ENHANCEMENT OF REMOVAL HEAVY METAL USING PHYTOREMEDIATION BY *PISTIA STRATIOTES Sp.* FROM SYNTHETIC WASTEWATER

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ABSTRACT

In today's modern or developing country, concept of phytoremediation is still the economic way in treating industrial wastewater. Heavy metals such as iron and chromium that contaminated in industrial wastewater can cause serious health problem to living organism. The objective of this research was to perform the removal efficiency of iron and chromium from the synthetic wastewater. The synthetic wastewater was made by following the standards of industrial wastewater to make sure it acts like the genuine industrial wastewater. The aim of the study was to determine the removal efficiency of iron and chromium as the quantities of plant were increased and to study the effect of pH change in constructed wetland. The wetland plant used for the research was water lettuce (*pistia stratiotes*). For analysis, atomic absorption spectroscopy was used to determine the concentration of iron and chromium. The research was conducted for seven days. Each parameter with varying quantity of plants and pH were carried out in three containers including control. The control container setup with no water lettuce (*pistia stratiotes*) was to compare the effectiveness. The results for varying quantity of plant for iron removal were 15 plants achieved highest removal efficiency (98.97%), 10 plants (81.23%) and the control (32.33%). For effect of pH experiment for iron removal, the highest removal efficiency achievement was pH 7 (98.97%), pH 4 (45.45%) and pH 10 (37.14%).The results for varying quantity of plant for chromium removal were 15 plants achieved highest removal efficiency (47.95%), 10 plants (35.45%) and the control (19.08%). For effect of pH experiment for iron removal, the highest removal efficiency achievement was pH 7 (47.95%), pH 4 (32.89%) and pH 10 (31.97%). The removal of iron was more effective than chromium. As a conclusion, water lettuce (*pistia stratiotes*) shows a good result in removing of iron and chromium in wastewater.

ABSTRAK

Di Negara yang moden atau membangun hari ini, konsep phytoremediation masih cara yang ekonomi dalam merawat air sisa industri. Logam berat seperti besi dan kromium yang tercemar dalam air sisa industri boleh menyebabkan masalah kesihatan yang serius kepada organisma hidup. Objektif kajian ini adalah untuk melaksanakan kecekapan penyingkiran besi dan kromium daripada air sisa sintetik. Air sisa sintetik akan dibuat dengan mengikut piawaian air sisa industri untuk memastikan ia bertindak seperti air sisa industri yang tulen. Matlamat kajian ini adalah untuk menentukan kecekapan penyingkiran besi dan kromium sebagai kuantiti tumbuhan meningkat dan untuk mengkaji kesan perubahan pH dalam tanah lembap dibina. Kilang paya digunakan untuk penyelidikan bagi adalah salad air (*stratiotes pistia*). Untuk analisis, spektroskopi penyerapan atom digunakan untuk menentukan kepekatan besi dan kromium. Kajian ini dijalankan tujuh hari. Setiap parameter yang berbeza-beza kuantiti tumbuhan dan pH telah dijalankan dalam tiga bekas termasuk kawalan. Persediaan bekas kawalan tanpa salad air (*stratiotes pistia*) adalah untuk membandingkan keberkesanan. Keputusan untuk pelbagai kuantiti loji untuk pembuangan besi adalah 15 kilang mencapai penyingkiran tertinggi kecekapan (98.97%), 10 tumbuh-tumbuhan (81.23%) dan kawalan (32.33%). Untuk kesan eksperimen pH untuk penyingkiran besi, tertinggi pencapaian kecekapan penyingkiran adalah pH 7 (98.97%), pH 4 (45.45%) dan pH 10 (37.14%). Keputusan untuk pelbagai kuantiti tumbuhan untuk penyingkiran kromium adalah 15 kilang dicapai penyingkiran tertinggi kecekapan (47.95%), 10 tumbuh-tumbuhan (35.45%) dan kawalan (19.08%). Untuk kesan eksperimen pH untuk penyingkiran besi, tertinggi pencapaian kecekapan penyingkiran adalah pH 7 (47.95%), pH 4 (32.89%) dan pH 10 (31.97%). Penyingkiran besi adalah lebih berkesan daripada kromium. Kesimpulannya, salad air (*stratiotes pistia*) menunjukkan keputusan yang baik dalam menghapuskan besi dan kromium dalam air sisa.

