

**BIOSORPTION OF CHROMIUM (VI) FROM AQUEOUS SOLUTION BY
DRIED WATER HYACINTH (*Eichhornia Crassipes*)**

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JUDUL: **BIOSORPTION OF CHROMIUM (VI) FROM AQUEOUS SOLUTION BY DRIED WATER HYACINTH (*Eichhornia Crassipes*)**

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**BIOSORPTION OF CHROMIUM (VI) FROM AQUEOUS SOLUTION BY
DRIED WATER HYACINTH (*Eichhornia Crassipes*)**

MOHD ZAMRI BIN ZAINUDDIN

**A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering**

**Faculty of Chemical & Natural Resources Engineering
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MAY, 2009

I declare that this dissertation entitled “*Biosorption of Chromium (VI) From Aqueous Solution By Dried Water Hyacinth (Eichhornia Crassipes)*” 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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Date: 30 April 2009

*Special Dedication to my family members,
my friends, my fellow colleague
and all faculty members*

For all your care, support and believe in me.

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ABSTRACT

Metal ions in wastewater can cause serious toxicological problem which are dangerous to the environment and human being. Hexavalent chromium Cr (VI) is very toxic and mutagenic for most organisms. It is essential to remove this metal from wastewater. The purpose of this study is to investigate the performance of dried water hyacinth (*Eichhornia crassipes*) in biosorption of hexavalent chromium, Cr (VI). The effect of biosorbent dosage, initial concentration, initial pH of the solution, and time contact were studied and the optimum conditions for biosorption process were indentified. Only the stems and leaves of the water hyacinth were use as the biomass in this study. Biomass is mixed with the chromium solution at specific condition before the supernatant is taken. Supernatant were analyzed using atomic absorption spectrophotometer (AAS) in order to determine the concentration of chromium in the solution. Results show that biosorption of chromium (VI) highly depends on parameter studied. The amount of chromium adsorbed depends on the dosage. High loading of biomass will increase the removal of chromium. Low initial concentration also will make sorption yield higher. Biosorption of chromium (VI) is greatly depending on pH value because at pH more than, 2 the amounts of chromium remove is lower. When the time contact between biosorbent and solution increase, the removal of chromium also increase. The optimum condition for biosorption of chromium were at 0.7g biosorbent loading, initial concentration at 5mg/L, 1.8 pH value and 75 minutes of time contact.

ABSTRAK

Ion-ion logam di dalam air sisa buangan industri boleh menyebabkan masalah pencemaran toksik yang berbahaya kepada alam sekitar dan kehidupan manusia. Kromium Heksavalens, Cr (VI) adalah sangat toksik dan mutagenik kepada hampir semua organism. Oleh yang demikian kromium mesti diasingkan dari air sisa industri sebelum dibuang. Tujuan kajian ini adalah untuk menyiasat keupayaan keladi bunting (*Eichhornia crassipes*) yang telah dikeringkan dalam proses menjerap Kromium Heksavalens, Cr (VI). Parameter yang dikaji ialah kesan dos biomass, kepekatan ion kromium pada awal eksperimen, pH awal larutan, dan kesan masa terhadap proses menjerap kromium. Penjerap yang digunakan di dalam kajian ini adalah campuran batang dan daun keladi bunting. Penjerap dicampurkan dalam larutan kromium dalam keadaan tertentu bergantung kepada parameter yang dikaji seperti nilai pH dan dos biomas yg berbeza sebelum ditapis untuk mendapatkan sampel yang seterusnya dianalisa menggunakan AAS. Keputusan kajian ini menunjukkan penjerapan Kromium Heksavalens bergantung kepada keempat-empat parameter yang dikaji. Keadaan yang optimum untuk penjerapan kromium adalah pada 0.7 g dos biomas, kepekatan larutan pada 5 mg/L, nilai pH 1.8 dan masa tindak balas pada 75 minit.

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LIST OF SYMBOLS/ABBREVIATIONS

| | | |
|--------------|---|-------------------------------------|
| AAS | - | Atomic Absorption Spectrophotometer |
| $K_2Cr_2O_7$ | - | Potassium Dichromate |
| HCl | - | Hydrochloric acid |
| NaOH | - | Sodium Hydroxide |
| % | - | Percent |
| mg/L | - | milligram per liter |
| C_i | - | Initial Concentration |
| C_e | - | Concentration at equilibrium |
| Rpm | - | rotation per minutes |

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CHAPTER 1

INTRODUCTION

1.1 Background

The discharge of heavy metals into aquatic ecosystems has become a matter of concern over the last few decades. The presence of extremely toxic elements can seriously affect plants and animals and have been involved in causing a large number of afflictions. Increased knowledge about toxicological effects of heavy metals on the environment is well recognized and therefore, it is unavoidable to search for different methods to reduce water pollution. The major sources of heavy metal contaminations are the industrial effluents. Due to their persistence in nature, it becomes essential to remove them from wastewaters. Various kind of heavy metal such as Lead, Zinc, Ferrum, Nickel, and also Chromium can be found in waste water.

Chromium containing solutions are used in a number of industries usually for chrome plating steels or for inhibiting corrosion in steel vessels. Because of the effect of the chromium to the environment, it is essential to treat wastewater contain Chromium before it can discharge to the drain system. Malaysian-Environmental Quality Act 1974 (Sewage and Industrial Effluents) 1979 stated that the concentration of Chromium (VI) in wastewater must below 0.05 mg/L for both standard A and standard B.

In this study, we use dried water hyacinth (*Eichhornia Crassipes*) as an adsorbent for biosorption of Chromium (VI) as an alternative method for conventional method for treating wastewater from industries that containing Chromium (VI). Biosorption make use of the ability of biological material to accumulate heavy metals from wastewater streams by either metabolically mediated or purely phsico-chemical pathway of uptake.

1.2 Problem statement

Wastewater from industry may contain dangerous and hazardous chemical. Wastewater from industries may cause pollution to the environment if this wastewater not treated seriously. The existence of heavy metal such as Chromium (VI) in the wastewater can caused toxic and mutagenic effect for most organisms. Before discharged to the drain system, this contaminated wastewater must be treated in order to make sure it is not harmful to the environment.

There are several way was developed in order to treat this wastewater and the common method is chemical precipitation using lime or caustic soda. Other method of treatment that available for wastewater treatment are such as ion exchange, electrolysis and reverse osmosis (RO) are high in operation cost and capital investment (V. K. Gupta *et al.*, 1999). In this study, dried water hyacinth will be used as an adsorbent because this plant is a good biosorbent for removal of heavy metal like Chromium (VI) (Cycle Keith *et al.*, 2006).

Treatment of wastewater using living water hyacinth need a large area such as water pond, and also can cause environmental problem. This plant can cause a problem like hindrance for water transport, microhabitat for a variety of disease factor such as mosquitoes, also reduction of biodiversity. In order to overcome this problem, it is possible to use dried water hyacinth in this study. Treatment using dried water hyacinth also is more convenient compare to using the living water hyacinth because it is easy for transportation of the biosorbent.

1.3 Objectives

Objectives of this study are:

1. To investigate the performance of dried water hyacinth as a biosorbent.
2. To study the biosorption of Chromium (VI) using dried water hyacinth.
3. To identify the optimum condition for biosorption of chromium (VI) using dried water hyacinth.

1.4 Scope of the study

To achieve the objectives stated above, the following scope had been identified:

1. Effect of pH.
2. Effect of dried water hyacinth dosage.
3. Effect of time.
4. Effect of initial concentration.

1.5 Rationale and Significance

In this study we want to remove the Chromium (VI) from aqueous solution by using dried water hyacinth. It is important to remove this heavy metal due to the environmental problem. The rationale we use dried water hyacinth in this study is because this plant is good for biosorption process based on previous finding of other researcher (Cycle Keith *et al.*, 2006). The significance of these studies is to prove that dried water hyacinth can act as a biosorbent in biosorption process of chromium from aqueous solution.

From this study, the potential of dried water hyacinth as a biosorbent for removing Chromium (VI) from waste water can be utilized. Once the potential of water hyacinth in treating chromium containing solution proven, it can replace the conventional method of treating wastewater containing Chromium (VI). On the other hand, environmental problem caused by living water hyacinth can be solved because we used dried water hyacinth.

CHAPTER 2

LITERATURE REVIEW

This chapter will review the research and study that has already been done in order to gain information about this study. It provides background about wastewater, Chromium IV, biosorbent, biosorption and also biosorption mechanism.

2.1 Wastewater

Wastewater is any water that has been adversely affected in quality by anthropogenic influence. It comprises liquid waste discharged by domestic residences, commercial properties, industry, and/or agriculture and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from different sources. Wastewater from industry usually contains heavy metal such as Copper, Nickel and Chromium.

2.1.1 Wastewater Regulation

The electroplating industry has been reported as one of the major polluter to the environment. This industry generates pollutants such as heavy or trace metals including chromium (Parinda Suksabye, 1995). This heavy metal especially the Cr (VI) species has been known as toxic heavy-metal and being carcinogenic. Because of their high toxicity, the industrial wastewaters containing heavy metals are strictly regulated and must be treated before being discharged to the environment. The industrial wastewaters must follow the limits as stated in the Environmental Quality (Sewage and Industrial Effluents) Regulations 1978. Table 2.1 show the limit of the parameter for standard A and standard B. Standard A is applied when wastewater is released at upper stream of the river and there is water intake to a Drinking Water Treatment Plant, while Standard B applied when wastewater released at the downstream of the river. This table below shows that for both standard A and B, wastewater must contain less than 0.05mg/L Chromium hexavalent.

