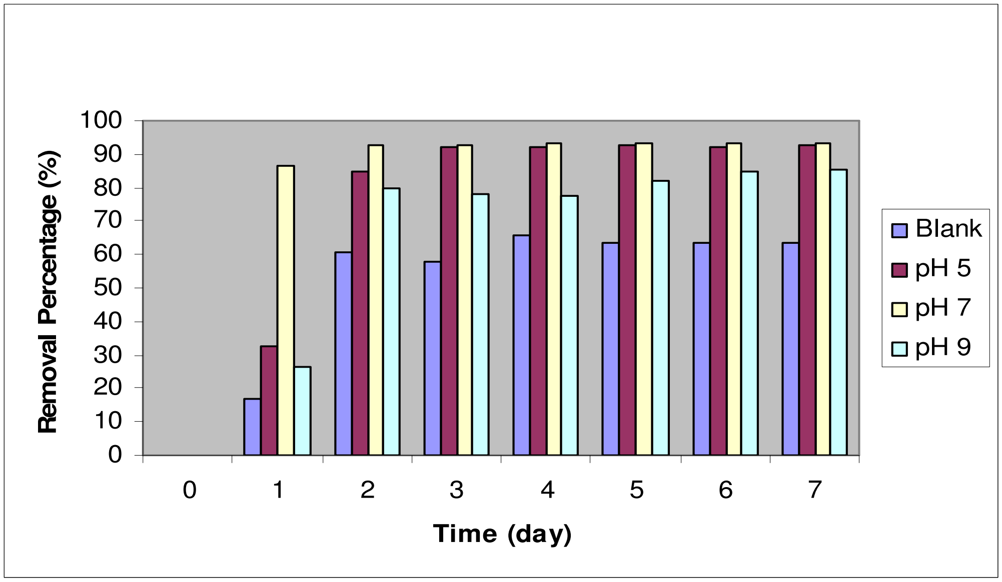

Figure 4.4: Graph of removal efficiency of copper (pH effect)

Figure 4.4 showed that pH 7 achieved highest removal efficiency in the copper removal. As expected, the result showed in zinc removal, pH 7 is also suitable in copper removal. By using 15 plants of water lettuce in a week, system can reduce the heavy metal up to 94% removal efficiency. Meanwhile the pH 5 and pH 9 conditions can remove the heavy metal up to 92 % and 85 % removal efficiency. For the blank, it only can remove the heavy metal to 64 %. Once again the result show the removal of copper is more effective than zinc. This result indicated that copper is accumulated more effectively in comparison to zinc (Kara *et al*., 2005)

4.2.3 Period of 7 days

The result that shows for 7 days, the removal efficiency will be increasing until it reach constant value and the remaining heavy metals will decrease. The result for both scopes of studies shows that the constant value is achieved before day 7 and this will prove that 7 days treatment is reliable (Kara *et al.,* 2005).

4.2.4 Heavy Metals

As a result, zinc removals in batch mode system of constructed wetland often less effective then removal of copper (Odjedba and Fasidi, 2003).

In the varying quantity of plants experiment, copper achieved 92 % removal meanwhile zinc achieved only 70 % removal. For the varying pH condition, copper achieved 93 % removal meanwhile zinc achieved only 80 % removal.

CHAPTER 5

CONCLUSION

5.1 Conclusion

According to the result in Chapter 4, the study about removal of zinc and copper in batch mode systems in constructed wetland using water lettuce (*pistia stratiotes*) can be consider as successful and useful study. The highest percentage can be achieved with 15 plants is 74.77 % removal of zinc and 92.94 % removal of copper meanwhile in pH 7 condition, the highest percentage can be achieved is 80.41 % removal of zinc and 93.36 % removal of copper. The potential to remove heavy metals like zinc and copper will attract many people from industries to use constructed wetland for their wastewater treatment. The great performance using water lettuce can make the plant to be one of the wetland plants which will be using in constructed wetland. The advantages using constructed wetland will make the system as alternative system in treatment industrial wastewater.

5.2 Recommendation

There were some recommendations for further successful studies as follow:

a) Another system can be used for designing the constructed wetland rather than batch system such as free water surface system or sub surface system.

b) Another plant species such as water hyacinth, duckweed and others wetland plants can be used to compare the effectiveness for each plant.

c) Add more heavy metals in a solution when making the synthetic wastewater to compare the percentage removal for each metal.

REFERENCES

Bastian, R. K., Shanaghan, P. E., and Thompson, B. P. (1989). *Use of wetland for municipal wastewater treatment and disposal- regulatory issues and EPA policies. In D. A. Hammer (Ed.), Constructed wetland for wastewater treatment: municipal. Industrial and agricultura*l. Chelsea: Lewis Publishers. 36-42.

Beharrell, M. A. (1996). Wetland Plants. In: Wong M. H: *Course Notes Constructed Wetlands Workshop. Quarantine Station North Head, Sydney*. Sydney: Department Land and Water Conservation. 24-26.