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LIST OF SYMBOLS

L	Liter
mg	Milligram

LIST OF ABBREVIATIONS

BOD	Biochemical Oxygen Demand
DO	Dissolved Oxygen
CWs	Constructed Wetlands
AAS	Atomic Absorption Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Polluted water has always been an issue of environmental concern all over the world. Environmental issue is mostly enhanced in the developing countries such as Malaysia. As known, Malaysia has a well-developed oil and gas sector and petrochemical industry which wastes from industry will actually pollute the water.

The 'kidneys of Earth' is the best way to describe natural wetlands due to the system filter pollutants from water just like the kidney did for humans. The natural wetland is known to be able to improve the quality of water thus the system is constructed to replicate the function of natural wetlands. Constructed wetlands are engineered system that have been designed and constructed to utilize the natural processes involving wetland vegetation, soils, and their associated microbial assemblages to assist in treating wastewater (Vymazal, 2007). In short, constructed wetland is a man-made wetland. A constructed wetland as 'purpose build 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' (White, 1998). Besides, constructed wetland can be an attractive landscape for visit purpose.

In these few years, much concern has been made on constructed wetlands for removing toxic heavy metals from wastewater (Raskin and Ensley, 2000). The bioaccumulation, phytoextraction, phytostabilization and rhizofiltration are the main aspects used by wetland plants to filter and store the toxic heavy metals.

However, the wastewater problem can be controlled through phytoremediation. Phytoremediation was carried out by a basic concept which the plant absorb the wastes or contaminants by roots.

The wetland plants play an important role in phytoremediation. The plant that germinate and grow in soil which is in saturated condition for long period can be considered as wetland plant (Sainty and Beharrel, 1998). Water-lettuce, scientific name called *Pistia stratiotes* is an aquatic plant which grows by floating on the water. Its characteristic of extensive root system helps in enhancing the removal of heavy metals in wastewater.

This technique still need more research before it able to be accepted as remediation technique for wastewater pollution. In this case, the research focuses on synthetic wastewater due to difficulty on getting genuine industrial wastewater.

1.2 Problem Statement

In the near future, the development of industry in Malaysia increases year by year. With the increase of industry, the toxicity heavy metal in surface and groundwater rapidly increases as well. Human health, property and environment will be seriously affected by the industrial wastes that containing toxic heavy metal.

Many activities in industries lead to the increases of concentration of heavy metals. Heavy metal can actually harm human health. Although some metal might be essential to human, over consumed could be fatal. The extra build up of iron in body can cause diseases such as anaemia and blood disorder while chromium poisoning can cause kidney and liver damage.

Phytoremediation is one of the treatment technology that being experimented recently. In order to overcome the problem, the treatment system has to be efficient enough. This system is known to be economical and low maintenance cost. However, the wetland plants will be the main concern in this treatment system. Thus, well selection of wetland plant species can exploit the removal potential of heavy metals from the wastewater (Liu et al., 2007). However, this research was carried out on synthetic wastewater. It is difficult to get the real industrial wastewater and the amount needed hardly obtained, thus only synthetic wastewater was used for this research.

1.3 Objectives of Study

The objectives of this study are:

- To investigate the effects of pH on the removal of heavy metal from the synthetic wastewater.
- To determine the removal efficiency of iron and chromium from the synthetic wastewater.

1.4 Scope of Study

This study was concerning on the effect of phytoremediation in treating synthetic wastewater by designing a wetland. The constructed wetland will be designed with the selected wetland plant species, which is water lettuce species. Water lettuce in scientific term is known as *Pistia stratiotes*. Firstly, the wetland with water lettuce plant species (*Pistia stratiotes*) will be constructed. Then, the treatment of wastewater containing iron and chromium will be focused. After that, the removal efficiency of iron and chromium when the numbers of water lettuce plants increases and the varies of pH will be studied. This experiment was carried out at Faculty of Civil Engineering and Natural Resources Laboratory, University Malaysia Pahang.

1.5 Research Significance

The main purpose of this research is to introduce an alternative method of treating wastewater by using constructed wetlands. Constructed wetland should be implemented in the wastewater treatment system of our country. The reason is that constructed wetland is well known to be economical and already widely used by western country.