Table 2.1: Environmental Quality Act 1974.

| | Parameters | Units | Standards | |
|----|---------------------------|----------------|-----------|-----------|
| | | | A | B |
| 1 | Temperature | ⁰ C | < 40.0 | < 40.0 |
| 2 | pH | pH | 6.0 – 9.0 | 5.5 – 9.0 |
| 3 | BOD ₅ at 20 °C | mg/L | < 20.0 | < 50.0 |
| 4 | COD | mg/L | < 50 | < 100 |
| 5 | Suspended Solids | mg/L | < 50 | < 100 |
| 6 | Mercury | mg/L | < 0.005 | < 0.05 |
| 7 | Cadmium | mg/L | < 0.01 | < 0.02 |
| 8 | Chromium, hexavalent | mg/L | < 0.05 | < 0.05 |
| 9 | Arsenic | mg/L | < 0.05 | < 0.10 |
| 10 | Cyanide | mg/L | < 0.05 | < 0.10 |
| 11 | Lead | mg/L | < 0.10 | < 0.50 |
| 12 | Chromium, trivalent | mg/L | < 0.20 | < 1.00 |
| 13 | Copper | mg/L | < 0.20 | < 1.00 |
| 14 | Manganese | mg/L | < 0.20 | < 1.00 |
| 15 | Nickel | mg/L | < 0.20 | < 1.00 |
| 16 | Tin | mg/L | < 0.20 | < 1.00 |
| 17 | Zinc | mg/L | < 2.00 | < 2.00 |
| 18 | Boron | mg/L | < 1.00 | < 4.00 |

Table 2.1 (Continued): Environmental Quality Act 1974

| | | | | |
|----|----------------|------|----------------|---------|
| 19 | Iron | mg/L | < 1.00 | < 5.00 |
| 20 | Phenol | mg/L | < 0.001 | < 1.000 |
| 21 | Chlorine, Free | mg/L | < 1.00 | < 2.00 |
| 22 | Sulphide | mg/L | < 0.50 | < 0.50 |
| 23 | Oil & Grease | mg/L | Not Detectable | 10.0 |

2.2 Chromium

The name of the element is derived from the Greek word "chrōma" (χρῶμα) meaning color, because many of its compounds are intensely colored. It was discovered by Louis Nicolas Vauquelin in the mineral crocoite (*lead chromate*) in 1797.

Chromium is an element that can be found naturally in rocks, animals, plants, soil, and also in volcanic dust and gases. There are several forms of chromium that exist in our environment such as chromium (III), chromium (VI) and chromium (0).

Chromium (VI) or their compounds have been used extensively by various metal-finishing, mining and chemical industries. Chromium has characteristic that is high corrosion resistance and hardness. A major development was the discovery that steel could be made highly resistant to corrosion and discoloration by adding chromium and nickel to form stainless steel. This has led to a sharp increase in the contamination of water. Because of their toxicity, the presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water (Hamidi *et al.*, 2007). Chromium is still widely used eventhough it has potential of toxicity.

2.2.1 Hexavalent Chromium

Hexavalent chromium refers to chemical compounds that contain the element chromium in the +6 oxidation state. Virtually all chromium ore is processed via conversion to sodium dichromate. Approximately 136,000,000 kg of hexavalent chromium was produced in 1985. Other hexavalent chromium compounds are chromium trioxide and various salts of chromate and dichromate. Hexavalent chromium is used for the production of stainless steel, textile dyes, wood preservation, leather tanning, and as anti-corrosion and conversion coatings as well as a variety of niche uses.

Hexavalent chromium is recognized as a human carcinogen via inhalation. Workers in many different occupations are exposed to hexavalent chromium. Exposure to chromium can occur from ingesting the contaminated food or drinking water or breathing contaminated workplace air. High level of Chromium (VI) exposure can cause cancer and damage the nose. Ingesting large amount of Chromium (VI) can cause stomach upset and ulcers, convulsions, kidney and liver damage, and also possible of death.

2.2.2 Toxicity of Hexavalent Chromium

Hexavalent chromium is transported into cells via the sulfate transport mechanisms, taking advantage of the similarity of sulfate and chromate with respect to their structure and charge. Trivalent chromium, which is the more common variety of chromium compounds, is not transported into cells.

Inside the cell, Cr (VI) is reduced first to metastable pentavalent chromium (Cr (V)), then to trivalent chromium (Cr (III)). Trivalent chromium binds to proteins and creates haptens that trigger immune response. Once developed, chrome sensitivity can be persistent. In such cases, contact with chromate-dyed textiles or wearing of chromate-tanned leather shoes can cause or exacerbate contact dermatitis.

Vitamin C and other reducing agents combine with chromate to give Cr (III) products inside the cell.

Hexavalent chromium compounds are genotoxic carcinogens. Chronic inhalation of hexavalent chromium compounds increases risk of lung cancer (lungs are especially vulnerable, followed by fine capillaries in kidneys and intestine). It appears that the mechanism of genotoxicity relies on pentavalent or trivalent chromium. According to some researchers, the damage is caused by hydroxyl radicals, produced during reoxidation of pentavalent chromium by hydrogen peroxide molecules present in the cell. Zinc chromate is the strongest carcinogen of the chromates used in industry. Soluble compounds, like chromic acid, are much weaker carcinogens. Figure 2.1 show an example of Chromium (VI) compound which is Chromium trioxide.



Figure 2.1: An example of a chromium (VI) compound: chromium trioxide

2.3 Biosorption

2.3.1 Introduction

Biosorption is processes that use the ability of biological material to accumulate heavy metal from wastewater stream by either metabolically mediated or purely physic-chemical pathways of uptake. Biosorption is a potential alternative to traditional treatment processes of metal ions removal. The phenomenon of

biosorption has been showed in a wide range of non-living biomass like bark, lignin and peanut hulls as well as of living biomass like fungi, and bacteria also in living aquatic plant. One of these aquatic plants is water hyacinth (*Eichhornia crassipes*). Biosorption can also uses biomass raw materials which are either abundant such as seaweeds or wastes from other industrial operations like fermentation wastes. The major advantages of biosorption over other conventional treatment methods are lowcost, high efficiency of metal removal from dilute solutions, no additional nutrient requirements, regeneration of biosorbent, and possibility of metal recovery. (Kaustubha *et al.*, 2005)

The biosorption process involves a solid phase (sorbent or biosorbent; usually a biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, a metal ion). Due to higher affinity of the sorbent for the sorbate species the latter is attracted and bound with different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. While there is a preponderance of solute (sorbate) molecules in the solution, there are none in the sorbent particle to start with. This imbalance between the two environments creates a driving force for the solute species. The heavy metals adsorb on the surface of biomass thus, the biosorbent becomes enriched with metal ions in the sorbate (Alluri *et al.*, 2007).

2.3.2 Biosorbent

Activated carbon has been standard adsorbent for treating wastewater for almost three decades. However, activated carbon remains an expensive material. There are various types of sources of biosorbent for biosorption process such as Seaweeds, microorganisms (bacteria, fungi, yeast, and molds), activated sludge, fermentation waste, and other specially propagated biomasses. Table 2.2 show that some of biomass that has been study for removal of Chromium (VI) from wastewater. Other biomass also has been studied for removing heavy metal from

wastewater especially chromium (VI). This biomass are including, olive oil waste, rice husk and also seaweed. All of this biomass shows the potential of adsorption of chromium. However, some of these adsorbents do not contain high adsorption capacities. Biosorbents were characteristic as broad sources, low-cost, and rapid adsorption.

Table 2.1: Biosorbent use in Chromium (VI) removal

| No | Heavy metal studied | Adsorbent | Parameter studied | References |
|----|------------------------|--|---|---|
| 1 | Cu, Cr(VI), As | Living water Hyacinth | Concentration | Cycle Keith <i>et al.</i> (2006) |
| 2 | Cr(VI) | Dried Water Hyacinth | 1.pH 2.Sorbent dose 3. Contact time 4. Initial Concentration | Kaustubha Mohanty <i>et al.</i> (2006) |
| 3 | Cr(VI) | Coir Pith | 1.pH 2.Sorbent dose 3. Contact time 4. Temperature | Parinda Suksabye <i>et al.</i> (2006) |
| 4 | Cr(VI) | Green algae Spirogyra Speicies | 1.Dose 2. Time contact 3. Initial concentration 4. pH | V.K. Gupta <i>et al.</i> (2001) |
| 5 | Cr(VI) | Red Algae (<i>Ceramium virgatum</i>) | 1.pH 2.Sorbent dose 3. Contact time 4. Temperature | Ahmet Sari & Mustafa Tuzen (2008) |
| 6 | Ni(II), Zn(II), Cr(VI) | <i>Alternanthera philoxeroides</i> | 1.Particle size 1.pH 3. Contact time 4. Temperature | Xue-Song <i>et al.</i> (2006) |
| 7 | Cr(VI) | Coffe husk | 1.pH 2.Sorbent dose 3. Contact time | Waleska E. Olieveira <i>et al.</i> (2007) |

Kaustubha Mohanty *et al.* (2006) reported that dried water hyacinth can remove Chromium (VI) from aqueous solution. Higher percentage of removal was recorded at low initial concentration. Higher removal also achieved at pH 1 since negatively charge $\text{Cr}_2\text{O}_7^{-2}$ were attracted by positively charge functional group on the surface of biomass. At acidic condition more positively charge functional group was exposed. Adsorptions of chromium ions also increase with time. When the contact time between adsorbent and solution increase, it will cause more ion bind with the adsorbent surface wall.

Based on study done by Parinda Suksabye *et al.* (2006), biosorption process of chromium using coir pitch as adsorbent greatly depends on pH. 99.9% removal achieved at pH 2.

2.3.3 Biosorption Mechanism

Generally, there are various types of biosorption mechanisms that can involve in biosorption process such as ion exchange, chelation, precipitation, complex formation and physical adsorption.

2.3.3.1 Ion Exchange

Ion exchange is a reversible chemical reaction wherein an ion in a solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion-exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. Synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications.

Ion exchange reactions are stoichiometric and reversible, and as such they are similar to other solution-phase reactions.

Cell walls of microorganisms contain polysaccharides and bivalent metal ions exchange with the counter ions of the polysaccharides. For example, the alginates of marine algae occur as salts of K^+ , Na^+ , Ca^{2+} , and Mg^{2+} . These ions can exchange with counter ions such as CO^{2+} , Cu^{2+} , Cd^{2+} and Zn^{2+} resulting in the biosorptive uptake of heavy metals. (Kuyucak and Volesky, 1988).