Beharrell, M. A. (2004) Planting Selection and Plant Establishment In Constructed Wetland in Tropical Environment. . In: Wong M. H. *Wetland ecosystem in Asia: function and management*. Netherlands: Elsevier B.V. 311-329.

Brix, H. (1997). Macrophyte-mediated oxygen transfer in wetlands: transport mechanism and rates. In: G. A. Moshiri (Ed.). *Constructed Wetland for water quality improvement*. , Boca Raton: Lewis Publishers.391-399.

C. Polpraset (2004). Constructed Wetland for Wastewater Treatment: Principles and Practices. In Wong M.H. *Wetland ecosystem in Asia: function and management*. Netherlands: Elsevier B.V. 285-310.

Gersberg, R. M., Elkins, B. V., Lyon, S. R., and Goldman, C. R. (1986). Role of aquatic plants in wastewater treatment by artificial wetland. *Water Resources*, 20(3). 363-368.

Gunawardhana, W. D. D. H., Jayaweera, M. W., Kasturiarachchi, J. C., (2002). Heavy metals levels of groundwater in Ratmalana Moratuwa industrial area: A comprehensive carried out in 2002. In *Proceedings of the Eight Engineering Research Unit (ERU) Symposium 2002,* University of Moratuwa, Sri Lanka.

Gurzau, E. S., Neagu, C., Gurzau, A. E., (2003). *Essential metals- case study on iron. Ecotoxicology and environmental Safety* (56). 190-200.

Jain, S. K., Vasudeman P., Jha N. K., (1989) Removal of some heavy metals from polluted water by aquatic plants: studies on duckweed and water velvet. *Bioogical. Wastes*., 28: 115-119,

Kara, Y., (2004) Bioaccumulation of copper from contaminated wastewater by using Lemna minor (Aquatic green plant*). Bulletin Environment Containation. and Toxicology*, 72 (3): 467-471,

Kadlec, R. H., and Knight, R. L. (1996). *Treatment wetlands*. New York: Lewis Publishers. 685-697.

Kebbekus, B. B. and Mitra, S. (1998). *Environmental Chemical Analysis.* Boca Raton, Florida: CRC Press. 86 – 89.

Lamai Ca, Kruatrachue Ma, Prayad Pa,. Suchart Ub, and Soonthornsarathool V (2005) Toxicity and Accumulation of Lead and Cadmium in the Filamentous Green Alga Cladophora fracta (O.F. Muller ex Vahl) Kutzing*: A Laboratory Study* .31.121-127

Liu, J. Dong, Y. Xu, H. Wang, D. and Xu, J. (2007). Accumulation Cd, Pb, and Zn by 19 wetland plant species in constructed wetland*. Journal of Hazardous Material*. In press.

Mahesh W. J., Jagath C. K., Ranil K. A. , Suren L. J.,(2007) *Contribution of water hyacinth (Eichhornia crassipes (Mart.) Solms) grown under different nutrient condition to Fe-removal mechanism in constructed wetlands*. . In: Wong M. H. *Wetland ecosystem in Asia: function and management*. Netherland: Elsevier B.V.. 1-9.

Maine, M. A. Sune, N. L. and Langger, S. C. (2004*).* Chromium bioaccumulation: comparison of the capacity of two floating aquatic macrophytes*. Water Research*. 38: 1494 – 1501.

Malaysia (1975) , *Akta Kualiti Alam Sekeliling 1974 (Kumbahan dan Effluen-Effluen Perindustrian) 1979. Following the law 8(1), 8(2), 8(3) Parameter Limitation for Effluent Standard A and Standard B*

Mitsch, W. J., and Gosselink, J. G. (1993). *Wetlands*. New York: Van Nostrand Reinhold. 11.

Moshiri, G. A. (Ed.) (1993). *Constructed Wetlands for Water Quality Improvement. CRC Press*. Boca Raton: Lewis Publishers.632.

Nora, F. Y., Wong Y. S., (1997) Accumulation and distribution of heavy metals in a simulated mangrove system treated with sewage. *Hydrobiologia*, 352 (1): 67-75

Noor Ida Amalina, A.N (2006). *Leachate treatment using constructed wetland with magnetic field.* Universiti Teknologi Malaysia: Master thesis.

Odjegba, V. J. and Fasidi, I. O. (2004). Accumulation of Trace Elements by Pistia stratiotes: Implications for phytoremediation. *Journal of Ecotoxicology*. 13: 637-646.

Otte, M. L. and Jacob, D. L. (2006). Constructed wetlands for phytoremediation. Pytoremediation. *Rhizomediation*. 57 – 67.

Peavy, H. S. Rowe, D. and Tchobanoglous, G. (1985). *Environmental Engineering*. Singapore: McGraw-Hill Book Co. 37 – 38.

Peer, W. A. Baxter, I. R. Richards, E. L. Freeman, J. L. and Murphy, A. S. (2005). Phytoremediation and hyperaccumulator plants. *Topics in Current Genetics*. 14: 299 – 340.

