REMOVAL OF CADMIUM FROM AQUEOUS SOLUTION BY DRIED WATER HYACINTH, (*EICHHORNIA CRASSIPES)*

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PUTERI EMME MARINA BINTI MOHAMAD

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

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

MAY 2008

DECLARATION

I declare that this thesis entitled "Removal of Cadmium from Aqueous Solution by Dried Water Hyacinth, (*Eichhornia Crassipies)*" is the result of my own research except as cited in the 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

To my love, Khairul Azmil Adzmi and my dearest family
May Allah bless us all….

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ABSTRACT

Water hyacinth (*E. crassipes*) approaches being a scourge in many parts of the world, choking waterways and hindering transport upon them. At the same time it is known to readily abstract heavy metal ions from water and, thus, aids in the removal of heavy metals found in such waters. This study considers the possibility of using dried parts of the plant as an inexpensive adsorbent for the removal of heavy metals from cadmium solution. Water hyacinth is dried and used as biosorbent as removal of cadmium in aqueous solution. Parameters that are used for these studies are dosage of biosorbent, contact time, pH and temperature. The analysis was done by using Atomic Absorption Spectroscopy where initial concentration was 20 mg/L; the amount of biosorbent was from 0.4 to 4 g/L, pH range between 2 to 10, contact time between 10 until 50 min, and temperature range between 25 until 60 degree celcius. The best conditions were found to be biosorbent at dose of 2 g/L, pH of 7, and contact time of 40 min and 35^{o}C for temperature. The results obtained show that the dried Water Hyacinth performed well for the removal of cadmium as heavy metals. As a low cost adsorbent, Water Hyacinth can preferable for removal of heavy metals from wastewaters.

ABSTRAK

Keladi bunting *(E. crassipes)* merupakan tumbuhan yang sedang menular ke seluruh dunia, menyumbat saluran air dan juga menghalang pengangkutan di air terutamanya. Pada masa yang sama, keupayaan keladi bunting sebagai alat untuk menyerap cas logam berat dari air, dan seterusnya membantu menyerap segala logam berat yang ditemui di dalam air. Tesis ini juga mempertimbangkan keupayaan keladi bunting dalam bentuk yang kering atau serbuk sebagai alat penyerap logam berat yang murah khasnya untuk menyerap ion logam kadmium dalam air penyahkumbahan. Keladi bunting dikeringkan dan digunakan sebagai penyerap logam kadmium dalam larutan cecair. Parameter yang dikaji di dalam tesis ini ialah dos penyerapan keladi bunting, masa, pH dan suhu. Di mana, nilai optimum yang diperoleh daripada hasil kajian dianalisa menggunakan “Atomic Absorption Spectroscopy” dengan nilai awal kepekatan 20 mg/L; dengan dos 0.4 kepada 4 g/L, pH diantara 2 hingga 10, masa diantara 10 hingga 50 minit dan juga suhu diantara 25 hingga 60 darjah celcius. Hasil kajian menunjukkan keputusan nilai yang optimum iaitu pada dos 2 g/L, pH 7, masa pada 40 minit dan suhu optimum pada 35 darjah celcius. Ekperimen yang telah dijalankan telah menunjukkan keputusan yang baik iaitu keladi bunting sebagai alat penyerapan logam berat yang berkesan.

TABLE OF CONTENTS

3 METHODOLOGY

4 RESULTS AND DISCUSSIONS

5 CONCLUSION

APPENDICES

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

g - Gram
mol - Molar
cm - Centimeter
°C - Degree Celcius
nm - Nanometer
kJ - Kilo Joule
V - Voltan
in - Inch
T - Tonne
μ - micro
λ - Wavelength
ξ - Energy State
λ_E - Characteristic Wavelength
A - Absorbance
e - Molar Absorptivity
b - Path Length
μL - Micro Liter
ppm - part per million
m - Mass
$\mathcal{V}$ - Volume
M - Molarity
i - Initial
f - Final

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, Water Hyacinth or in scientific name *Eichhornia crassipes* have been disturbing mankind ecosystem especially making pollute to the lake, river and etc. Water hyacinth is believed has a potential to remove heavy metals from water such as Cadmium (Cd). Zhu *et al*. (1999) have studied the ability of water hyacinth to take up and translocate six trace elements namely As(V), Cd(II), Cr(VI), Cu(II), Ni(II) and Se(VI) under controlled conditions.

Nevertheless, the mobilization of heavy metals in the environment due to industrial activities is of serious concern due to the toxicity of these metals in human and other forms of life (Vieira and Volesky, 2000; Esterves *et al.*, 2000). Removal of toxic heavy metals from industrial wastewater is essential from the standpoint of environmental pollution control (Yuan *et al*., 2001). Many industries, especially electroplating, battery and plastic manufacturing release heavy metals such as cadmium and zinc in wastewater (Olguin and Hurnandoz, 1998; Prasad and Pandey, 2000).

However, heavy metals such as Cd^{2+}, Zn^{2+}, Fe^{2+} are essential micronutriens for plants but when it present in excess, they can become extremely toxic. Cd is one of the most toxic heavy metals and is considered non-essential for living organisms. Cd has been recognized for its negative effect on the environment where it accumulates throughout the food chain posing a serious threat to human health. Science Asia, 2004, also quote that Cd pollution has induced extremely severe effects on plants.

Recently, researcher has shown an interest in treating wastewater with benefit of cost effective and environmentally friendly technologies for the remediation of soil and wastewater polluted with heavy metals elements (ScienceAsia 30, 2004). Plants which have the ability to absorb and accumulate nonessential metals such as Cd and Pb, and this ability could contribute to environment by removing pollutant metals (Holan and Volesky , 1994).

Water hyacinth is a free floating aquatic plant well known for its production abilities and removal of pollutants from water (A. Malik *et al.*, 2007). It has been discovered that water hyacinth's quest for nutrients can be turned in a more useful direction. The plant has been shown to accumulate trace elements such as Ag, Pb, Cd and Zn.The focus on water hyacinth as a key step in wastewater recycling is due to the fact that it forms the central unit of a recycling engine driven by photosynthesis and therefore the process is sustainable, energy efficient and cost efficient under a wide variety of rural and urban conditions (ScienceAsia 30, 2004).

1.2 Objective of Study

The objectives of this study are to study the potential of water hyacinth as a wastewater treatment method to remove cadmium from aqueous solution.

1.3 Scope of Study

The scope of this study is to study the effects of biosorbent dosage, contact time, pH and temperature in the removal of cadmium from aqueous solution.

1.4 Problem Statement

Water hyacinth is listed as one of the most productive and active plants on earth and it are considered as one of the world's worst aquatic plants. It cans double its size in 5 days and a mat of medium sized plants may contain 2 million plants per hectare that weigh 270 to 400T (A. Malik, 2007). However, it is also known to be an accumulator of heavy metal ions and has been widely studied as such (Wolverton, 19751; Blake *et. al.*, 1987; Pinto *et. al.*, 1987). However, two main disadvantages emerge from this practice. First, ponds have to be constructed if they are not available in place and, second, heavy metals produce phytotoxic effects on plants resulting in inhibition of chlorophyll synthesis and necrosis (Blake *et. al.*, 1987; Satyakala *et al.*, 1992; Delgado *et. al.*, 1993). Additionally, the metal sorption capacity of the dried biomass of aquatic plants has been recently investigated (Scheinder *et. al.*, 1994). Compared to living systems, dried biomass presents advantages for conservation, transport and handling, being able to be applied in waste water treatment plants as a simple sorbent material. To date, however, the individual parts of *E. crassipes* (stems, roots, leaves of the plants) have not been studied. Also, there has been little direct comparison of the relative heavy metal biosorption by *E. crassipes* and its parts to biosorption by various other biosorbents.

CHAPTER 2

LITERATURE REVIEW

2.1 Background Study of Cadmium

Figure 2.1: Cadmium metal solid

Cadmium is a lustrous, silver-white (as shown in Figure 2.1), ductile, very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but insoluble in alkalis. It has similar in many physical to zinc but it forms more complex compounds. More details on properties of cadmium are shown in Table 2.1.

Cd has been recognized for its negative effect on the environment where it accumulates throughout the food chain posing a serious threat to human health (Holan and Volesky, 1994). Chronic dust or fume exposure can give permanently damage to the lungs, producing shortness of breath and emphysema. The risks of absorption via dermal contact are negligible.