2.3.3.2 Chelation

The word *chelation* is derived from the Greek word *chele*, which means *claw*, and is defined as the firm binding of a metal ion with an organic molecule (ligand) to form a ring structure. The resulting ring structure protects the mineral from entering into unwanted chemical reactions. Figure 2.2 show the example of ion involves in chelation such as carbonate (CO_3^{2-}) and oxalate ($C_2O_4^{2-}$) ions.

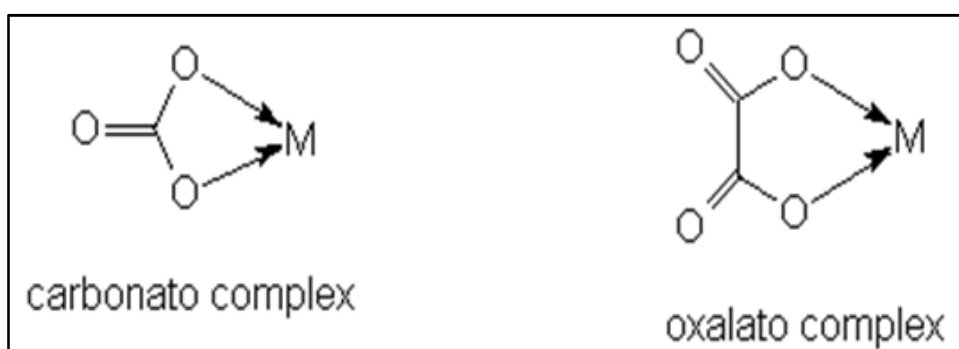
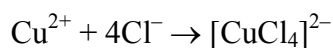
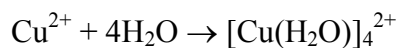


Figure 2.2: Resulting ring from carbonate (CO_3^{2-}) and oxalate ($C_2O_4^{2-}$) ions

2.3.3.3 Coordination (Complex Formation)

A coordination complex is any combination of cations with molecules or anions containing free pairs of electrons. Bonding may be electrostatic, covalent or a combination of both; the metal ion is coordinately bonded to organic molecules. Example of the formation of a coordination compound is:



where coordinate covalent bonds are formed by donation of a pair of electrons from H_2O and Cl^- (Lewis bases) to Cu^{2+} (Lewis acid).

2.3.3.4 Precipitation

Precipitation may be either dependent on the cellular metabolism or independent of it. In the former case, the metal removal from solution is often associated with active defense system of the microorganisms. They react in the presence of toxic metal producing compounds, which favour the precipitation process. In the case of precipitation not dependent on the cellular metabolism, it may be a consequence of the chemical interaction between the metal and the cell surface. The various biosorption mechanisms mentioned above can take place simultaneously. (N. Ahalya *et.al*, 2003)

2.3.3.5 Physical Adsorption

Physical adsorption takes place in biosorption process with the help of Van der Waals' forces. Electrostatic interactions between the metal ions in solutions and cell walls of biosorbent could result the removal of metal ions.

2.3.4 Factor Effecting Biosorption

The investigation of the efficacy of the metal uptake by the microbial biomass is essential for the industrial application of biosorption, as it gives information about the equilibrium of the process which is necessary for the design of the equipment.

The metal uptake is usually measured by the parameter 'q' which indicates the milligrams of metal accumulated per gram of biosorbent material and 'qH' is reported as a function of metal accumulated, sorbent material used and operating conditions.

Temperature seems not to effecting the biosorption performances in the temperature range of 20-35 °C (Aksu et al. 1992)

pH seems to be the most important parameter in the biosorptive process. It affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Friis and Myers-Keith, 1986, Galun et al. 1987)

Biomass concentration in solution seems to influence the specific uptake: for lower values of biomass concentrations there is an increase in the specific uptake (Fourest and Roux, 1992; Gadd et al. 1988). Gadd et al. 1988 suggested that an increase in biomass concentration leads to interference between the binding sites. Fourest and Roux, 1992 invalidated this hypothesis attributing the responsibility of the specific uptake reduce to metal concentration shortage in solution. Hence this factor needs to be taken into consideration in any application of microbial biomass as biosorbent.

Biosorption is mostly used to treat wastewater where more than one type of metal ions would be present; the removal of one metal ion may be influenced by the presence of other metal ions. For instance: Uranium uptake by biomass of bacteria, fungi and yeasts was not affected by the presence of manganese, cobalt, copper, cadmium, mercury and lead in solution (Sakaguchi and Nakajima, 1991).

2.4 Water Hyacinth

Water hyacinth is a non-native, invasive, free-floating aquatic macrophyte. With board, thick and glossy ovate leaves, water hyacinth may rise some 1 meter in height. The leaves are 10-20 cm across, supported above the water surface by long, spongy and bulbous stalks. The feathery, freely hanging roots are purplish black. As much as 50 percent of a single water hyacinth's biomass can be roots, which extend to a depth of up to 2 feet in the water. Moreover, its dramatic lavender flowers and shiny green leaves make it highly prized as an ornamental plant. Water hyacinth is known as one by way of runners, eventually forming daughter plants. The growing season for water hyacinth is typically from March to early December. However, the majority of plants do not die and carry over plants begin to grow in spring as the weather warms. Plants can tolerate extremes of water level fluctuation and seasonal variations in flow velocity, extremes of nutrient availability, pH, temperature and toxic substances. It spreads and grows rapidly under favorable temperature and nutrient condition (warmer temperatures and higher nutrient levels) (Ho Mai Anh *et al.*, 2007).



Figure 2.3: Water hyacinth

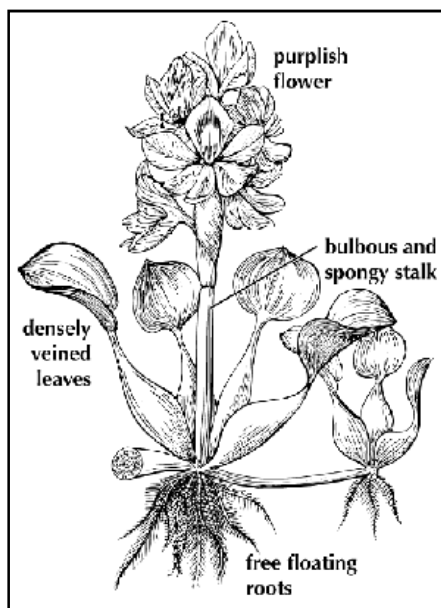


Figure 2.4: Structure of Water hyacinth plant

2.4.1 Impact of Water Hyacinth to the Environment

Water hyacinth can cause hindrance to water transport. Access to harbours and docking areas can be seriously hindered by mats of water hyacinth. Canals and freshwater rivers can become impassable as they clog up with densely intertwined carpets of the weed.

Water hyacinth can grow so densely that a human being can walk on it. When it takes hold in rivers and canals it can become so dense that it forms a herbivorous barrage and can cause damaging and dangerous flooding.

The diseases associated with the presence of aquatic weeds in tropical developing countries are among those that cause the major public health problems: malaria, schistosomiasis and lymphatic filariasis. Some species of mosquito larvae thrive on the environment created by the presence of aquatic weeds, while the link between schistosomiasis (bilharzia) and aquatic weed presence is well known. Although the statistical link is not well defined between the presence of aquatic

weeds and malaria and schistosomiasis, it can be shown that the brughian type of filariasis (which is responsible for a minor share of lymphatic filariasis in South Asia) is entirely linked to the presence of aquatic weeds. (Ho Mai Anh *et al.*, 2007).

Where water hyacinth is prolific, other aquatic plants have difficulty in surviving. This causes an imbalance in the aquatic micro-ecosystem and often means that a range of fauna that relies on a diversity of plant life for its existence will become extinct. Diversity of fish stocks is often affected with some benefiting and others suffering from the proliferation of water hyacinth. People often complain of localised water quality deterioration. This is of considerable concern where people come to collect water and to wash. (Ho Mai Anh *et al.*, 2007).

2.4.2 Potential of Water Hyacinth in Heavy Metal Accumulation

Phytoremediation or phytoextraction is a new and promising method that has been drawing interest in many years. Phytoextraction is the use of plants to remove contaminants from water by pulling the contaminant out of the water through the root system and the plant body. This makes disposal easier and much less expensive because properly destroying the plants and the contaminants held within is a relatively simple process. The major contaminants that are removed from water by plants are various carcinogenic metals such as copper, chromium, arsenic, mercury, and others (Cyle keith *et al.*, 2006).

Cyle keith *et al.*, 2006 study the effect of a floater plant like water-hyacinth for removal of chromium, and copper. Water-hyacinths do not seem to remove large amounts of arsenic or copper from contaminated water. Post-analysis levels of arsenic were close to the beginning levels of arsenic, and it was concluded that water-hyacinth will not remediate arsenic contaminated water. The water-hyacinth appeared to be a good choice for removing chromium from polluted water. At low concentrations, the plant removed about 70% of the chromium in the water. As the concentrations increased, the plant appeared not to be able to take up as much

percent chromium, but the amount the plant was able to take up was still significant which is around 25% (Cyle keith *et al.*, 2006).

The copper data showed directly opposite results when compared to chromium and arsenic. It seems that when a plant such as a water-hyacinth is in the presence of large amounts of copper, levels of copper in water are greater than when copper is present without any plants. With no plants present, copper is much more likely to precipitate out of an aqueous solution (Tucker and Hargreaves, 2003). The samples that had plants present had the higher values because of how plants and copper react with each other. Root exudates from the water hyacinth could have kept copper soluble or suspended in water, thus showing higher amount of copper in the samples with plants (Cyle keith *et al.*, 2006).

CHAPTER 3

METHODOLOGY

3.1 Introduction

This study focused on 4 parameter which are absorbent dosage, initial concentration, pH and time contact.