CHAPTER 2

LITERATURE REVIEW

2.1 Wetland

Wetland is an area where the ground surface covered with water for a long period of time every year. An area developed into a catchment after rain storm could not listed as a wetland. Due to long period presence of water, it establishes a favor condition for aquatic plants and owned the characteristic of wetland soils. However, some of the wetlands are only wet seasonally. Wetland acts as a transition zone between land and water. The ecosystem of wetland is specialized by the unique environment and condition such as the soils, hydrology and vegetation. Wetlands perform various ecological functions and it is known to be the most productive ecosystem in the world. Besides that, the groundwater is directly linked to wetland systems and groundwater is essential for human drinking purpose. The hydrology properties of wetlands are basically slow flow and shallow water. This condition would let the sediments settled indirectly. All in all, wetlands are places for groundwater recharge, absorb water, purify pollutants, control floodwater and erosion, and provide feeding protection yet reproductive habitats for several type of wildlife (Chin, 2006).

2.1.1 Natural Wetland

Natural wetland is formed naturally on earth and it is transition between land and water (Figure 2.1). This system can function like human's kidney to purify or filter pollutants from the water that passes through it. Due to the great effect, engineers are work on it to replicate the function of the system.

Wetlands benefit both human and wildlife naturally. One of the main concerns is filtration of water. With the hydrology properties of slowing down the water flow, the suspended solids will be settled down. Some of the pollutants are then absorbed by the plants. The storm water runoff from a fertilized area will carry the nutrients together and deposited by the wetland plants for growing purpose. The nitrogen can be converted by microbes into inorganic nitrogen which helps in plants growth.

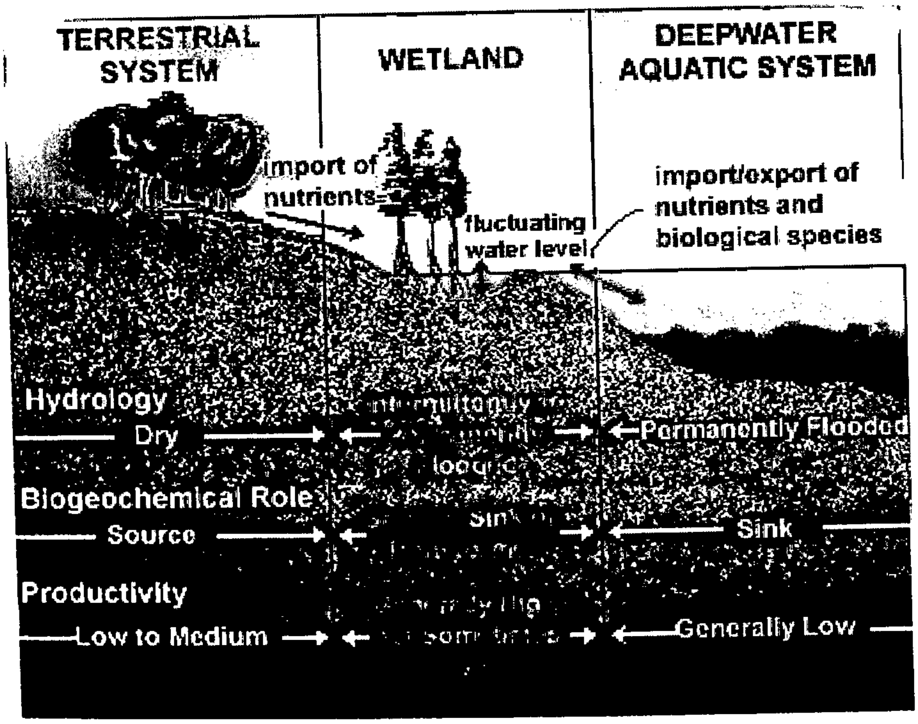

Figure 2.1: Wetland (NS Wetland Partners Society, 2013)

2.1.2 Constructed Wetland

Constructed wetlands (CWs) are engineered systems that have been designed and constructed to exploit the natural processes involving wetland vegetation, soils and associated microbial assemblages for treating wastewaters (Guittonny-Philippe et al., 2013). They are designed to take the benefit of the same function that occur in natural wetlands, but provided in controlled environment. CWs for wastewater treatment can be categorized depend on the life form such as free-floating, rooted emergent and submerged macrophytes (Brix and Schierup, 1989). CWs can be defined as purpose built structures, utilizing the soil and biota, which perform the desired process and functions of natural wetlands to achieve objectives (White, 1998). Typically, CWs should perform better than a natural wetland because all the conditions are under controlled.