In every year, a very large amount of cadmium is released into the environment, about 25,000 tons. Cadmium is one of the most toxic metals affecting the environment. Mining and metallurgy of cadmium, cadmium electroplating, battery and accumulator manufacturing, pigments and ceramic industries waste waters contain undesired amounts of Cd2+ ions (G.H. Pino *et al*., 2006)

While, in aquatic ecosystems cadmium can bio accumulate in mussels, oysters, shrimps, lobsters and fish. The susceptibility to cadmium can vary greatly between aquatic organisms. Salt-water organisms are known to be more resistant to cadmium poisoning than freshwater organisms. Mean time, animals that eating or drinking cadmium also sometimes gets high blood-pressures, liver disease and nerve or brain damage. This scenario shows that the damage affects of cadmium not only to environment but to animals and aquatic.

Meantime, when humans expose to cadmium exposure, kidneys and lungs are the most effected organs. As mentioned above, cadmium poisoning may be acute by ingestion or inhalation or the poisoning may be chronic at lower levels, which can cause kidney damage by the mechanism described above. In chronic exposure, cadmium accumulates in the body, particularly the kidneys and liver.

Other health effects that can be caused by cadmium are:

1) Diarrhoea, stomach pains and severe vomiting
2) Bone fracture
3) Reproductive failure and possibly even infertility
4) Damage to the central nervous system
5) Damage to the immune system
6) Psychological disorders

7) Possibly DNA damage or cancer development
8) muscle cramps

Table 2.1: Chemical properties of cadmium

Items	**Properties**
Atomic number	48
Atomic mass	112.4 g.mol $^{-1}$
Electronegativity according to Pauling	1.7
Density	8.7 g.cm^{-3} at 20°C
Melting point	321 °C
Boiling point	767 °C
Vanderwaals radius	0.154 nm
Ionic radius	0.097 nm (+2)
Isotopes	15
Electronic shell	[Kr] 4d^{10} 5s^{2}
Energy of first ionisation	866 kJ.mol $^{-1}$
Energy of second ionisation	1622 kJ.mol $^{-1}$
Standard potential	-0.402 V
Discovered	Fredrich Stromeyer in 1817

2.1.1 Cadmium in Water

WHO, 1992 said that the average cadmium content in the world's oceans has variously been reported as low as <5 ng/L and 5-20 ng/L by OECD (1994), Jensen and Bro-Rasmussen (1992), to as high as 110 ng/L (CRC 1996), 1 00 ng/L (Cook and Morrow 1995) and 10 to 100 ng/L (Elinder 1985). These high levels have been noted found by Elinder (1985), around certain coastal areas and meanwhile WHO (1992), and OECD (1994), found that the variations of cadmium concentration with the ocean depth, presumably due to patterns of nutrient concentrations, have also been measured. Even greater variations are quoted for the cadmium contents of rainwater, fresh waters, and surface waters in urban and industrialised areas. Levels from 10 ng/L to 4000 ng/L have been quoted in the literature depending on specific location and whether or not cadmium totals or dissolved cadmium is measured.

As in natural way, cadmium usually is a minor constituent of surface and groundwater. It believe OECD (1994), that cadmium may exist in water as the hydrated ion, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or as organic complexes with humic acids. Cadmium can also enter aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition direct discharge from industrial operations, leakage from landfalls and contaminated sites, and the dispersive use of sludge and fertilizers in agriculture. Since cadmium is a major compound that usually been used in industry, and so it is highly contributed to problematic environment supported by WHO (1992), also state that much of the cadmium entering fresh waters from industrial sources may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment. Cook and Morrow (1995) also have shown of some data that recent sediments in lakes and streams range from 0.2 to 0.9 ppm in contrast to the levels of generally less than 0. 1 ppm cited above for fresh waters.

The rivers which believe have excess cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, dumping of dredged sediments or flooding. It has also been demonstrated that rivers can transport cadmium for considerable distances, up to 50 km, from the source (WHO 1992). Nonetheless, studies of cadmium contamination in major river systems over the past twenty to thirty years have conclusively demonstrated that cadmium levels in these rivers have decreased significantly since the 1960s and 1970s (Cook and Morrow 1995, Elgersma *et al*., 1992, Mukunoki and Fujimoto 1996, Van Assche and Ciarletta 1992). For example, studies on the Rhine River Basin from 1973 through 1987 indicated that the point source cadmium discharges to the Rhine River decreased from 130 to 11 mt per year over that 14-year time span, a reduction of over 90% (Elgersma *et al*., 1992). Similarly, data on total cadmium and dissolved cadmium at the Dutch/German border over the period from 1971 to 1987 have shown comparable reductions (Van Urk and Marquenie 1989) (Levels of cadmium in environment, http://www.cadmium.org/). The distribution of cadmium to waters play big role whether cadmium emitted to waters is able or unable to enter the food chain and affect human health.

2.2 Background Study of Water Hyacinth (*Eichhornia crassipe*)

Figure 2.2: Water Hyacinth in purplish black color.

Water hyacinth with broad, thick and glossy ovate leaves, water hyacinths can be raise till 1 metre in height. The leaves also can rise to 10-20 cm across, supported above the water surface by long, spongy and bulbous stalks. While the feathery, freely hanging roots are purplish black color. An erect stalk supports a single spike of 8-15 conspicuously attractive flowers, mostly lavender to pinkish in colour with six petals. Water hyacinth grows over a wide variety of wetland types and prefers nutrient-enriched waters. However, it can tolerate considerable variation in nutrients, temperature and pH levels. The optimum pH for growth of water hyacinth is 6–8. It can grow in a wide range of temperature from 1 to 40°C (optimum growth at 25–27.5°C) but it is thought to be cold-sensitive (Wilson *et al.*, 2005). Fruit a 3-celled capsule with many seeds. When not in bloom, water hyacinth may be mistaken for frog's-bit (*Limnobium spongia*). Water Hyacinths are the only large aquatic herb that can float on the water unattached to the bottom. They float on bloated air-filled hollow leaf stalks that give them their Malay name that means "pregnant tuber". Their roots trail underwater in a dense mat.

The Water Hyacinth has special adaptations which are allowing them to grow and spread rapidly in freshwater. They can withstand extremes of nutrient supply, pH level, temperature, and can even grow in toxic water. They grow best in still or slow-moving water. Water hyacinth also known as one of the fastest growing plants, water hyacinth can reproduces primarily by way of runners or stolons, eventually forming daughter plants. They may also reproduce via seeds. The common water hyacinth (*Eichhornia crassipes*) is a vigorous grower known to double its population in two weeks. Water hyacinth grows over a wide variety of wetland types and prefers nutrient-enriched waters.

2.2.1 Environmental Problems by Water Hyacinth

Water hyacinth is listed as one of the most productive and active plants on earth and it are considered as one of the world's worst aquatic plants. It cans double its size in 5 days and a mat of medium sized plants may contain 2 million plants per hectare that weigh 270 to 400T (A. Malik, 2007). These dense mats interfere with navigation, recreation, irrigation, and power generation (Epstein, 1998). Many large hydropower schemes have to devote significant time and money in clearing the weed in order to prevent it from entering the turbine and causing damage and power interruptions. The blockage of canals and rivers can even cause dangerous flooding. On the other hand, increased evapotranspiration due to water hyacinth can have serious implications where water is already scarce. Water hyacinth can also present many problems for the fisherman such as decreased fish population, difficult access to the fishing sites and loss of fishing equipment, resulting in reduction in catch and subsequent loss of livelihood (A. Malik / Environment International 33, 2007).

Water hyacinth is blamed for the reduction of biodiversity as well. These mats competitively exclude native submerged and floating-leaved plants and its associated fauna, thereby causing an imbalance in the aquatic micro-ecosystem. Diversity of fish stocks is also affected. Low oxygen conditions beneath the mats create good breeding conditions for mosquito vectors of malaria, encephalitis and filariasis. Lately the hyacinth has invaded many tropical lakes including Lake Victoria, East Africa where it caused several of the above described problems such as reduction in fish catch, interference with transportation and water supply and breeding of snails, mosquitoes and snakes (Mailu, 2001, and Mironga, 2004). Plummer (2005) reported that the density of snails Biomphalaria sudanica (hosts of the disease organism *Schistosoma mansoni*) was increased in the vicinity of water hyacinth in Lake Victoria, East Africa. Until only a few years ago, Simberloff *et al.*, 1997; Langeland and Burks, 1998 reported that the major problem with water hyacinth in Florida were actually covering as many as 125,000 acres of water with up to 200T of hyacinths per acre.