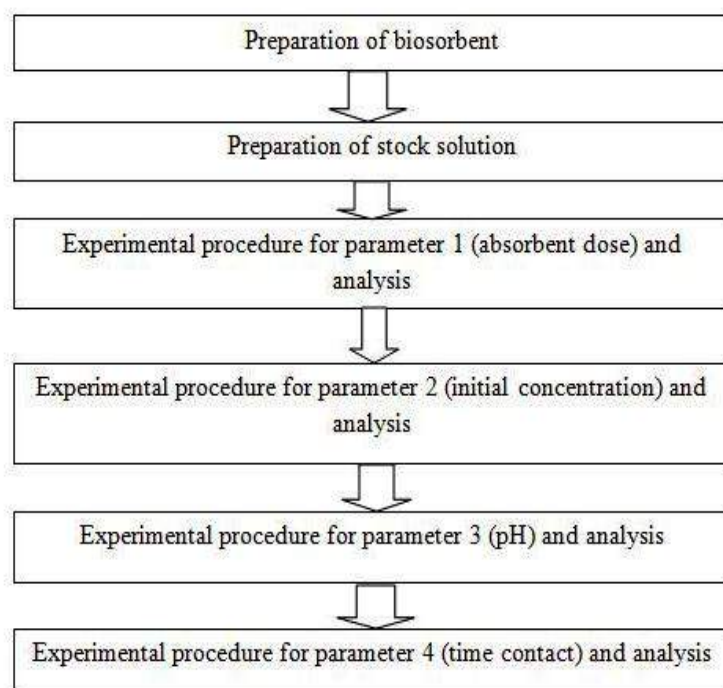


Figure 3.1 Simplified flow diagram of the experiment

Figure 3.1 above show the overview diagram for the experimental procedure of this study. The methodology of this study was based on study by Kaustubha *et al.*, 2006 and V.K. Gupta *et al.*, 2001 with some modification was done. This study started with collection of water hyacinth and preparation of the biosorbent. In this study the stem and leave of the water hyacinth were used as biosorbent. After stock solution has been prepared the study started with first parameter which is to find the biosorbent dosage. The second parameter is effect of initial concentration. The third parameter is the effect of pH value and the final parameter is effect of time contact. In this study, result from each parameter will be used in the following parameter. Atomic Absorption Spectrophotometer (AAS) were used in order to determine the concentration of Chromium in the sample.

3.2 Equipment / Apparatus

In this study, the equipment/apparatus below were used through the experiment:

1. pH meter
2. Orbital shaker
3. Atomic Absorption Spectrophotometer (AAS) model Hitachi Z-5000
4. Conical Flask
5. Measuring cylinder

3.3 Reagent

In this study, the reagent/chemical below was used:

1. Potassium Dichromate, $K_2Cr_2O_7$
2. 0.1M Hydrochloric acid, HCL

3. 0.1M Sodium Hydroxide, NaOH

3.4 Preparation of Dried Water Hyacinth (Biosorbent)

Living water hyacinth was collected at Pekan, Pahang. Then, the water hyacinth was washed with deionized water in order to remove dirt. Then, this fresh water hyacinth was cut to small pieces before undergo oven dried for 24 hour at 60 °C. Roots of water hyacinth were separated from the stem and leaves of the plant. Finally, the dried stem and leave of water hyacinth was reduced to powder form by conventional blender. Only stem and leave of the water hyacinth has used as biosorbent in this study.

3.5 Preparation of Chromium Stock Solution

This experiment used chromium solution in the form of $K_2Cr_2O_7$. Potassium dichromate was mixed with distilled water in volumetric flask to produce stock solution with concentration of 50 mg/L. All working solution obtained by varying the concentration of this stock solution by dilution process using distilled water.

3.6 Biosorption experiment

3.6.1 Effect of Adsorbent Dosage

For studying the effect of absorbent dose, concentration of potassium chromate was adjusted to 5 mg/L by dilution and was put conical flasks. pH for working solution were adjusted to 2. This adjustment had been made by using HCl

before the biomass was added. Each of the conical flasks contains 50 mL of the solution. Each of the conical flasks was added with different of amount of adsorbent range from 0.2 g to 0.7 gram. These conical flasks were closed before placed on the orbital shaker and were shaken for 30 minutes at 150 rpm. After that the solution was filter using filter paper and the supernatant was filtered again using 0.45 μ m nylon syringe filter. After that the supernatant was analyzed using Atomic Absorption Spectrophotometer (AAS).

3.6.2 Effect of Initial Concentration

Chromium solution with different initial concentration was prepared. The initial concentration is ranging from 2.5 to 27.5 mg/L. Using HCl, the pH value of the solution was adjusted to 2. The chromium solutions were mixed with 0.7 gram adsorbent. These conical flasks were closed before placed on the orbital shaker and were shaken for 30 minutes at 150 rpm. After that the solution was filter using filter paper and the supernatant was filtered again using 0.45 μ m nylon syringe filter. After that the supernatant was analyzed using Atomic Absorption Spectrophotometer (AAS).

3.6.3 Effect of pH

For effect of pH, 50 mL of Chromium solution with initial concentration 5 mg/L was prepared and put into several different conical flask. By using HCl or NaOH, the pH value of the solution was adjusted so each of the conical flasks has the different value of pH ranging from 1 to 8. Each flask was added with 0.7 gram of adsorbent. These conical flasks were closed and placed on the orbital shaker for 30 minutes at 150 rpm. After that the solution was filter using filter paper and the supernatant was filtered again using 0.45 μ m nylon syringe filter. After that the supernatant was analyzed using Atomic Absorption Spectrophotometer (AAS).

3.6.4 Effect of Time Contact

Chromium solution with concentration 5 mg/L and pH 1.8 was mixed with 0.7 gram biosorbent. This solution was shaken at different time contact range from 5 minutes to 180 minutes at 150 rpm. After that the solution was filter using filter paper and the supernatant was filtered again using 0.45µm nylon syringe filter. After that the supernatant was analyzed using Atomic Absorption Spectrophotometer (AAS).

3.7 Analysis

The chromium concentration in the solution was determined at the beginning of the experiment (C_i) and also at the equilibrium state (C_e). Sample was analyzed using atomic absorption spectrophotometer (AAS). The equation below was used to calculate the percent removal of chromium ion in the solution by the adsorbent.

$$\% \text{ Removal} = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (\text{eq 3.1})$$

CHAPTER 4

RESULT AND DISCUSSION

4.1 Effect of Adsorbent Dosage

Figure 4.1 show the graph of percentage removal versus of biosorbent dosage at different concentration which are 5 mg/L, 15 mg/L, and 25 mg/L. At concentration 5 mg/L, the maximum adsorption is at 0.7 gram adsorbent which has 72% removal of Chromium. For solution with 15 mg/L concentration, the removal ranged from 48.73% to 54.67% while for solution with concentration 25 mg/L the removal ranged from 34.99% to 51.4%. Result show that the biosorption process is highly dependent on biosorbent dosage. As the biosorbent mass increased, the surface area of the biosorbent also increased which provide more exchangeable site for the anions. In this study the biosorption of chromium is maximum at higher dosage. However for the concentration og 15mg/L and 25 mg/L, there are slightly decrease in biosorption efficiency at higher biosorbent dosage. This can be explained by a result of partial aggregation of biomass which caused the decrease of surface are for the biosorption process. The same trend also was reported previously by by Kaustubha *et al.*, (2005).

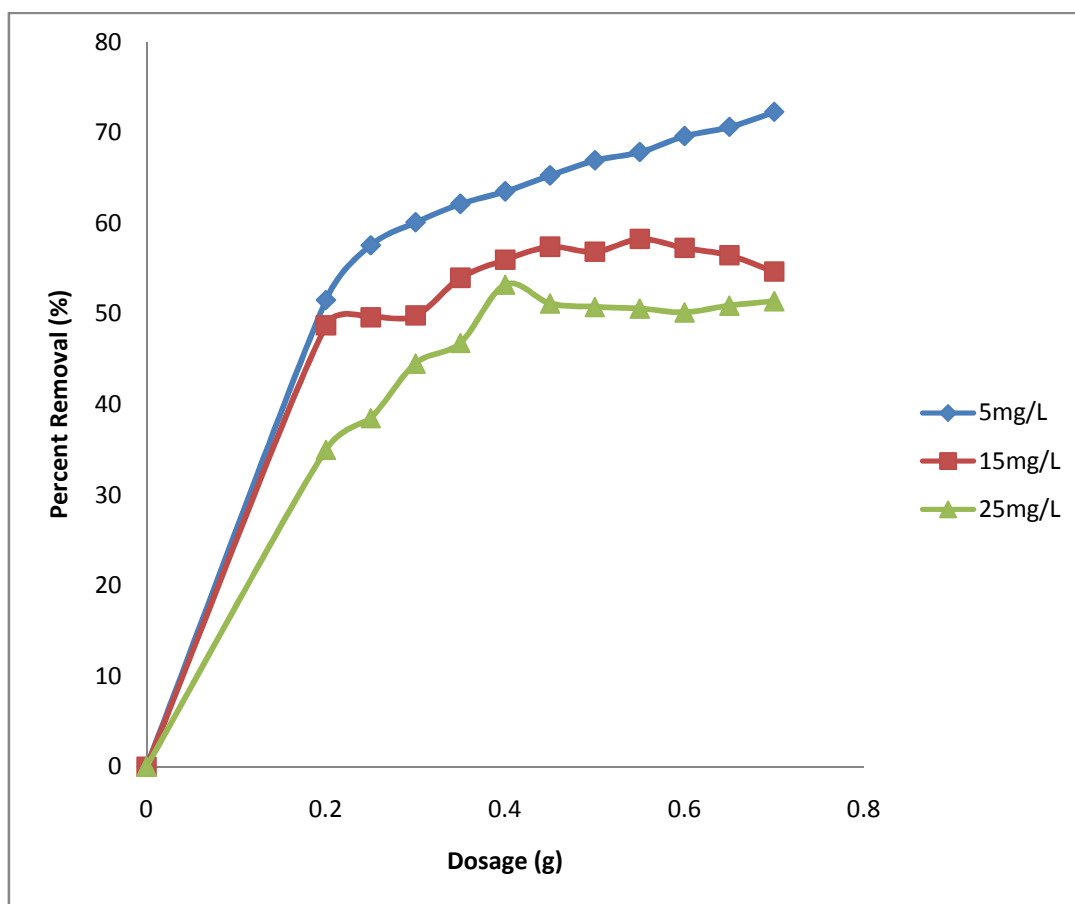


Figure 4.1: Graph of percentage removal of Cr (VI) at different amount of biosorbent dosage (initial concentration is 5mg/L, 15 mg/L and 25mg/L, time contact 30 minutes and pH=2)

4.2 Effect of Initial Concentration

At different initial concentration, the amount of chromium ions in the solution also differs. The amounts of chromium remove increase from concentration 2.5 mg/L to 5 mg/L. However, when the concentration of the solution increase from 5 mg/L to 27.5 mg/L, the percent removal of chromium is decreased. The optimum initial concentration is 5 mg/L which recorded 71.106 % removal. The decrease of chromium removal result from lack of surface area available to adsorbed chromium ion since the amount of biosorbent is fixed for all concentration which is 0.7 mg/L.