There are two types of CWs which are free water surface system and subsurface flow system. The types are as follows:

2.1.2.1 Free Water Surface System

This system is actually consists of a channel or basin which function with a barrier to prevent seepage to support emergent vegetation and water will be at a comparatively depth flowing through the soil surface. The flow path is horizontal and water surface is always exposed to the atmosphere (Sherwood, 1993). Figure 2.2 (a) & (b) show the free water surface system with different types of macrophyte.

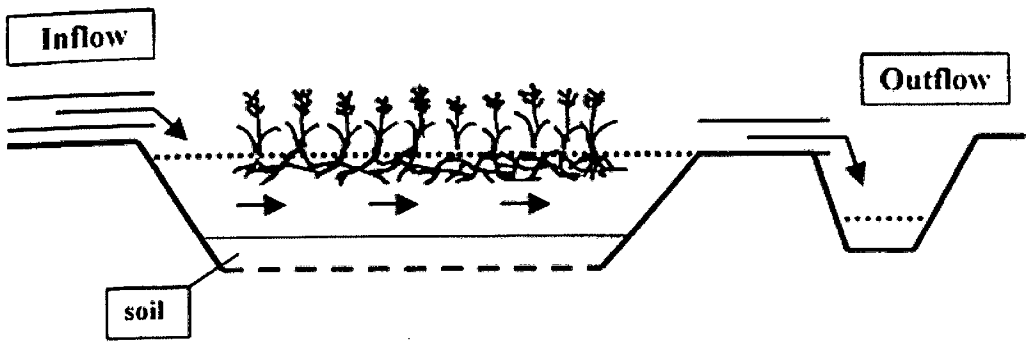

Figure 2.2 (a): Free water surface system with free floating plants (Vymazal, 2007)

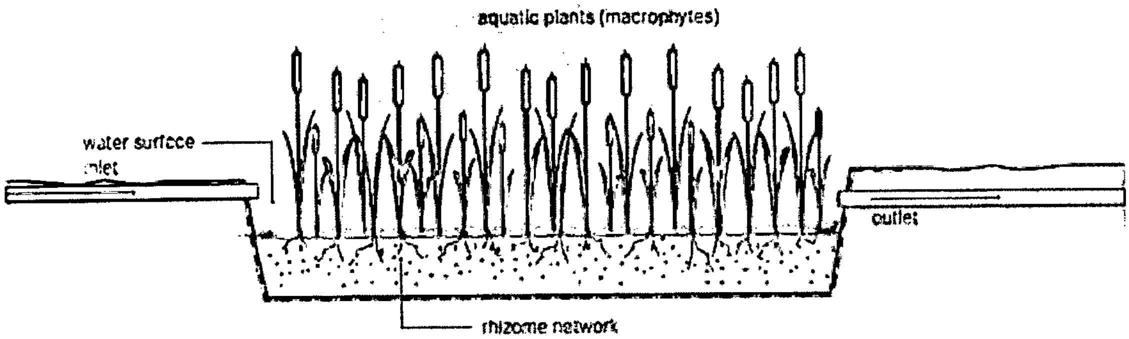

Figure 2.2 (b): Free water surface system with emergent macrophytes (Tilley et al., 2008)

2.1.2.2 Subsurface Flow System

Basically, subsurface flow system also consists of channel or basin with barrier to prevent seepage, but with a porous medium. The media normally made of rock or gravel. The root of the emergent macrophytes will get the support from the media as well. This kind of design presumes that the water level will remain below the top of the rock media (Sherwood, 1993).

Subsurface flow system has two flowing mode which are vertical and horizontal flow. Further information can refer to figure 2.3 (a) & (b).