Reed, R. C., Middlebrooks, E. J., and Crites, R. W. (1988). *Natural systems for waste management and treatment.* New York: McGraw Hill. 234-241.

Sainty, G., and Beharrel, M. (1998). Wetland Plants. In: *NSW department of land and water conservation constructed wetland manual.*Sydney: Orbital Offset press Pty Ltd.374-381.

U.S. EPA (1988). Design manual – *constructed wetland and aquatic plant systems for municipal wastewater treatment*. Cincinnati: United States Environmental Protection Agency. EPA/625/1-88/022

White, G. (1998). Design for urban water wetland. In *NSW department of land and water conservation constructed wetlands manual*. Sydney: Orbital offset Press Pty Ltd.233-252.

APPENDICES

APPENDIX A1: GANTT CHART FOR PSM I

No.	Activities	Final Year Semester 1															
		W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15	W16
1	Conformation of the PSM title																
2	PSM briefing by the coordinator																
3	Information searching and preparation of Chapter 1.																
4	Submit the Chapter 1 to the Supervisor for correction																
5	Information searching and preparation of the project's 1st draft																
6	Submit the project's 1st draft to the supervisor for evaluation																
7	Project's 1st draft correction and preparation for project draft presentation																
8	Project's draft presentation and correction by the examiner																
9	Final draft preparation																
10	Submit the project's final draft to the supervisor and examiner for evaluation																
11	Project's draft correction and preparation of PSM II																

APPENDIX A2: GANTT CHART FOR PSM II

No.	Activities	Final Year Semester 2															
		W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15	W16
1	Design the constructed wetland																
2	Water-lettuce collection																
3	Varying number of plant experiment																
4	Varying waste concentration experiment																
5	Varying pH concentration experiment																
6	Water sampling and analysis																
7	Writing the project report																

Appendix A.3: Table percentage removal for zinc in varying quantity of plant experiments

Day	Blank (%)	5 plants (%)	10 plants (%)	15 plants (%)
0	0.00	0.00	0.00	0.00
0.5	1.01	2.06	3.12	3.60
1	3.03	11.34	26.04	38.74
1.5	3.03	15.46	26.04	43.24
2	5.05	19.59	28.13	49.55
2.5	3.03	22.68	38.54	57.66
3	5.05	11.34	36.46	59.46
4	3.03	16.49	42.71	63.96
5	3.03	27.84	58.33	74.77
6	5.05	32.99	69.79	73.87
7	6.06	32.99	66.67	71.17

Appendix A.4: Table percentage removal for copper in varying quantity of plant experiments

Day	Blank (%)	5 plants (%)	10 plants (%)	15 plants (%)
0	0.00	0.00	0.00	0.00
0.5	6.75	8.92	18.20	21.98
1	27.15	40.14	38.50	40.19
1.5	37.62	43.51	55.34	74.88
2	38.68	51.08	56.24	82.42
2.5	40.00	58.24	84.36	87.76
3	42.38	59.59	85.11	88.70
4	42.52	70.54	86.47	87.76
5	47.15	80.14	90.38	92.94
6	47.15	82.57	81.05	90.42
7	47.95	81.35	86.32	90.58

Appendix A.5: Table percentage removal for zinc in varying pH condition experiment

Day	Blank (%)	pH 5 (%)	pH 7 (%)	pH 9 (%)
0	0.00	0.00	0.00	0.00
1	4.14	6.86	48.45	30.56
2	4.14	62.75	74.23	52.78
3	8.88	67.65	74.23	52.78
4	48.52	73.53	75.26	55.56
5	59.17	74.51	76.29	66.67
6	61.54	75.49	79.38	63.89
7	70.41	76.47	80.41	72.22

Appendix A.6: Table percentage removal for copper in varying pH condition experiment

Day	Blank (%)	pH 5 (%)	pH 7 (%)	pH 9 (%)
0	0.00	0.00	0.00	0.00
1	16.86	32.57	86.71	26.54
2	60.50	84.59	92.52	79.62
3	57.69	92.16	92.86	78.08
4	65.45	92.16	93.02	77.31
5	63.47	92.43	93.19	81.92
6	63.64	92.30	93.36	85.00
7	63.47	92.43	93.36	85.38

Appendix A.7: Picture of Atomic Absorption Spectrophotometer (AAS)

Appendix A.8: Picture of initial condition of water lettuce for varying plant experiment

(a) 5 plants (b) 10 plants (c) 15 plants

Appendix A.9: Picture of final condition of water lettuce for varying plant experiment

(a) 5 plants (b) 10 plants (c) 15 plants

Appendix A.10: Picture of initial condition of water lettuce for varying pH experiment

(a) pH 5 (b) pH 7 (c) pH 9

Appendix A.11: Picture of final condition of water lettuce for varying pH experiment

(a) pH 5 (b) pH 7 (c) pH 9