Generally, when the initial concentration increased, the removal is decreasing. This is because the number of chromium ion in the solution increase when the concentration increased, so more surface area needed to remove more chromium ion. K. S. Low *et al.*, 1995 and V. K. Gupta *et al.*, 2001 reported the same trend previously.

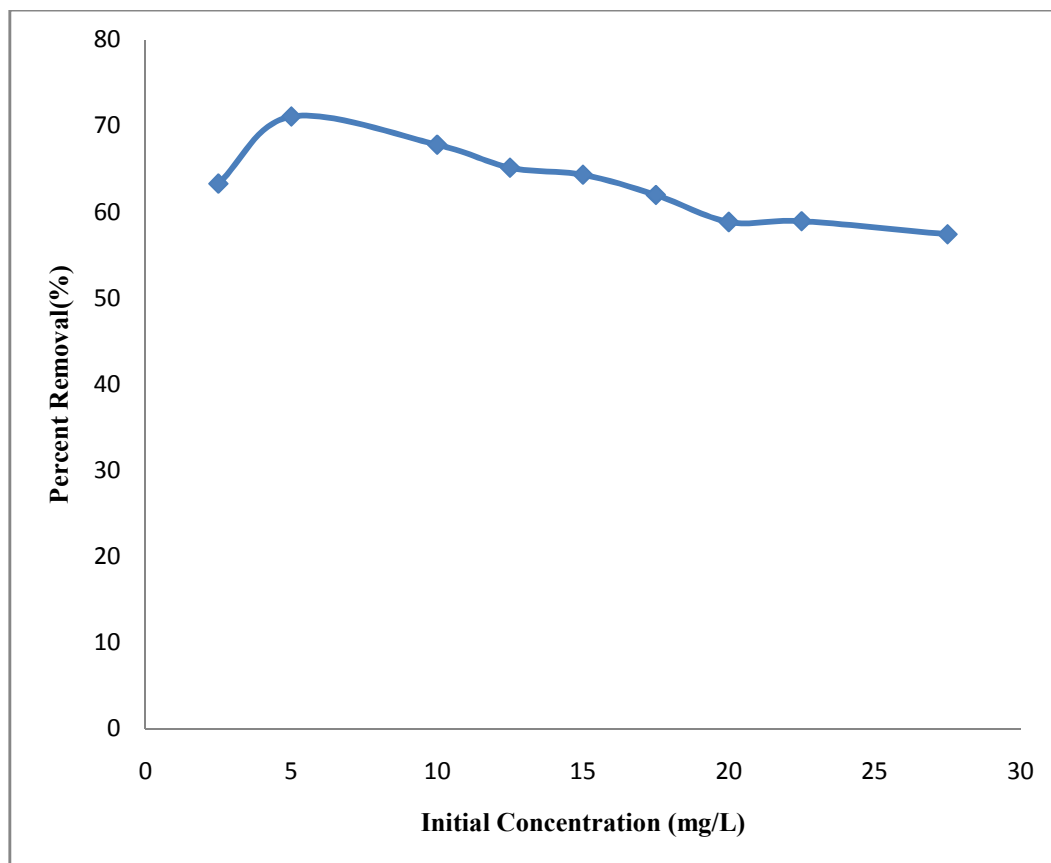


Figure 4.2: Graph of percentage removal of Cr (VI) at different initial concentration (pH=2, time contact =30 minutes, and 0.7 gram biosorbent dosage)

4.3 Effect of pH

Figure 4.3 shows the removal of Chromium at different pH value. From the figure we can see that the optimum pH for absorption of Chromium (VI) was at 1.8. At pH 1-2, the dominant species is HCrO_4^- (Ahmet & Mustafa; 2008), while the dried water hyacinth should be positive at low pH and this will promoted the binding of negatively charge HCrO_4^- . The HCrO_4^- species are most easily exchanged with OH^- ions at active surface under acidic condition.

The amount of Chromium ions sorbed decreased when the pH is higher than 2 until 8. This is because Chromium present in anionic form in the solution and the surface become more negatively charge within that range. So the chromium ions and the surface area will repulse each other and cause the amount of chromium adsorbed decreased. However, there are still chromium had adsorbed by the biosorbent at pH more than two. This is because other mechanism like physical adsorption has take placed and ion exchange mechanism has reduced at that pH. The same trend was reported by Kaustubha *et al.*, 2005 and Parinda Suksabye *et al.*, 2006.

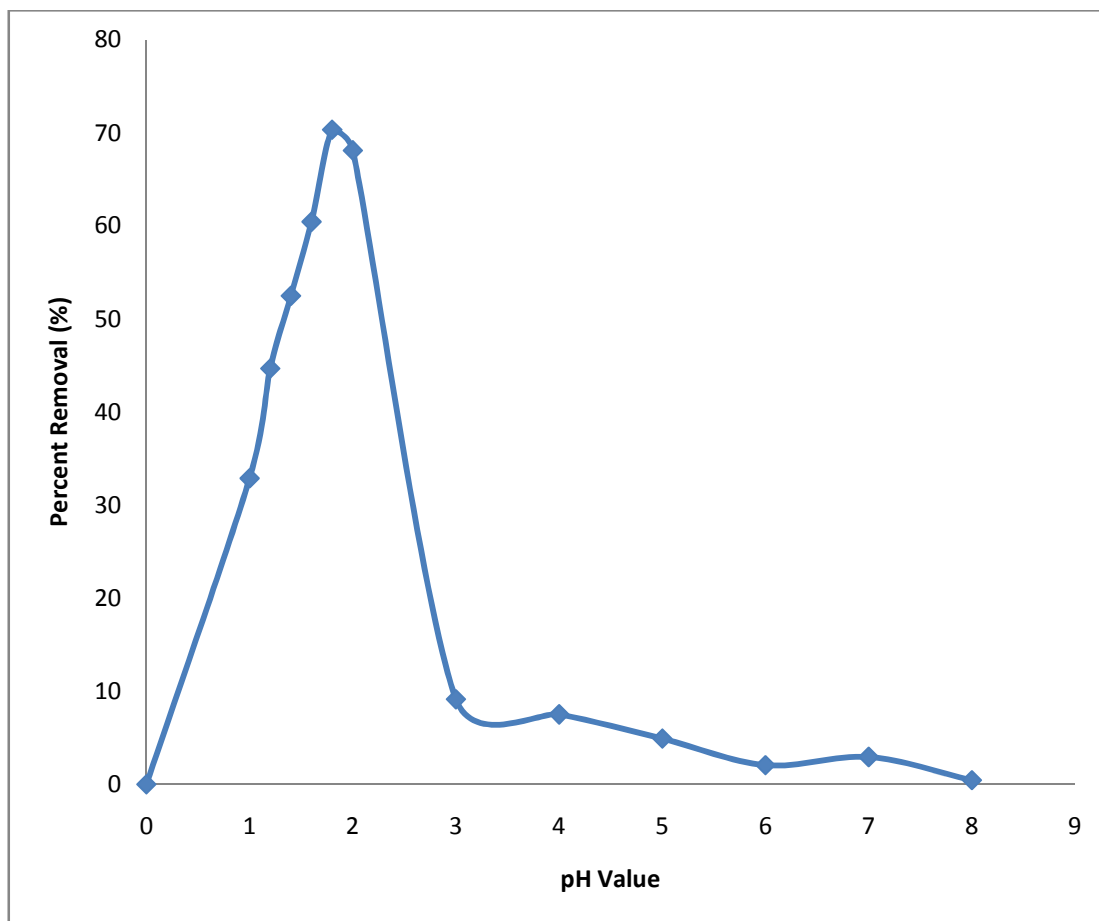


Figure 4.3: Graph of percentage removal of Cr (VI) at different pH (time contact=30 min, initial concentration 5mg/L, and 0.7 gram biosorbent dosage)

4.4 Effect of Time Contact

Time contact was evaluated as one of the most important factor affecting biosorption process. Figure 4.4 show the graph for removal at different time contact. The process is rapid at the beginning of the process. After 5 minutes, the removal is 50.49 % and continues to increase along with contact time. After 75 minutes of time contact, the removal is 74 % and no significance different recorded after that. We can conclude that the optimum time for biosorption reach equilibrium is 75 minutes. Increasing time contact will caused the removal increase because chromium ions

were exposed to the surface area of the biosorbent longer and more chromium ion will bind with the surface wall. There is no addition of chromium removal after 75 minutes maybe because the biosorbent already saturated with chromium ion and no longer can adsorb more ions. The same trend was reported by V. K. Gupta *et al.*, 2001.