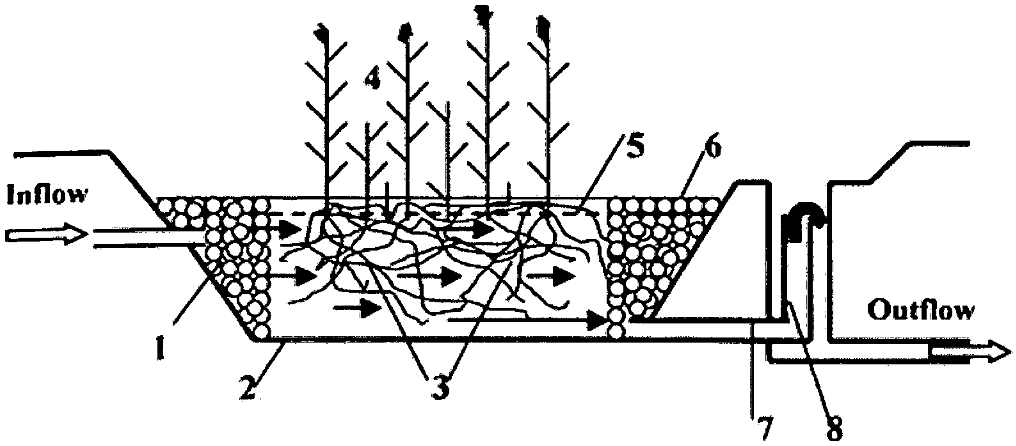

Figure 2.3 (a): Subsurface horizontal flow system (1 Distribution zone filled with large stones, 2 impermeable liner, 3 filtration medium (gravel or rock), 4 vegetation, 5 water level in bed, 6 collection zone with large stones, 7 collection drainage pipe, 8 outlet structure for maintaining the water level in bed.) (Vymazal, 2007)

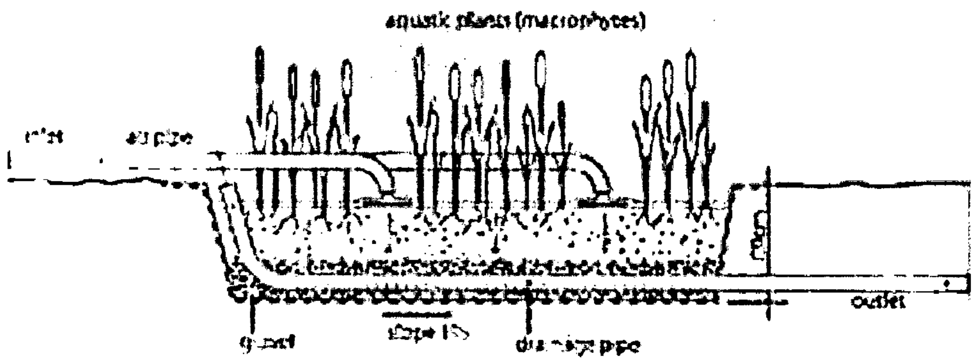

Figure 2.3 (b): Subsurface vertical flow system (Tilley et al., 2008)

2.2 Phytoremediation

Phytoremediation is a process which uses plants to purify the pollution in the environment. The plants help to prevent wind and rain from bringing the pollution away to the other areas. Phytoremediation works best at low or medium of pollution condition. Plants remove the harmful chemicals by absorbing water and nutrients from the water or ground that was polluted. Tree roots grow deeper than smaller plants, so they used to reach pollution that deeper in the ground (EPA, 2001). The chemical that absorbed by plants can be stored in some parts of plants such as leaves, stems and roots. The chemical can be changed into less harmful thing or release into the air through transpiration (EPA, 2001). Basically phytoremediation uses only one basic concept by taking pollutants with their roots.

2.3 Wetland Plants

Wetland plants play an important role in metal removal by the processes of filtration, absorption, cation exchange and root-induced chemical changes in rhizosphere (Dunbabin and Bowmer, 1992). Different plant will have different capability of removing heavy metals, such as salix can take much more heavy metals than the other species (Stoltz and Greger, 2002). Some heavy metal might need some particular of species to remove. Thus, the species of plant that used in the constructed wetland may affect the performance of the wetland for removing the heavy metals from wastewater.

In general, wetland plants can be divided into four different groups which are free floating plants, floating leave plants, emergent plants and submerged plants (Vymazal, 2007).