2.2.2 Water Hyacinth as Metals Removal

In the last few decades, significant progress in bioremediation of metals and radionuclide has been made (Prasad and De Oliveira Freitas, (2003); Malik, 2004). Aquatic plants are known to accumulate metals from their environment and affect metal fluxes through those ecosystems. Water hyacinth has exceptionally high affinity and accumulation capacity for several metals (Zaranyika *et al.,* (1994); Polprasert and Katiwada, 1998; Zhu *et al*., 1999). Therefore, it is used as a biomarker and is introduced in wetlands for water phytoremediation (Satyakala and Jamil, 1992).

Due to these reasons, investigations on metal sorption capacity of the dried biomass of water hyacinth have gained momentum (Table 2.2). Compared to living systems, dried biomass presents advantages for conservation, transport and handling. Metals are mostly concentrated at the roots of water hyacinth, indicating that the root system could act as an efficient biosorbent for various materials which are soluble in water (Low and Lee, 1990; Hao *et al*., 1993; Low *et al*., 1994).

Therefore, the usefulness of the dried biomass of non-living water hyacinth roots in removing metal ions from solution has been actively researched in the last decade (Table 2.2). The efficient sorption of uranium, copper as well as basic dyes by dead water hyacinth roots has been demonstrated (Low et al., 1994; Shawky et al., 2005). Al Rmalli et al. (2005) have shown that more than 93% of arsenite (As(III)) and 95% of arsenate (As(v)) were removed from a solution containing 200µg As/L within 60min of exposure to a powder produced from dried roots. There has been little direct comparison of the relative heavy metal biosorption by water hyacinth or its parts with biosorption by various other biosorbents. Schneider et al. (1995) however, have shown that dried roots and aerial parts of water hyacinth are better biosorbent than yeast (*Candida parapsilosis*), bacterial (*Mycobacterium phlei*) and fungal (*Rhizopus oryzae*) strains. The authors suggested that the dried biomass of the plant might be placed in simple bags and used in a very low-cost metal ion removal system for decontamination of chemical and mining industry wastewaters. Udaya Simha et al. (2002) showed that the root of water hyacinth is an effective and attractive proposition compared to activated carbon in removing fluoride from water bodies. Further, activated carbon prepared from water hyacinth plant has been found to show better adsorption of pollutants like dyes and phenol than commercial activated carbon and the same has been used for the removal of metals like Hg and Pb also (Table 2.2).

Table 2.2: Pollutants biosorption by dried/processed water hyacinth plant part (A. Malik, 2007)

Pollutant	**Water hyacinth part**	**Maximum sorption capacity/removal**	**Reference**	**Comments**
Basic dyes (methylene blue and Victoria blue)	Dried roots	Methylene blue (128.9mg g^{-1}) and Victoria blue (145.4 mg g^{-1})	Low et al. (1995)	Sorption depends on pH, sorbent dose and dye conc.
Pb, Cd, Cu, Zn	Dried roots and aerial parts	Pb (47 mg g^{-1}), Cd (27), Cu (23), Zn(20)	Schneider et al. (1995)	WH found to be better biosorbent than yeast, bacterial and fungal strains
Pb, Cu, Zn, Cd, Cr, Mn, Ni, Co, Au, Ag (5 mg l^{-1})	Treated roots	Acidic and basic treatments increased the metal uptake	Yao and Ramelow (1997)	
Lead (15-25 mg l^{-1})	Activated carbon prepared from water hyacinth	16.61 mg g^{-1} at pH 5, particle size (125-180µm)	Shekinah et al. (2002)	Pb removal increased with increase in pH from 2 to 4
Mercury (10-40 mg l^{-1})	Activated carbon prepared from water hyacinth	28.4 mg g^{-1} at pH 5, particle size (125-180µm)	Kadirvelu et al. (2004)	Sorption dependent on contract time, pH, Hg(II) and carbon conc. Data fitted both Freundlich and Langmuir isotherm models
Organic pollutants viz methylene blue (MB), Congo red (CR), p-	Activated carbon prepared from water hyacinth	MB (139 mg g^{-1}), CR (154), PNP (149), P (59)	Al Rmalli et al. (2005)	Activated carbon prepared from WH showed better adsorption than commercial activated carbon

nitrophenol (PNP), phenol (P)				
Arsenic	Powdered dried root	93% of As(III) and 95% of As(v) removal from 200µg As l^{-1} within 60 min	Shawky et al. (2005)	As conc. In treated solution < 10 µg l^{-1} (WHO guideline limit value)
Uranium (20-100µgml^{-1}))	Dried roots	64000U^{6+} µg g^{-1}		Rapid sorption depends on pH, sorbent dose and U conc.; follows Langmuir isotherm

2.3 Biosorption

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992). Algae, bacteria and fungi and yeasts have proved to be potential metal biosorbents (Volesky, 1986). The major advantages of biosorption over conventional treatment methods include (Kratochvil and Volesky, 1998 a):

1) Low cost;
2) High efficiency;
3) Minimisation of chemical and lor biological sludge;
4) No additional nutrient requirement;
5) Regeneration of biosorbent; and
6) Possibility of metal recovery.

The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases. (Biosorption of heavy metals, N. Ahalya, T.V. Ramachandra* l and R.D. Kanamadi 2., http://www.ces.iisc.ernet.in/energy/water/paper/biosorption/biosorption.htm#6)

2.3.1 Mechanism of Metal Biosorption

Adsorption and desorption studies invariably yield information on the mechanism of metal biosorption: how is the metal bound within the biosorbent. This knowledge is essential for understanding of the biosorption process and it serves as a basis for quantitative stoichiometric considerations which constitute the foundation for mathematical modeling of the process.

A number of different metal-binding mechanisms have been postulated to be active in biosorption such as:

1) Chemisorptions by ion exchange, complexation, coordination, chelation
2) Physical adsorption, microprecipitation.

Boya Volesky, 1999, said that there are also a possibility oxidation/reduction reactions taking place in the biosorbent. Due to the complexity of the biomaterials used it is quite possible that at least some of these mechanisms are acting simultaneously to varying degrees depending on the biosorbent and the solution environment.

2.3.1.1 Ion Exchange

Cell walls of microorganisms contain polysaccharides and bivalent metals 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+}, and Zn^{2+} resulting in the biosorptive uptake of heavy metals (Kucuyak and Volesky, 1988). The biosorption of copper by fungi *Gaboderma Iucidium* (Muraleedharan and Venkobachr, 1990) and Aspergillus niger was also up taken by ion exchange mechanism. Ion exchange reactions are stoichiometric and reversible, and in that way they are similar to other solution phase reactions.

For example:

$$NiSO_4 + Ca(OH)_2 = Ni(OH)_2 + CaSO_4 \quad \textbf{(2.1)}$$

2.3.1.2 Complexation

The metal removal from solution may also take place by complex formation on the cell surface after the interaction between the metal and the active groups. Aksu et al. 1992 hypothesized that biosorption of copper by C. vulgaris and Z. ramigera takes place through both adsorption and formation of coordination bonds between metals and amino and carboxyl groups of cell wall polysaccharides. Complexation was found to be the only mechanism responsible for calcium, magnesium, cadmium, zinc, copper and mercury accumulation by Pseudomonas syringae. Micro-organisms may also produce organic acids (e.g., citric, gluonic, fumaric, lactic and malic acids), which may chelate toxic metals result in the formation of metallo-organic molecules. These organic acids help in the solubilisation of metal compounds and their leaching from their surfaces. Metals may be absorbed or complexed by carboxyl groups found in microbial polysaccharides and other polymers.

2.3.1.3 Chelation

Chelation(from Greek, chele. Meaning claw) is the binding - or complexation – of a bi – or multidentate ligand. These ligands which are often organic compounds are called chelant, chelator, chelating agent, sequestering agent form a chelate complex. The term is reserved for complexes in which the metal ion is bound to two or more atoms of the chelating agent, although the bonds may be any combination of coordination or ionic bonds. Figure 2.3 shows the example of chelation.