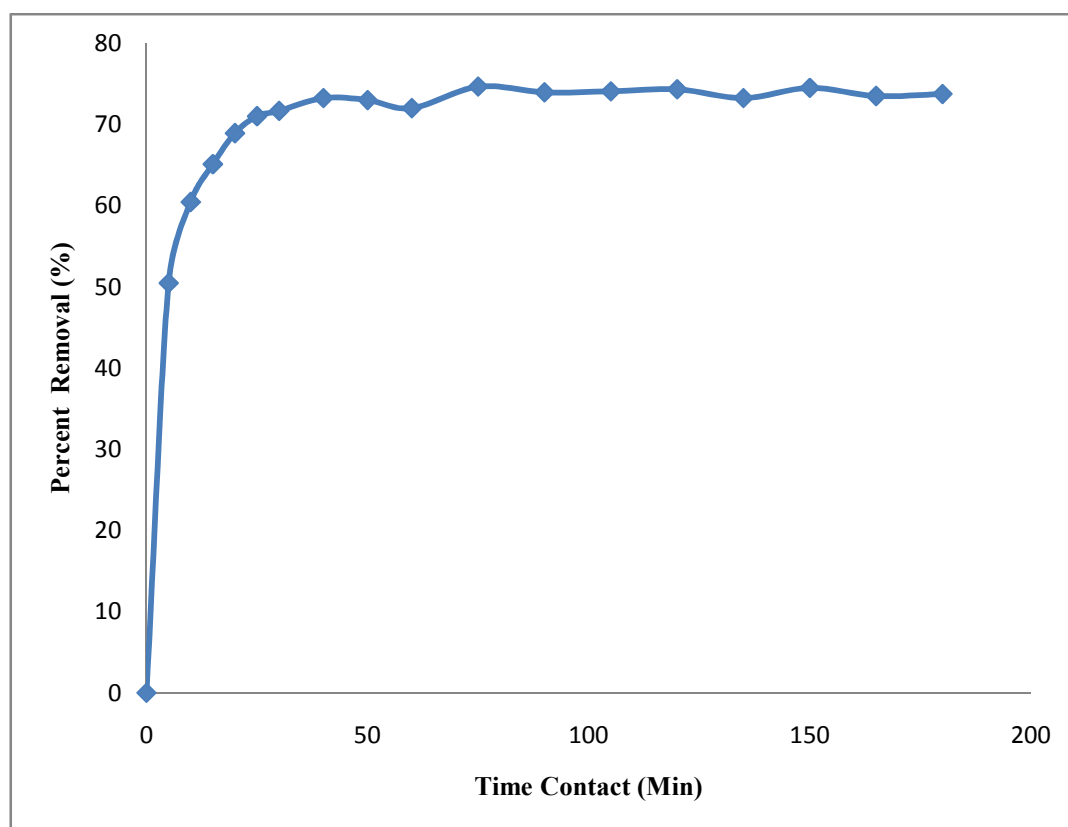


Figure 4.4: Graph of percentage removal of Cr (VI) at different time contact (pH=1.8, initial concentration 5mg/L and 0.7 gram biosorbent dosage)

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study focused on the biosorption of hexavalent Chromium, Cr (VI) onto the dried water hyacinth from aqueous solution. The removal of Cr (VI) increase when the biosorbent dosage increases. The amount of chromium remove from the solution is high at when the initial concentration of solution is low compare to solution with high initial concentration. Biosorption of Cr (VI) also depends on pH. High removal of Cr (VI) achieved at lower pH which is acidic condition. The biosorption rate is high at the beginning of the reaction. When the time contact between biosorbent and solution increase, the binding rate of Cr (VI) will slow until it achieved equilibrium.

From this study we can conclude that the biosorption process of hexavalent Chromium, Cr (VI) depends on biosorbent dosage, initial concentration of the solution, pH value and also time contact between biosorbent and solution. The optimum condition for biosorption of hexavalent Chromium, Cr (VI) using dried water hyacinth achieved at 0.7gram of boisorbent dosage, initial concentration at 5mg/L, pH at 1.8 and equilibrium time is 75 minutes.

The results from this study also show that the dried water hyacinth (*Eichhornia Crassipes*) is suitable for removal of hexavalent Chromium, Cr (VI) from wastewater and can be developed for future utilization of this water hyacinth plant.

5.2 Recommendation

There are some other parameters than can be studied further in order to determine the performance of dried water hyacinth as a biosorbent. This parameter includes effect of particle size, and effect of temperature on biosorption process. The speed of rotation while shaking also can be studied as a parameter affected biosorption process.

Since this study only focused on water hyacinth stem and leaves as a biosorbent, further study can assess the performance of water hyacinth roots in biosorption of hexavalent Chromium, Cr (VI). The mixture of both stems and roots of water hyacinth also can be used as biosorbent of hexavalent Chromium, Cr (VI).

Sample must be preserve if it cannot be analyze right away using AAS after the biosorption process. A small droplet of Nitric acid must be added to the supernatant before keeping it in the refrigerator for preservation of the sample.