2.3.1 Water Lettuce (*Pistia stratiotes*)

In this research, the wetland plant used will be as titled, water lettuce (*Pistia stratiotes*). Water lettuce as shown in figure 2.4, belong to the family of *Araceae*. It is a free floating aquatic plant. It is widely grown in tropical and subtropical countries (Mitsch and Gosselink, 1993). The plant reproduces sexually and vegetatively. The leaves are pale yellow-green and fan-shaped with prominent veins on the underside. The short white hair which traps air will provide buoyancy to the plant. Water lettuce is an ideal plant species to remove or accumulate the heavy metals in the wastewater because it grows rapidly and with an extensive root system (Odjegba and Fasidi, 2004). Table 2.1 shows the characteristic of the water lettuce.

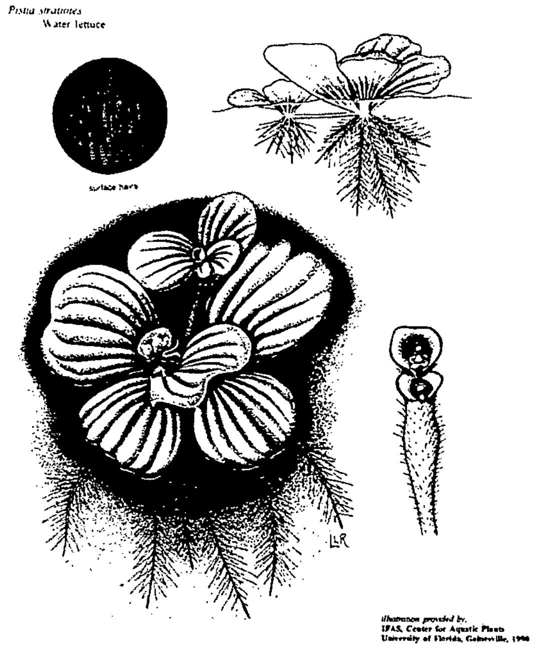

Figure 2.4: Water lettuce (Florida, 2011)

Table 2.1: Characteristic of water lettuce

Common name	Water lettuce
Scientific name	*Pistia stratiotes*
Size	Can range from 2" to 18" individually.
Light	Does best with shade but can adapt to full sun

2.4 Heavy Metals

Heavy or toxic metals would harm to human and other living organism even in small amount. Toxic metals that may dissolved in water included cadmium, lead, mercury, iron and chromium. All these metals are concentrated by gone through the food chain, therefore it would possesses the greatest danger to the organism near the top of the chain (Peavy et al., 1985).

2.4.1 Iron

Iron is a metallic element which listed in the periodic table with the symbol of Fe and atomic number of 26. It is an element in transition series. Iron is the most common element forming the Earth as a whole and the fourth most common element in the Earth's crust. Iron appears in lustrous silvery-grey and easy being oxidize in normal environment, we called it rust. Iron metal has been applied to human life since ancient time. Pure iron is soft but after smelted with carbon will be hardened and strengthened.

Iron is essential to human and other living organism as it forming complex with oxygen in hemoglobin. It is the way to transport oxygen in blood to all of body. However, large amount of consuming iron can cause increases level of iron in the blood. This can damage DNA, protein, lipids and other cellular components. The significant effects including coma, liver failure, long-term organ damage and even could be fatal.

2.4.2 Chromium

Chromium is a chemical element with the symbol of Cr and atomic number of 24. It is in steely-grey, lustrous, hard and brittle. Chromium oxide was used to coat metal weapons by the Chinese in Qin dynasty. Chromium can be used to produce dye and pigment. The yellow pigment is the mixed of chrome yellow and cadmium yellow. The chromium oxide also being used as a green colour in glassmaking.

Chromium has no verified biological role and has been categorized as not essential for mammals. High concentration of chromium in cell can lead to DNA damage. The chromium poisoning can caused kidney and liver damage as well.

2.5 Metal Analysis

For elemental analysis especially metal determination, it is most recommended to decompose the molecule sample into atoms and measure the emission of its radiant energy. This method is worked with the focus of atomic spectra. This would make the selection of individual elements from a complex mixture become easier with less interfere. Atomic absorption is normally used to analyze metals in air, water and solid samples (Kebbekus and Mitra, 1998).