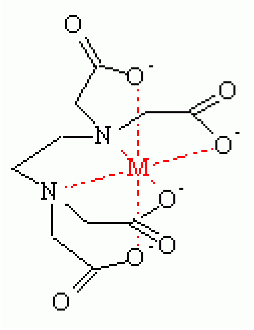


Figure 2.3: Metal-EDTA chelate

Virtually all biochemicals exhibit the ability to dissolve metals cations. Thus proteins, polysaccharides, and polynucleic acids are excellent polydentate ligands for many of the metal ions. In addition to these adventitious chelators, several are produced to specifically bind certain metals. Such chelating agents include the porphyrin rings in hemoglobin or chlorophyll and the Fe^{3+}-chelating siderophores secreted by microorganisms.

2.3.2 Factors Affecting 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.

The following factors affect the biosorption process:

1. Temperature seems not to influence the biosorption performances in the range of 20-35 ^{0}C (Aksu *et al*. 1992)

2. 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)

3. 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 decrease to metal concentration shortage in solution. Hence this factor needs to be taken into consideration in any application of microbial biomass as biosorbent.

4. Biosorption is mainly 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 example: 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). In contrast, the presence of Fe^{2+} and Zn^{2+} was found to influence uranium uptake by *Rhizopus arrhizus* (Tsezos and Volesky, 1982) and cobalt uptake by different microorganisms seemed to be completely inhibited by the presence of uranium, lead, mercury and copper (Sakaguchi and Nakajima, 1991).

2.4 Atomic Adsorption Spectroscopy (AAS)

Atomic absorption (AA) is the standard method for the analysis of specific metals. It is widely practiced in environmental analysis. The general aspects of the techniques are:

a) mg/L to μg/L detection is routine

b) analysis is generally very specific to a given element (although interferences are common)
c) some techniques offer multiple compound analysis for one injection
d) the techniques are fast and relatively inexpensive

(Refer to appendix D for further explanation on AAS method and applications)

2.5 Current Studies of Biosorption of Cadmium

2.5.1 Sorption of Cadmium and Zinc from Aqueous Solutions by Water Hyacinth (S.H. Hasan *et al*., 2007)

The water hyacinth (*Eichchornia crassipes*) has been successfully utilized for the removal of Cd(II) as well as their admixture from samples of aqueous solutions. The growth of the plant after 16 days of exposure to the metal ions showed an increasing trend up to 2.5 ppm of Cd(II) concentrations, however, the growth became nondetectable or inhibited above these concentrations. The overall metal uptake by the plant was dependent upon the concentration of the metal and the duration of the exposure time. The metal uptake from a mixture of Cd(II was reflected by a rate constant quite different from those solutions containing only one metal ion. A water hyacinth based system can be used to remove Cd(II) and Zn(II) from water/wastewater.

2.5.2 Removal of Cadmium and Zinc by Water Hyacinth, *Eichhornia crassipes* (ScienceAsia 30, 2004)

Toxic heavy metal pollution of water and soil is a major environmental problem, and most conventional remediation approaches do not provide acceptable solutions. Wetland plants are being used successfully for the phytoremediation of trace elements in natural and constructed wetlands. This study demonstrates the phytoremediation potential of water hyacinth Eichhornia crassipes, for the removal of cadmium (Cd) and zinc (Zn). The phytoaccumulation of heavy metals, Cd and Zn, by water hyacinth E. crassipes, was studied. Water hyacinths were cultured in tap water, which was supplemented with 0.5, 1, 2 and 4 mg/L of Cd and 5, 10, 20, and 40 mg/L of Zn, and were separately harvested after 0, 4, 8 and 12 days. The experiment showed that both Cd and Zn had effects on plant relative growth. Removal of metals from solution was fast especially in the first four days. The accumulation of Cd and Zn in shoots and roots increased with the initial concentration and also with the passage of time. Plants treated with 4 mg/L of Cd accumulated the highest concentration of metal in roots (2044 mg/kg) and shoots (113.2 mg/kg) after 8 days; while those treated with 40 mg/L of Zn accumulated the highest concentration of metal in roots (9652.1 mg/kg) and shoots (1926.7 mg/kg) after 4 days. The maximum values of bioconcentration factor (BCF) for Cd and Zn were 622.3 and 788.9, respectively, suggesting that water hyacinth was a moderate accumulator of Cd and Zn and could be used to treat water contaminated with low Cd and Zn concentrations.

2.5.3 Sorption of Cd ions onto akagan´eite-type nanocrystals (Deliyanni, Matis, 2005)

The aim of this paper is to remove cadmium ions from aqueous solutions by sorption onto synthetic akagan´eite-type nanocrystals. This material was shown to be a promising inorganic adsorbent due to its favourite characteristics. Synthetic akagan´eite was prepared in the laboratory according to a newmethod. In this paper, the effects of adsorbent amount, initial cadmium concentration, pH value of solution, concentration of background electrolyte ions and temperature variation on the treatment process of cadmium removal by akagan´eite were investigated. Typical adsorption isotherms (Freundlich and Langmuir) were determined for the mechanism of sorption process. From the aforementioned results, the following can be concluded: Sorption depended greatly on the solution pH value, increasing as pH increased; for a change of around 2.5

pH units, cadmium removal varied between 0 and 100%. Cadmium removal was shown to decrease with the increase of the electrolyte ions in solution.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The experiment was conducted start from the preparation of biosorbent of dried water hyacinth, where the water hyacinth was dried, cut, grind and stored. Then, 100 mg/L cadmium solution as stock solution was prepared. The parameters that have been studied are; dosage of biosorbent, contact time, pH and temperature. Lastly, the experiment was analyzed using AAS to measure the percent removal of biosorbent water hyacinth as a removal of cadmium solution. Figure 3.1 show the overall process for this experiment.

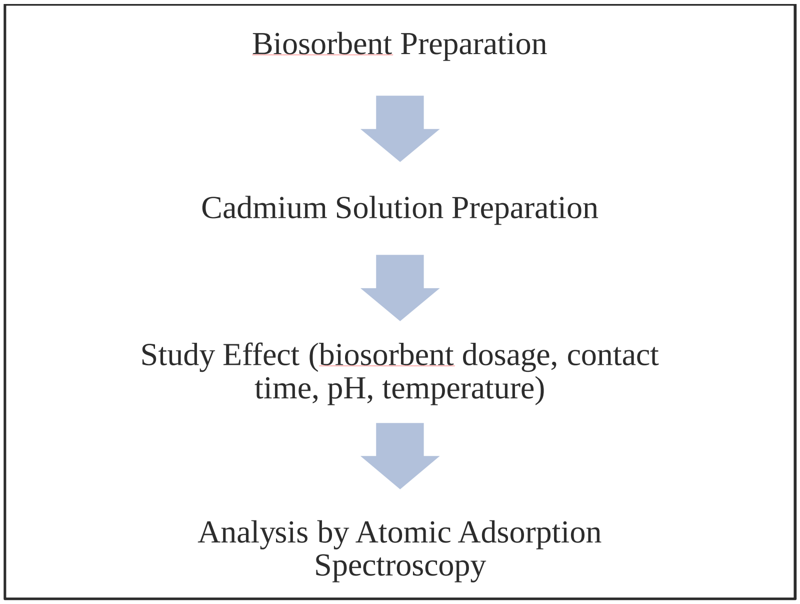


Figure 3.1: Overall process diagram of experiment.

3.2 Equipments Requirement

Equipments used in this experiment;

1. Jar Test
2. Z-5000 Polarized Zeeman Atomic Absorption Spectrophotometer
3. Hybridization Incubator Shaker
4. pH meter (HM 30P)
5. Erlenmeyer Flask
6. Micro pipette (range 100µL)
7. Electric balance Shimadzu (AW220)
8. Oven
9. Octagon siever (OCT-DIGITAL 4527-01)

3.3 Chemicals Requirement

Chemicals used in this experiment;

1. Cadmium Nitrate Tetrahydrate (solid)
2. Cadmium Standard Solution
3. Distilled Water
4. NaOH
5. HCL
6. Dried Water Hyacinth (solid)

3.4 Experimental Procedure

3.4.1 Biosorbent Preparation

The *Eichhornia crassipes* used in the experimentation was obtained from wild specimens growing in Pekan, Pahang. The roots, the aerial parts (stems plus leaves) or the whole plant were washed,dried at 60°C and ground in a bladed mixer to less than 0.59 mm (Tyler 28 mesh). The biomass preparation scheme is shown schematically in Figure 3.2. No pretreatment is used in this experimental.