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APPENDIX A

Data from AAS

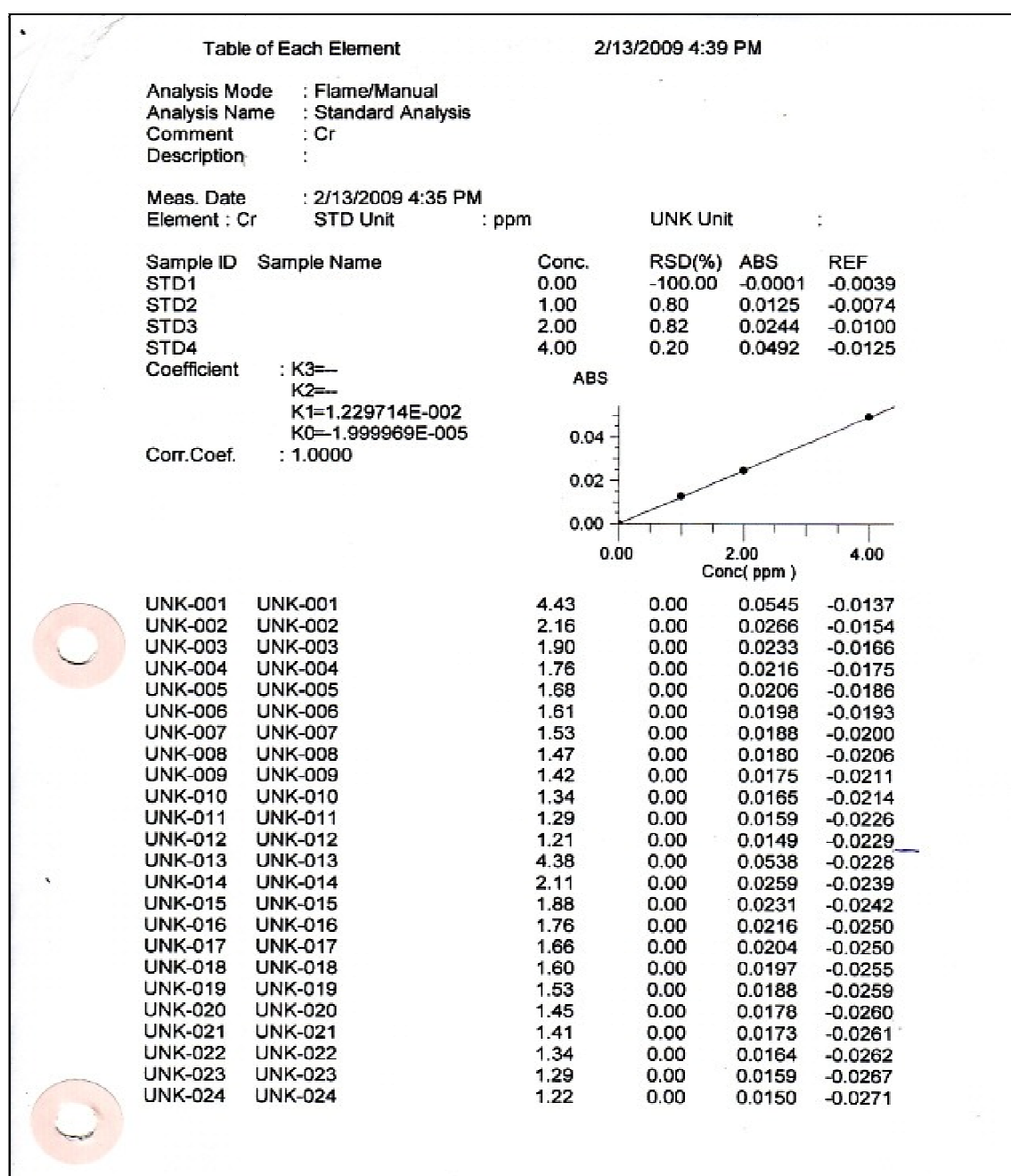


Figure A.1: Result AAS for different dosage at concentration 5mg/L

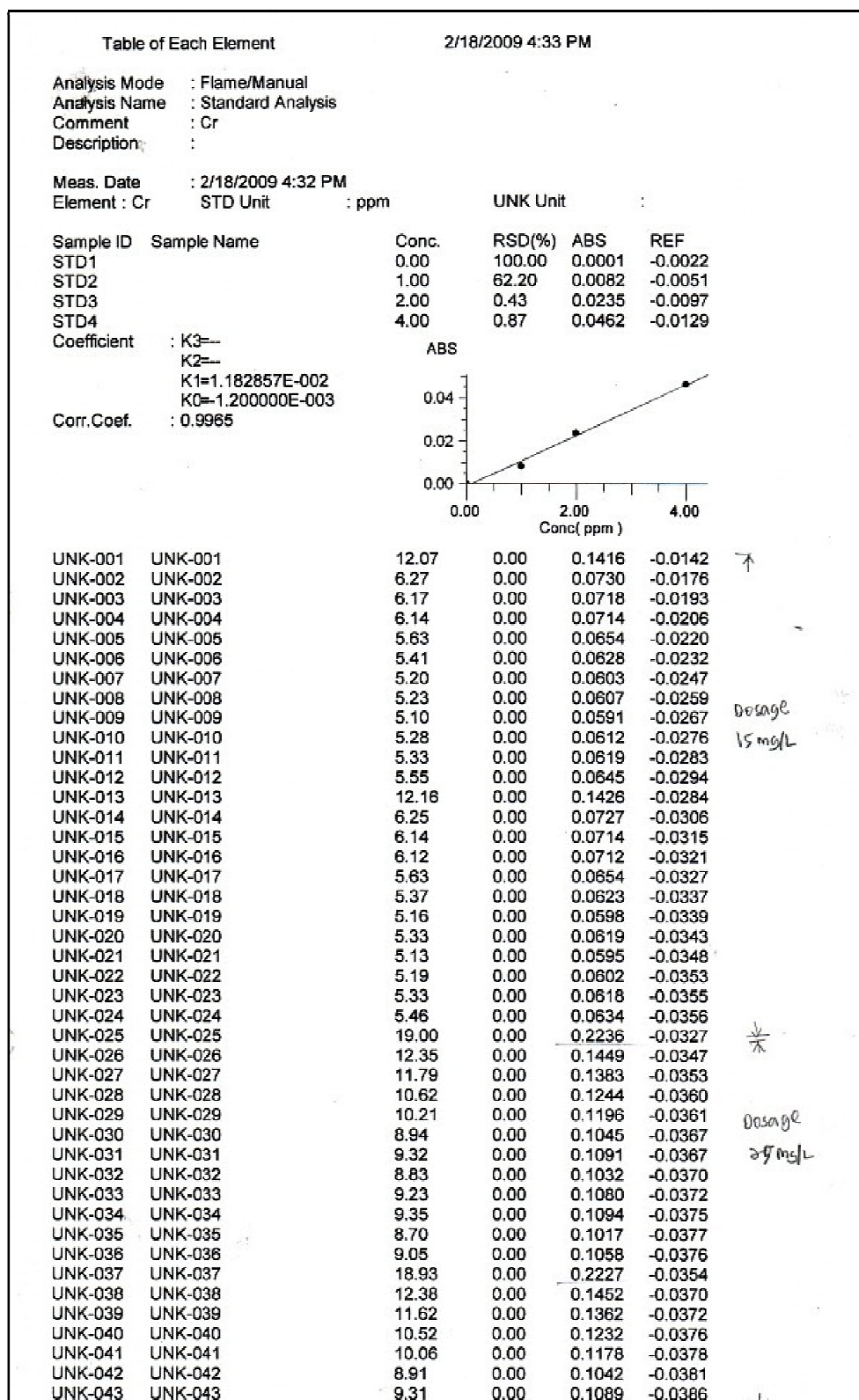


Figure A.2: Result AAS for different dosage at concentration 15mg/L and 25 mg/L

| Sample ID | Sample Name | Conc. | RSD(%) | ABS | REF |
|-----------|-------------|-------|--------|--------|---------|
| UNK-044 | UNK-044 | 8.86 | 0.00 | 0.1036 | -0.0385 |
| UNK-045 | UNK-045 | 9.31 | 0.00 | 0.1089 | -0.0386 |
| UNK-046 | UNK-046 | 9.41 | 0.00 | 0.1101 | -0.0388 |
| UNK-047 | UNK-047 | 8.51 | 0.00 | 0.0995 | -0.0388 |
| UNK-048 | UNK-048 | 9.05 | 0.00 | 0.1058 | -0.0388 |
| UNK-049 | UNK-049 | 9.22 | 0.00 | 0.1079 | -0.0392 |
| UNK-050 | UNK-050 | 9.21 | 0.00 | 0.1077 | -0.0388 |
| UNK-051 | UNK-051 | 9.16 | 0.00 | 0.1072 | -0.0388 |
| UNK-052 | UNK-052 | 5.06 | 0.00 | 0.0587 | -0.0399 |
| UNK-053 | UNK-053 | 5.14 | 0.00 | 0.0596 | -0.0398 |
| UNK-054 | UNK-054 | 5.22 | 0.00 | 0.0606 | -0.0396 |
| UNK-055 | UNK-055 | 5.06 | 0.00 | 0.0587 | -0.0398 |
| UNK-056 | UNK-056 | 5.43 | 0.00 | 0.0630 | -0.0397 |
| UNK-057 | UNK-057 | 5.50 | 0.00 | 0.0638 | -0.0396 |