2.5.1 Atomic Absorption Spectroscopy

In order to analyze with atomic absorption spectroscopy, the sample required to be atomized and broken down into atoms before passed into radiation beam for absorbance measurement. In flame atomic absorption, a sample of liquid solution is aspirated into a flame. This is achieved by using nebulizer and mixes the sample with gaseous fuel and oxidant to form a mixed aerosol solution. Each drop first dries to a small particle of salt, after that evaporates completely. The ion cluster keep heating until energy absorption enough to dissociate into free atoms in vapor state. The beam is passed through the flame and absorbance by the atomized species is measured. It should be noticed that the absorbance is proportional to the concentration of ground state atoms in the flame (Kebbekus and Mitra, 1998).

Due to the atomic absorption measurements in the flame are done in a dynamic system, it is important to ensure that the samples and standards are in similar matrix. The viscosity of the solution, behavior of the mist, its evaporation and drying characteristic and droplet size can all have an effect on the rate of formation atom. Normally all standards and samples are made up in dilute acidic aqueous solutions (Kebbekus and Mitra, 1998).

2.6 Chemical Characteristic

2.6.1 Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand (BOD) is the amount of oxygen being consumed by the organism in stabilizing waste. The aerobic biological decomposition of an organic waste will keep continue until all the waste is consumed if the oxygen available is sufficient. The determining of a sample through BOD is to discover the difference in dissolved oxygen (DO) concentration between the initial and final time after incubation of 5 days at temperature of 20°C. The difference will be converted to mass of oxygen per unit volume sample (mg/L).

BOD used to determine the quantity of oxygen that required to biologically stabilizing the organic matter in wastewater. The result of BOD tests are not only used to measure the efficiency of treatment facilities, but also used to find out the compliance with wastewater discharge permits (Tamimi, 2003).

2.7 Synthetic Wastewater

The synthetic wastewater can be known as artificial wastewater is described as the wastewater that human-made and not originally from industries. Table 2.2 shows the references in making synthetic wastewater.

Table 2.2: Parameter limitation for iron and chromium for standard A and B (Akta Kualiti Alam Sekeliling 1974 (Kumbahan dan Effluen-Effluen Perindustrian) 1979).

Metal	Unit	Standard A	Standard B
Iron (Fe)	mg/L	1.0	5.0
Chromium (Cr) Trivalent	mg/L	0.2	1.0

Standard A defines that the factories or industries activities use water sources from the river after the factories location while standard B is that the factories or industries activities use water sources from the river before the factories location (Figure 2.5).

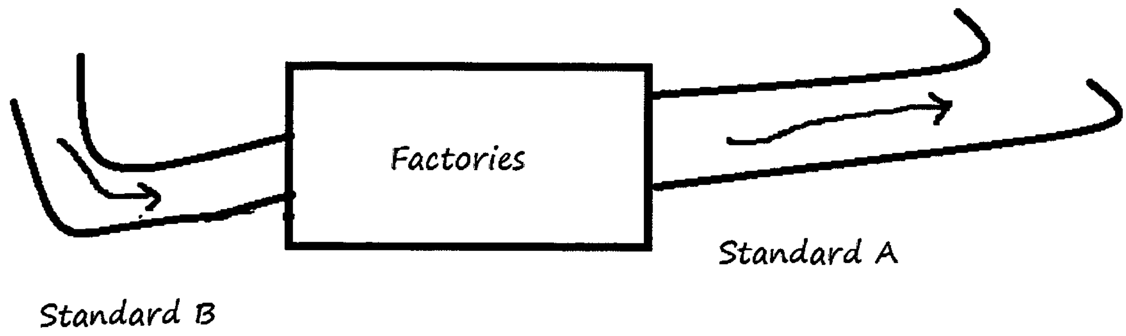

Figure 2.5: Definition of standard A and B

2.8 Conclusion

In conclusion, constructed wetlands have been found to be able to filter or purify wastewater and it is already being used by western countries. However, the result of efficiency of removing heavy metals especially iron and chromium still not obvious enough to convince the society or investor to invest constructed wetland as their wastewater treatment plant.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The methodology is divided into 4 phases as shown in Figure 3.1. The experiment is carried out at Faculty of Civil Engineering and Environmental Resources (FKASA) Environmental Laboratory, Universiti Malaysia Pahang (UMP).

The objective of the study is to determine the efficiency heavy metal removal in synthetic wastewater. The wetland is constructed using plastic container or basin, which means no soil will be used. The control sample is setup without water lettuce.