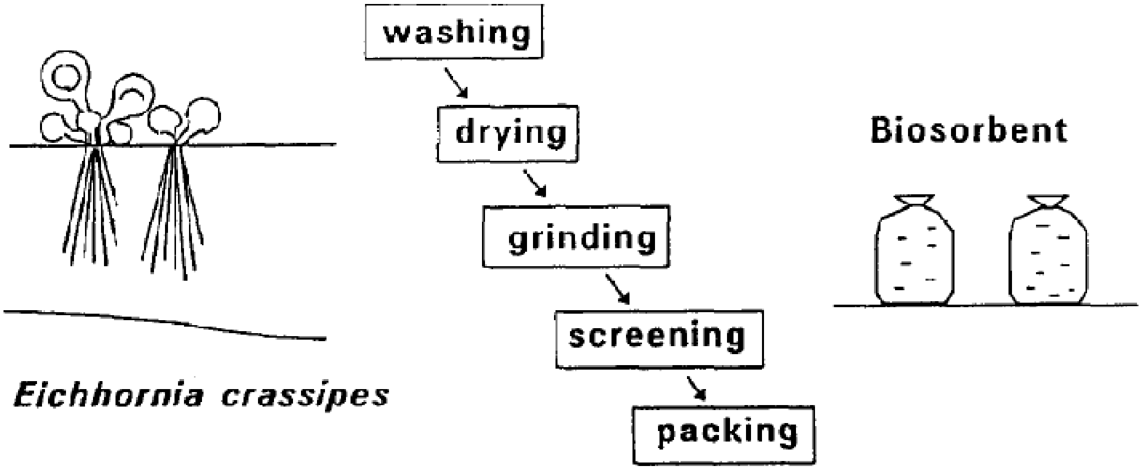


Figure 3.2: Procedure for preparation of *Eichhornia crassipes* biomass.

3.4.2 Cd solutions preparation

A stock solution of cadmium was prepared by dissolving AR grade of Cadmium Nitrate Tetrahydrate, $Cd(NO_3)_2.4H_2O$ in distilled water, respectively at an initial concentration of 1000 mg/mL. For the experimental initial concentration used is at 20 mg/L.

The concentration is measured as below:

$$\text{Concentration} = \frac{m}{\mathcal{V}}$$

(3.1)

Where;

m = mass

$\mathcal{V}$ = volume

For dilution to determined initial concentration, this equation is used:

$$M_iV_i = M_fV_f \quad \textbf{(3.2)}$$

Where M is molarity, V is volume, and the subscripts i and f refer to the initial and final values.

3.4.3 Effect of Water Hyacinth Dosage

To determine the effect of the cadmium ions from solution by the biosorbents, 500 ml of a cadmium solution was stirred using Jar test for 30 min at room temperature, 25^{o}C with different range (0.4 g/L, 0.8 g/L, 1.2 g/L, 1.6 g/L, 2.0 g/L, 2.4 g/L, 2.8 g/L, 3.2 g/L, 3.6 g/L and 4.0 g/L) of water hyacinth biosorbent. The concentration of heavy metal ions in solution was determined both before the introduction of the biosorbent and after the reaction of the biosorbent with the metal containing solution. The amount of heavy metal ions abstracted from solution was determined, using atomic adsorption spectroscopy, by the difference in metal ion concentration from the two analyses performed before and after introduction of the biomass.

3.4.4 Effect of Contact Time

Contact time is one of the important parameter needed in order to remove cadmium ions from solutions. In this experiment, 5 samples of 20 mg/L cadmium solution are prepared with 1.0 g biosorbent at 25^oC. Each sample is stirred in Jar Test with varies time started for 10 minutes with 10 minutes interval time until 50 minutes.

3.4.5 Effect of pH

To determine the effect of pH on the removal of cadmium solution 500 mL of Cd solution was stirred for 30 min with 2.0 g/L of biosorbent. The initial concentration is 20 mg/L. 5 samples were prepared with different range of pH start from pH 2 until pH 10, two solution of HCl and NaOH is used to adjust pH. pH is measured by pH meter and the conclusion analyzed of Cd is using atomic adsorption spectroscopy.

3.4.6 Effect of Temperature

Parameter of temperature is determined to see the effect of biosorbent water hyacinth in removal cadmium ions in cadmium solution. 20 mg/L of cadmium solutions is stirred for 30 minutes with 1.0 g of biosorbent. Temperature is set with variables from 20^oC, 30^oC, 40^oC, 50^oC and 60^oC, for this purpose the samples is shake using shaker incubator.

3.4.7 Summary of Parameters

Table 3.1: Summary Parameter on Methodology

Parameter	Characteristics
1. Biosorbent Dosage	T: 25^{o}C, pH: 5.5 ± 0.2, Time: 30 min Dosage range: 0.4 g/L, 0.8 g/L, 1.2 g/L, 1.6 g/L, 2.0 g/L, 2.4 g/L, 2.8 g/L, 3.2 g/L, 3.6 g/L and 4.0 g/L
2. Contact Time	T: 25^{o}C, pH: 5.5 ± 0.2, Dosage: 2.0 g/L Time range: 10 min, 20 min, 30 min, 40 min and 50 min
3. pH	T: 25^{o}C, Time: 30 min, Dosage: 2.0 g/L, pH range: 2, 4, 6, 7, 8, 10
4. Temperature	pH: 5.5 ± 0.2, Time: 30 min, Dosage: 2.0 g/L Temperature range: 25^{o}C, 30^{o}C, 35^{o}C, 40^{o}C, 45^{o}C, 50^{o}C, 55^{o}C, 60^{o}C

3.5 Analyzing the Cadmium Removal

Concentration of Cd solution is determined by using absorbance value measured before and after treatment at 228.8 nm with Atomic Adsorption Spectroscopy. Before analyze the sample by AAS, the biosorbent will be filtered using filter paper. *Refer appendix details on usage of AAS*

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The factors that influenced the removal of cadmium by using water hyacinth are;

1. Biosorbent dosage
2. Contact time
3. pH
4. temperature

4.2 Effect of Biosorbent Dosage

The biosorption of cadmium by Water Hyacinth as biosorbent was initially determined. Data obtained is depicted in Table 4.1. It is readily noted that *E. crassipes* is a particularly good adsorbent for these divalent metals (SCHNEIDER *et al.*, 1995)

TABLE 4.1: Sorption of Cd(II) by Water Hyacinth as biosorbent; 30 min reaction with agitation, rpm = 80 rpm, initial pH 5.5 ± 0.2

Sample	Dosage (g/L)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal (%)
1	0.0	20	20	0.00
2	0.4	20	1.25	93.75
3	0.8	20	0.86	95.70
4	1.2	20	0.59	97.05
5	1.6	20	0.52	97.40
6	**2.0**	**20**	**0.46**	**97.70**
7	2.4	20	0.65	96.75
8	2.8	20	0.62	96.90
9	3.2	20	0.62	96.90
10	3.6	20	0.58	97.10
11	4.0	20	0.56	97.20

There is general consensus that dosage is the key parameter, along with metal concentration and solution composition, in determining biosorption levels. Accordingly the objective of this work was evaluating the biosorption of Cd^{2+} by dried water hyacinth from aqueous solution and to determine the effects biosorbent dosage on uptake levels.

Result obtained shows that the optimum dosage of dried water hyacinth is 2.0 g/L with percent removal of 97.70%. First sample act as control for this experiment. With initial concentration at 20 mg/L, the biosorption of Cd^{2+} range at (93 – 97) % show the excellent removal capacities of Cd^{2+} by dried water hyacinth. From I.A.H Scheneider *et. Al* (1995), considering the large surface area of the *E. crassipes* parts, it is not surprising that these materials are excellent biosorbents for multivalent metal ions. Figure 4.1 show the graph of the biosorption of Cd^{2+}, the effect of dosage biosorbent to cadmium metal solution. The decreasing of percentage present in figure 4.1 show that at more than 2.0 g/L of dosage, dried water hyacinth is slightly inefficient to remove the Cd^{2+}. In this case, higher metal adsorption from these particles is attributed to mass transport inside the sorbent particles (G.H. Pino *et al.* / Minerals Engineering 19, 2006).