Figure A.3: Result AAS for different dosage at concentration 25 mg/L

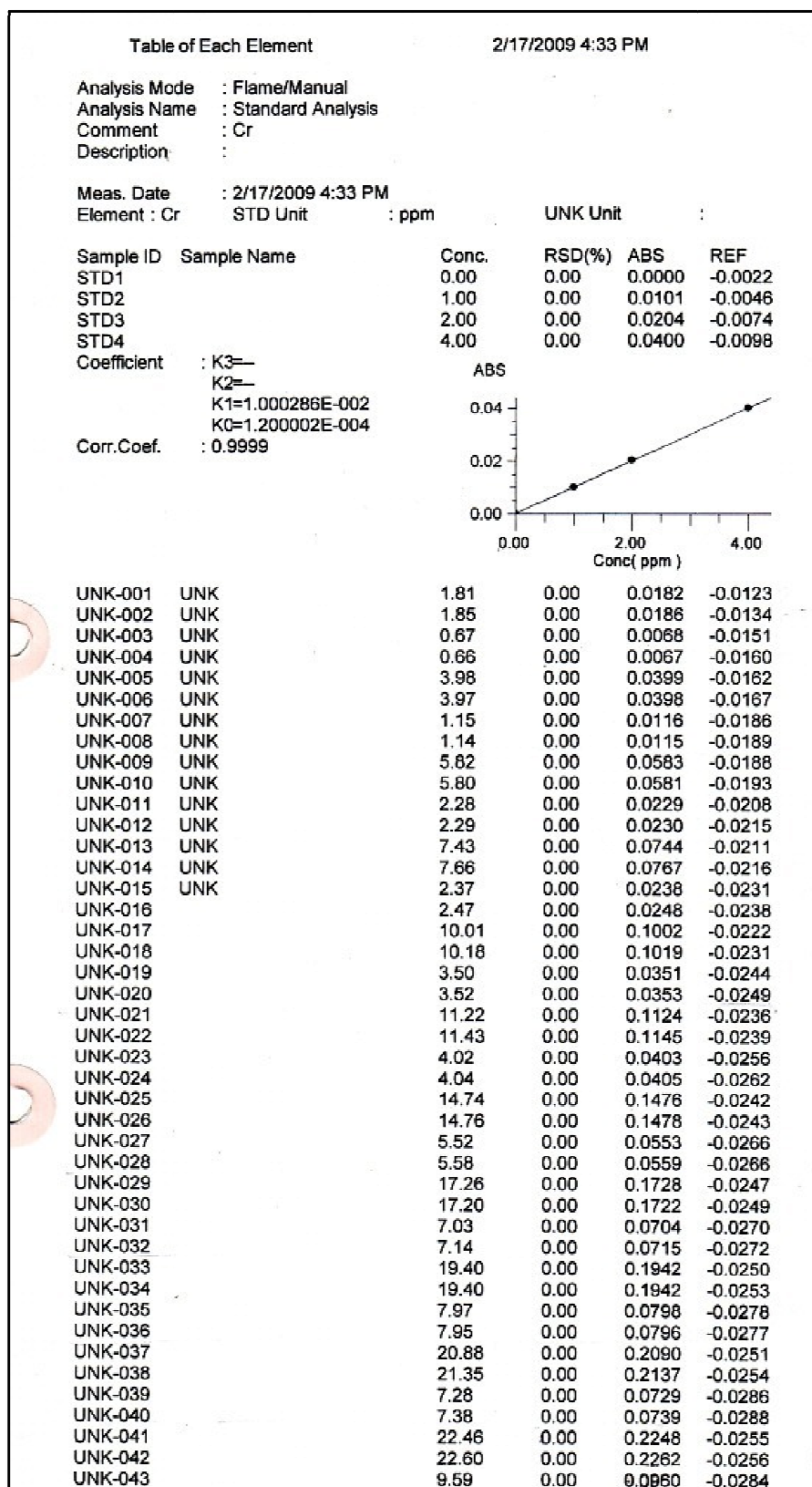


Figure A4: Result AAS for different initial concentration

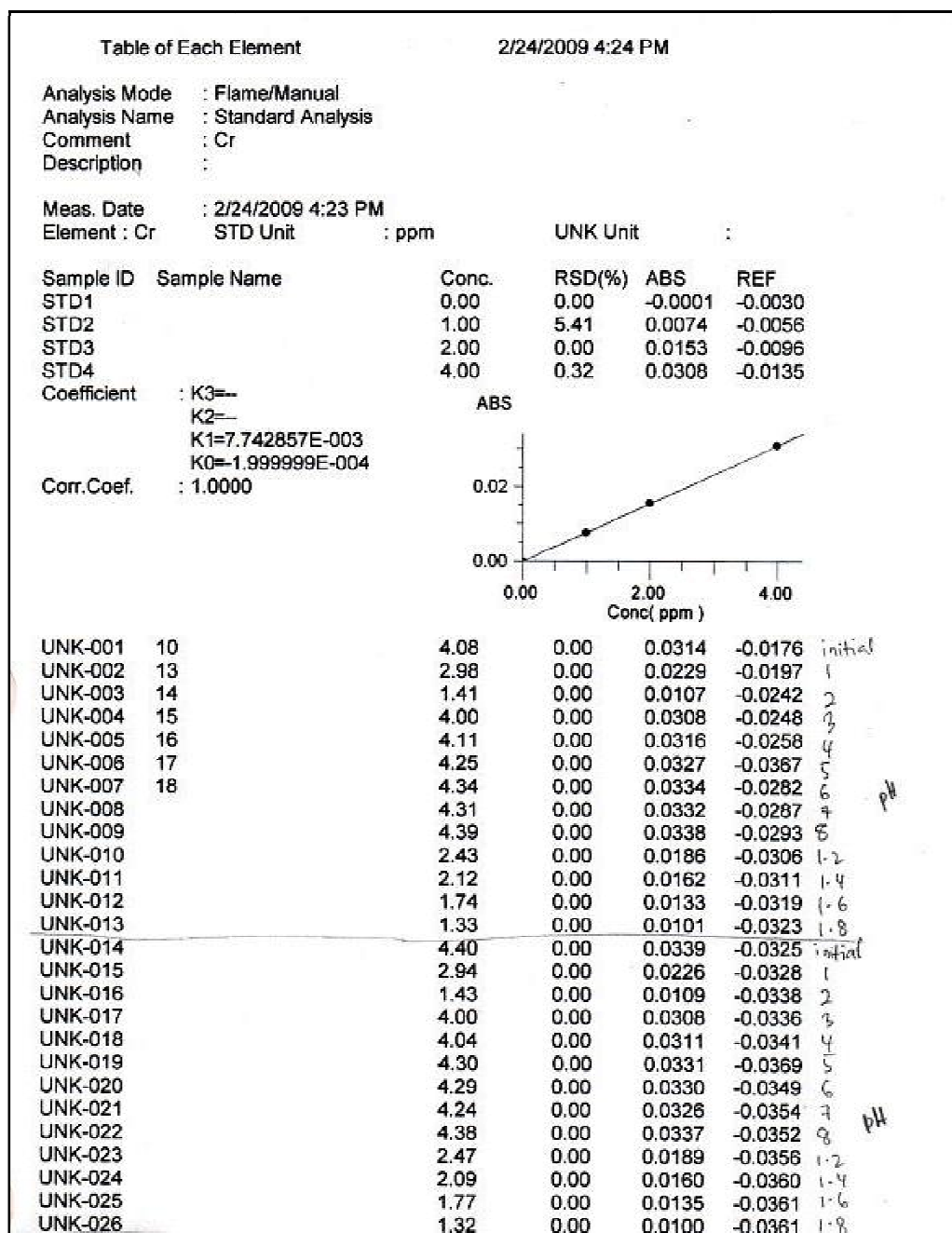


Figure A5: Result AAS for different pH value

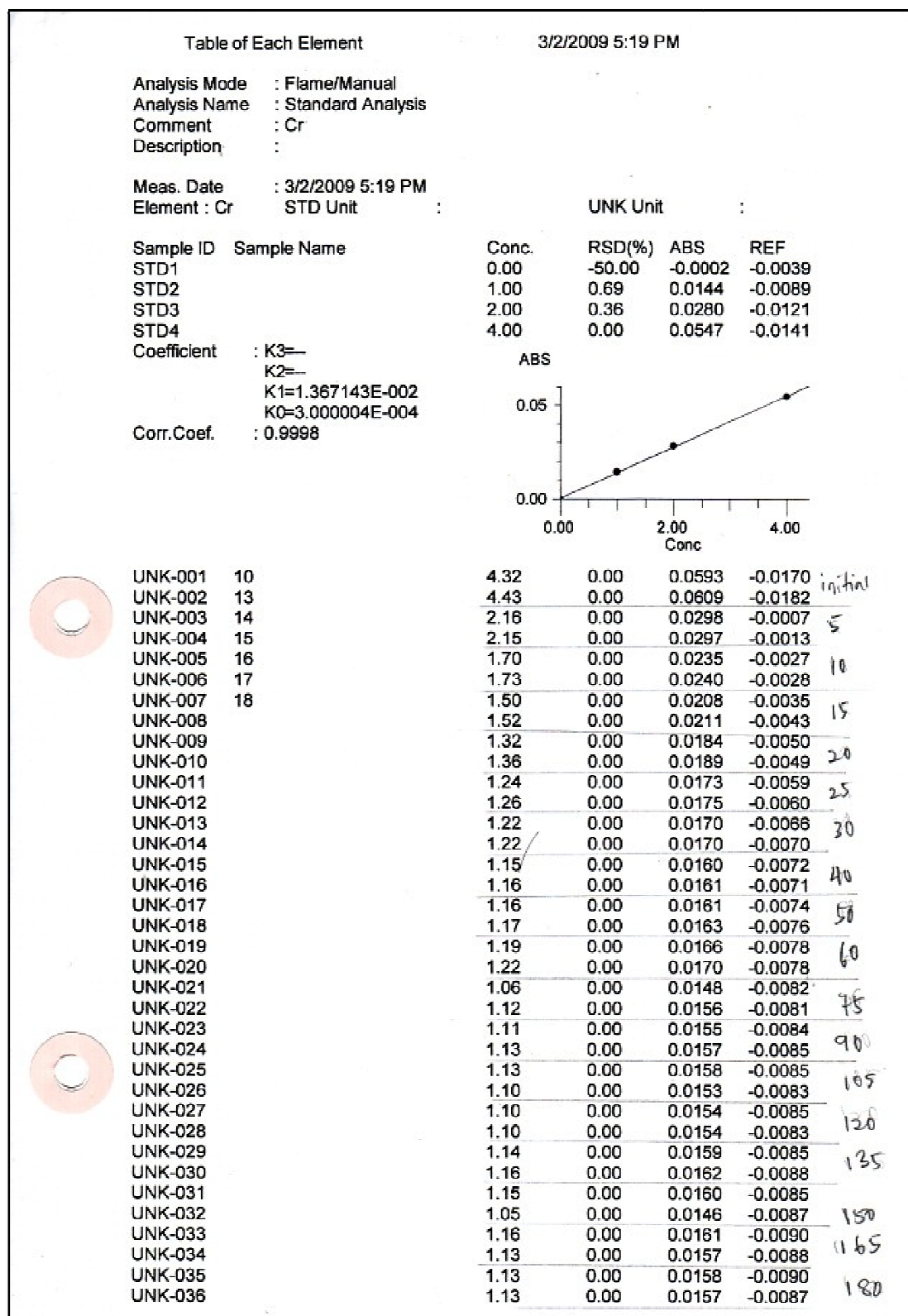


Figure A6: Result AAS for different time contact

APPENDIX B

Percent Removal for Each Parameter

B.1: Percent Removal with different biosorbent dosage at different concentration

| DOSAGE (gram) | PERCENT REMOVAL (%) | | |
|------------------|---------------------|--------|--------|
| | 5mg/L | 15mg/L | 25mg/L |
| 0 | 0 | 0 | 0 |
| 0.2 | 51.52 | 48.73 | 34.99 |
| 0.25 | 57.56 | 49.61 | 38.49 |
| 0.3 | 60.1 | 49.82 | 44.52 |
| 0.35 | 62.14 | 53.97 | 46.8 |
| 0.4 | 63.52 | 55.98 | 53.23 |
| 0.45 | 65.28 | 57.4 | 51.15 |
| 0.5 | 66.94 | 56.86 | 50.77 |
| 0.55 | 67.86 | 58.26 | 50.59 |
| 0.6 | 69.62 | 57.28 | 50.16 |
| 0.65 | 70.63 | 56.47 | 50.92 |
| 0.7 | 72.29 | 54.67 | 51.4 |

B.2: Chromium removal at different initial concentration

| Initial concentration (mg/L) | % Removal |
|------------------------------|-----------|
| 2.5 | 63.31 |
| 5 | 71.106 |
| 10 | 67.83 |
| 12.5 | 65.165 |
| 15 | 64.34 |
| 17.5 | 62 |
| 20 | 58.86 |
| 22.5 | 58.95 |
| 27.5 | 57.43 |

B.3: Chromium removal at different pH

| pH | % Removal |
|-----|-----------|
| 0 | 0 |
| 1 | 32.89 |
| 1.2 | 44.69 |
| 1.4 | 52.5 |
| 1.6 | 60.47 |
| 1.8 | 70.36 |
| 2 | 68.14 |
| 3 | 9.14 |
| 4 | 7.52 |
| 5 | 4.913 |
| 6 | 2.06 |
| 7 | 2.94 |
| 8 | 0.442 |

B.4: Chromium removal at different contact time

| Time contact (min) | % Removal |
|--------------------|-----------|
| 0 | 0 |
| 5 | 50.49 |
| 10 | 60.48 |
| 15 | 65.14 |
| 20 | 68.96 |
| 25 | 71.048 |
| 30 | 71.71 |
| 40 | 73.29 |
| 50 | 73.04 |
| 60 | 72.04 |
| 75 | 74.7 |
| 90 | 74 |
| 105 | 74.12 |
| 120 | 74.37 |
| 135 | 73.29 |
| 150 | 74.54 |
| 165 | 73.54 |
| 180 | 73.79 |

APPENDIX C

Preparation of biosorbent



Figure C 1: Water Hyacinth collected at Pekan



Figure C 2: Water Hyacinth dried in oven



Figure C 3: Water hyacinth after drying process



Figure C 4: Water hyacinth stems and leaves were cut into small pieces before blend

APPENDIX D

Biosorption process



Figure D 1: Mixture of Chromium solution and biosorbent



Figure D 2: Solution were shaken using orbital shaker



Figure D 3: Filtration process in order to get the supernatant

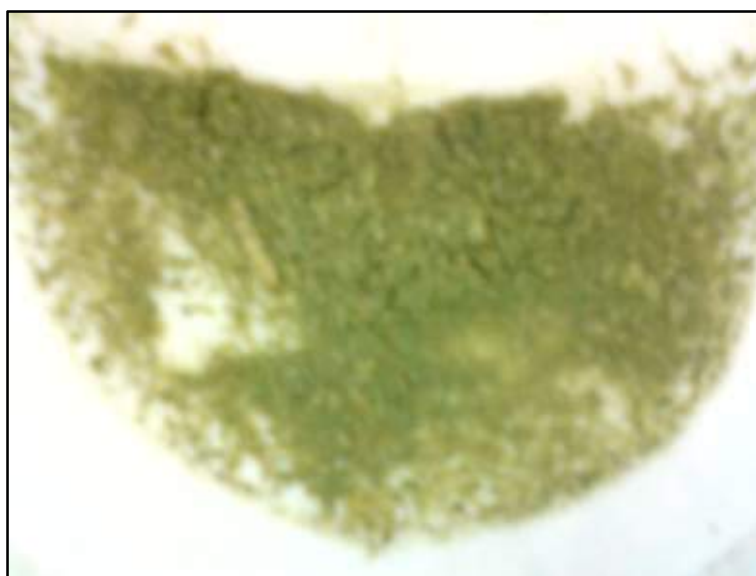


Figure D 4: Biosorbent after biosorption process



Figure D 5: Sample kept in universal bottle before analyzed

APPENDIX E

Analysis of the sample



Figure E 1: AAS use for sample analyzation