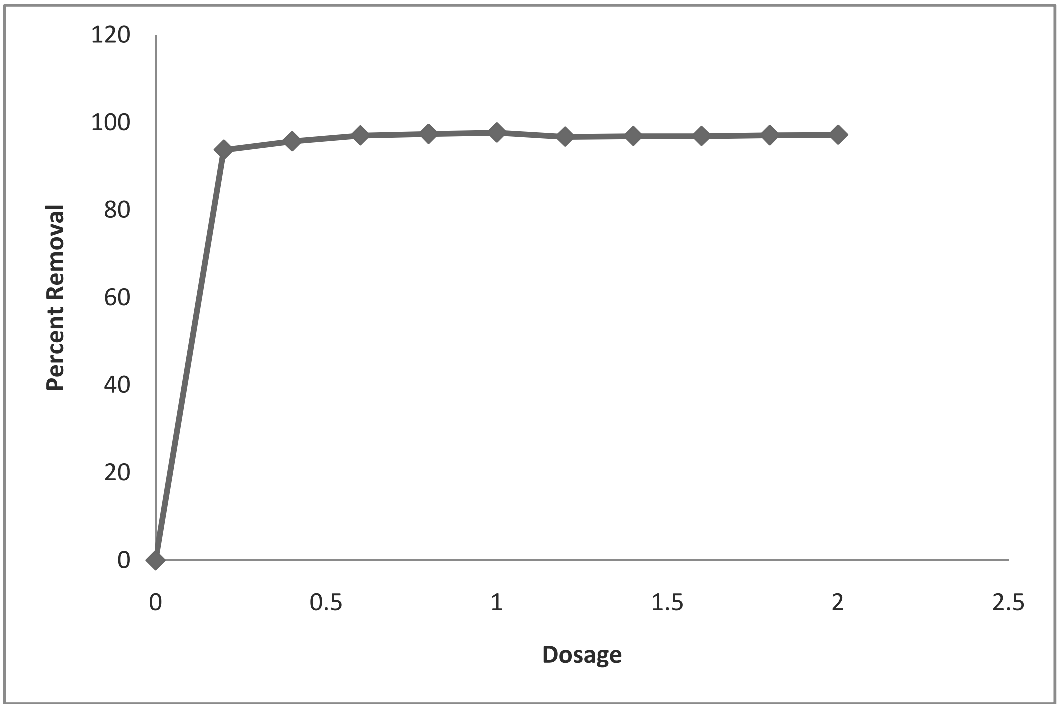


Figure 4.1: Effect of Water Hyacinth dosage on Cd removal (Initial Cd concentration = 20 mg/L, T = 25^oC, Contact Time = 30 min, pH = 5.5 ± 0.2, Mixing speed; rpm = 80)

4.3 Effect of Contact Time

Table 4.2: Sorption of Cd(II) by Water Hyacinth as biosorbent; 2.0 g/L of biosorbent dosage with agitation, rpm = 80 rpm, initial pH 5.5 ± 0.2

Sample	Contact Time (min)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal (%)
1	0	20	20.0	0.00
2	10	20	0.94	95.30
3	20	20	0.82	95.90
4	30	20	0.54	97.30
5	**40**	**20**	**0.51**	**97.45**
6	50	20	0.66	96.70

From Table 4.2, the optimum sorption of cadmium uptake from dried water hyacinth was observed at 40 minutes with percent removal of 97.45%. From research, G.H. Pino *et. al* (2006), the range contact time for removal of heavy metal by dried water hyacinth are at 30 minutes until 60 minutes. This experiment was conducted with different contact time at range from 0 minutes until 50 minutes with 10 minutes interval time. As illustrated in Figure 4.2, from 0 until 30 minutes, water hyacinth biosorbent absorb rapidly cadmium ions from the solution and then it continued at a relatively slower rate up to maximum sorption. In the beginning of experimental run adsorption values were not high but the percentage of metal ion adsorption increased with increasing time (S. Kocaoba, 2007).

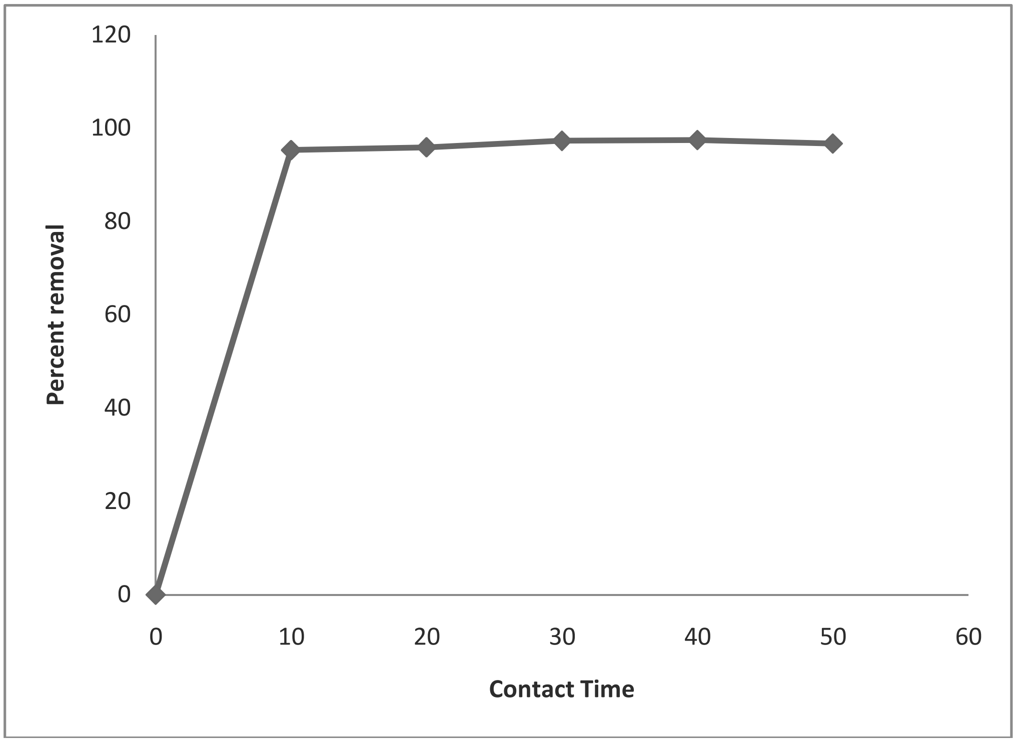


Figure 4.2: Effect of Water Hyacinth Contact Time on Cd removal (Initial Cd concentration = 20 mg/L, T = 25^{o}C, Dosage = 2.0 g/L, pH = 5.5 ± 0.2, Mixing speed, rpm = 80)

4.4 Effect of pH

Table 4.3: Sorption of Cd(II) by Water Hyacinth as biosorbent; 1.0 g of biosorbent dosage with agitation, rpm = 80 rpm, contact time 30 mins

Sample	pH	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal (%)
1	2	20	0.71	96.45
2	4	20	0.71	96.45
3	6	20	0.69	96.55
4	**7**	**20**	**0.53**	**97.35**
5	8	20	0.67	96.65
6	10	20	0.75	96.25

According to the objectives of this study was to evaluate the biosorption of Cd2+ by dried of water hyacinth from aqueous solution and to determine the effects of pH (in range 2–10) on uptake levels. From the study of pH effect, the optimum sorption by dried water hyacinth was observed at pH 7. This result was support by research G.H. Pino *et*. Al (2006), pH at 7 show the best pH of water hyacinth as biosorbent as removal of Cd^{2+}. The Cd^{2+} removal increased from 96.45%, at pH 4, to 97.35%, at pH 7. As illustrated in figure 4.3, there have been decreasing value after pH 7 until 10 from 97.35% to 96.25%, this because of the inefficiency of biosorbent in uptake cadmium from the solution. As pH is further raised, once the bulk solubility limit is reached, the sorption is greatly reduced because the metal ion is removed from solution by the bulk precipitation (I.A.H. Schneider *et al*., 2001). At lower pH, the amount of adsorbed was found to decrease because the surface area of the adsorbent was more protonated and competitive adsorption occurred between H+ protons and free metal ions towards the fixation sites (C.A. Coles and R.S. Yong, 2002). Therefore, H+ ions react with anionic functional groups on the surface of the adsorbent and result in restriction of the number of binding sites favorable for the adsorption of metal ions (S. Kocaoba, 2007).

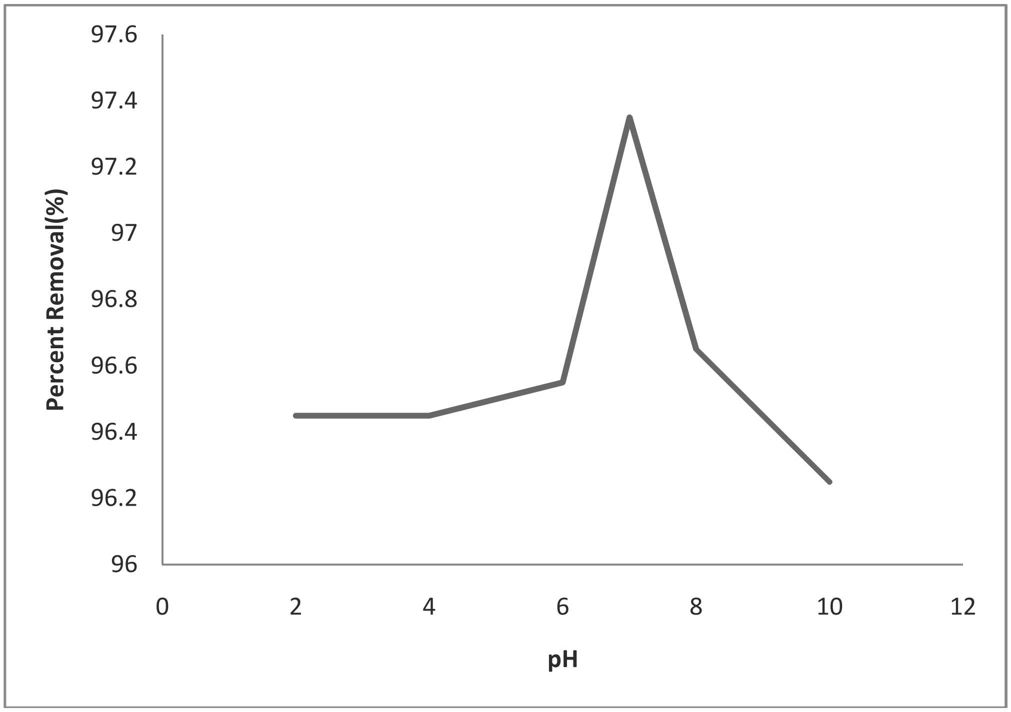


Figure 4.3: Effect of Water Hyacinth pH on Cd removal (Initial Cd concentration = 20 mg/L, T = 25^oC, Contact Time = 30 min, Dosage = 2.0 g/L, Mixing speed, rpm = 80)

4.5 Effect of Temperature

Table 4.4: Sorption of Cd(II) by Water Hyacinth as biosorbent; 2.0 g/L of biosorbent dosage with agitation, rpm = 175 rpm, initial pH 5.5 ± 0.2, contact time 30 mins

Sample	Temperature (^oC)	Initial Concentration (mg/L)	Final Concentration (mg/L)	Removal (%)
1	25	20	0.58	97.10
2	30	20	0.55	97.25
3	**35**	**20**	**0.53**	**97.35**
4	40	20	0.65	96.75
5	45	20	0.58	97.10
6	50	20	0.57	97.15
7	55	20	0.50	97.50

In order to find out the most suitable temperature, this experiment were run with different temperature start at room temperature, T=25^{o}C. From figure 4.4, the result above at T=35^{o}C shown the positive value as the best condition for the temperature parameter. From studies of effect temperature on precipitation of cadmium, the results show that yield decreases by an increase in the temperature and the optimal temperature is 30^{o}C, M. Abdalbake and O. Shino, 2004). These factors may simultaneously affect the binding sites on isolated fungal and bacterial species causing reduction in heavy metal removal. Energy-independent mechanisms are less likely to be affected by temperature since the processes responsible for removal are largely physiochemical in nature (Gulay *et al.*, 2003). The Langmuir and Freundlich constants for sorption of cadmium versus the temperature are presented. It comes out from this table that the value of *K*F, which consists a measure of the sorbent capacity, was increased as the temperature was rising, showing that the rate of adsorption also increased (Deliyanni, Matis, 2005). As illustrated in figure 4.4, after T = 35^{o}C, there have been decreasing in cadmium uptake by biosorbent water hyacinth, this is show that the biosorbent have reach to it maximum potential as absorbent.

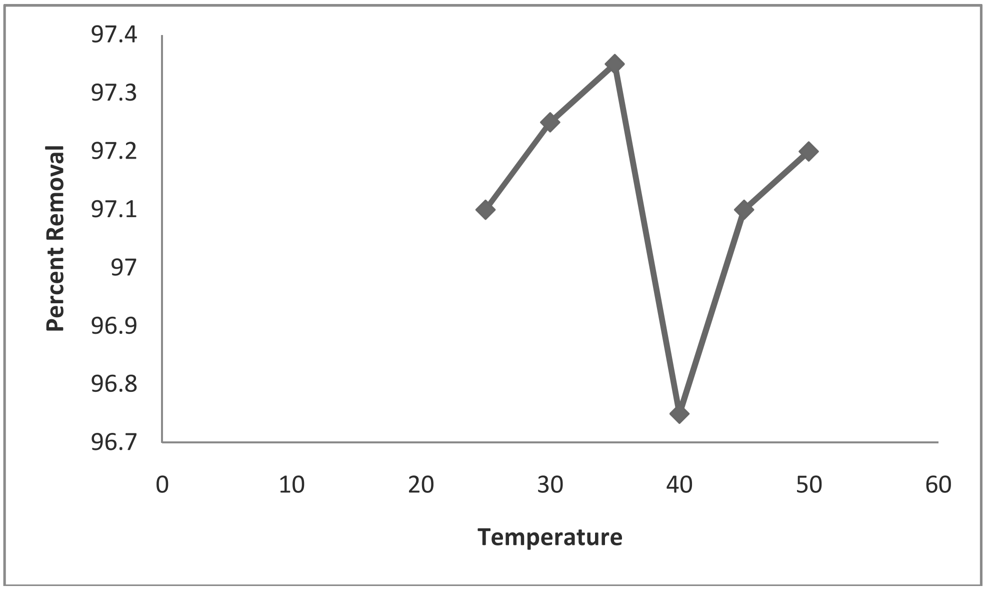


Figure 4.4: Effect of Water Hyacinth Temperature on Cd removal (Initial Cd concentration = 20 mg/L, Dosage = 2.0 g/L, Contact Time = 30 min, pH = 5.5 ± 0.2, Mixing speed, rpm = 175)

CHAPTER 5

CONCLUSION

5.1 Conclusion and Recommendation

The dried or nonliving water hyacinth has the potential to remove cadmium from aques solution. From the study, it shows that percent of removal of Cd increased by 98%. As for the best contact time in biosorption of Cd^{2+} is in range (30-40) minutes. The obtained results showed that pH highly affected the uptake capacity of the biosorbent. For Cd^{2+} ions the best value of pH for biosorption was 7 and temperature at $T=35^{o}C$ show as the best removal of ion Cd from cadmium solution. The obtained result shows that *E. crassipes* is excellent biosorbents for adsorption of metal ions in wastewater. The water hyacinth has been successfully used for the removal of Cd(II) from aqueous solutions.

In this study, dried water hyacinth is used as biosorbent without pretreatment, this can be improved by undergo pretreatment before it can be used as a removal of heavy metal. This is also suggested by Ali *et. al*, (2004), pretreatment with fungi or chemicals to increase the biodegradability of water hyacinth.

Water hyacinth is one of the plant species that attracted considerable attention because of its ability to grow in heavily polluted water together with its capacity for metal ion accumulation. As a result, one of its prime utility that has found world-wide acceptance is in treating wastewaters (Tchobanoglous *et al*., 1989). It is suggested that water hyacinth is used as one of the removal for heavy metals since it is economical and easy to use. The unique capacity of water hyacinth to scavenge and concentrate the pollutants from relatively low strength wastewaters has also been established. The progress in pilot/full-scale application of the water hyacinth-based wastewater treatment systems has revalidated their beneficial application (A. Malik, 2007). It is also recommended that the dried biomass of the plant might be placed in simple bags and used in a very low cost metal ion removal system.

This study have shows the ability of water hyacinth as a good biosorbent for removal of heavy metals. In this study, the usage of the whole water hyacinth is not fully utilized; leaves are the only part used in the experiment as a biosorbent while roots are not. From research Schneider *et. al*, (1995), the study shows that root have more ability to absorp heavy metal than leave. It is suggested that for the next study, can take this opportunity to learn about the differences and both ability as biosorbent, which one of them can be a better biosorbent for waste water treatment.

REFERENCES

Ali N, Chaudhary BL, Khandelwal SK, (2004). Better use of water hyacinth for fuel, manure and pollution free environment. *Indian J Environ Prot*;24:297–303.

Al Rmalli SW, Harrington CF, Ayub M, Haris PI. A biomaterial based approach for arsenic removal from water. J Environ Monit 2005;7:279–82.

Anushree Malik (2007). Environmental challenge vis a vis opportunity: The case of water hyacinth. *Environment International*. 33 (2007) 122–138.

Blake, G., Kaigate, B., Fourcy, A. & Boutin, C, (1987).Incorporation of Cadmium by Water Hyacinth, *Water Science Technology*, 19, 123-128.

B.Volesky and Z.R. Holan, (1995) Biosorption of heavy metals. *Biotechnol Prog.* 11 : 235-250

Cook, M. E., and Morrow, H., (1995) "Anthropogenic Sources of Cadmium in Canada," National Workshop on Cadmium Transport Into Plants, Canadian Network of Toxicology Centres, Ottawa, Ontario, Canada, June 20-21, 1995.

CRC Handbook of Chemistry and Physics 77th Edition, (1996) CRC Press, Inc., Boca Raton, Florida.

Delgado, M., Bigeriego, M. & Guardiola, E., (1993). Uptake of Zn, Cr, and Cd by Water Hyacinth, *Water Research*, 27, 269-272.

E.A. Deliyanni, K.A. Matis., (2005). Sorption of Cd ions onto akagan´eite-type nanocrystals. *Separation and Purification Technology* 45. (2005) 96–102

Elgersma, F., Anderberg, B. S., and Stigliani, W. M., (1992) ."Emission Factors for Aqueous Industrial Cadmium Emissions in the Rhine River Basin; A Historical Reconstruction for the Period 1970-1988," Edited Proceedings Seventh International Cadmium Conference - New Orleans, Cadmium Association, London, Cadmium Council, Reston VA, International Lead Zinc Research Organisation, Research Triangle Park NC.

Elinder, Cad-Gustaf (1985) "Cadmium: Uses, Occurrence, and Intake," Cadmium and Health: A Toxicological and Epidemiological Appraisal, CRC Press, Inc., Boca Raton, Florida.

Epstein P. Weeds bring disease to the east African waterways. Lancet 1998;351:577.

Esterves, A.J.P., Vaddman, E., Leite, S.G.F., 2000. Repeated removal of cadmium and zinc from industrial effluents by waste biomass Sargassum sp. Biotechnol. Lett. 22, 499–502.

Gabriela Huama´n Pino, Luciana Maria Souza de Mesquita, Mauricio Leonardo Torem, Gustavo Adolfo Saavedra Pinto, (2006). Biosorption of cadmium by green coconut shell powder. *Minerals Engineering 19*. 380–387.

Hao Y, Roach AL, Ramelow GJ, (1993). Uptake of metal ions by nonliving biomass derived from Sphagnum moss and water hyacinth roots. J Environ Sci Health;A28:2333–2343.

Holan ZR and Volesky B (1994) Biosorption of lead andnickel by biomass of marine alage. *Biotechnol Bioeng* 43,1001-9.

Jensen, A., and Bro-Rasmussen, F., (1992). Reviews of Environmental Contamination and Toxicology. *Environmental Contamination in Europe*. Volume 125, pages 101-181.

Langeland KA, Burks KC, editors. Identification and biology of non-native plants in Florida's natural areas. University of Florida; 1998. [165 p. UF/IFAS Distribution].

Low KS, Lee CK, Tai CH. Biosorption of copper by water hyacinth roots. *J Environ Sci Health* 1994;A29:171–88.

Low KS, Lee CK, Tan KK. Biosorption of basic dyes by water hyacinth roots. *Bioresour Technol* 1995;52:79–83.

Malik A. Water Hyacinth for phytoremediation. In: Teixeira da Silva Jaime A, editor. Floriculture, ornamental and plant biotechnology: advances and topical issues (vol. III). 1st edition. London, UK: Global Science Books Ltd.; 2006. p. 298–303.

Mailu AM. Preliminary assessment of the social, economic and environmental impacts of water hyacinth in the Lake Victoria basin and the status of control, biological and integrated control of water hyacinth, Eichhornia crassipes (2001) ACIAR Proceedings No. 102.

Mironga JM. Geographic information systems (GIS) and remote sensing in the management of shallow tropical lakes. *Appl Ecol Environ Res* 2004; 2:83–103.

Mukunoki, J., and Fujimoto, K., (1996). "Collection and Recycling of Used Ni-Cd Batteries in Japan," Sources of Cadmium in the Environment, Inter-Organisation Programme for the Sound Management of Chemicals (IOMC), Organisation for Economic Co-operation and Development (OECD), Paris, 1996.

M. Abdalbake, O. Shino, (2004). Removing the cadmium, arsenic and sulfate ions from wet process phosphoric acid. *PERIODICA POLYTECHNICA SER. CHEM. ENG.* VOL. 48, NO. 1, PP. 63–71.

N. Kuyucak and B. Vole sky, Biosorbents forrecovery of metals from industrial solutions. *Biotechnol Left.*, 10 (2), 137-142 (1988)

Olguin, E.J., Hurnandoz, E. (1998). Use of aquatic plants for recovery of nutrients and heavy metals from wastewaters. Round table on municipal water, Vancouver, Canada, March 15–17.

Organisation for Economic Co-operation and Development (OECD) (1994), Risk Reduction Monograph No. 5: Cadmium OECD Environment Directorate, Paris, France.

Organisation for Economic Co-operation and Development (OECD) (1996). Report From Session F, "Sources of Cadmium in Waste," Chairman's Report of The Cadmium Workshop, ENVIMCICHEMIRD(96)1, Stockholm, Sweden, October 1995.

Polprasert C, Kessomboon S, Kanjanaprapin W. Pig wastewater treatment in water hyacinth ponds. *Water Sci Technol* 1992;26:2381–4.

Plummer ML. Impact of invasive water hyacinth (Eichhornia crassipes) on snail hosts of schistosomiasis in Lake Victoria, East Africa. *Eco Health* 2005;2:81–6.

Pinto, C.L.R., Caqonia, A. & Souza, M.M., (1987). Utilization of Water Hyacinth for Removal and Recovery of Silver from Industrial Wastewater, *Water Science Technology*, 19, 89-101.

Prasad MNV, De Oliveira Freitas HM, (2003). Metal hyperaccumulation in plants — biodiversity prospecting for phytoremediation technology. *Electron J Biotechnol*;6:110–46.

Royal Chemical Society(RS.C).Atomic Absorption Spectrophotometer.

Satyakala G, Jamil K. Chromium-induced biochemical changes in *Eichhornia crassipes* (mart) solms and Pistia stratiotes L. Bull Environ Contam Toxicol 1992;48:921-8.

Sevgi Kocaoba, (2007). Comparison of Amberlite IR 120 and dolomite's performances for removal of heavy metals. *Journal of Hazardous Materials 147*. 488–496

S. H. Hasan, M. Talat, S. Rai (2007). Sorption of cadmium and zinc from aqueous solutions by water hyacinth *(Eichhornia crassipe)*. *Bioresource Technology*. 98 (2007) 918–928.

Shawky S, Geleel MA, Aly A. Sorption of uranium by non-living water hyacinth roots. *J Radioanal Nucl Chem* 2005;265:81–4.

Schneider IAH, Rubio J, Misra M, Smith RW, (1995). Eichhornia crassipes as biosorbent for heavy metal ions. *Miner Eng*;8:979–88.

Schneider, I.A.H., Souza, M.L. & Rubio, J., (1994).Sorption of Copper Ions from Aqueous Solution by *Potomogenton luscens* Biomass, *Proceedings of the IV Meeting of the Southern Hemisphere on Mineral Technology,* eds. S.Castro and F. Concha, University of Concepcion - Chile, Volume I, 341-353.

Simberloff D, Schmitz DC, Brown TC. Strangers in paradise: impact and management of nonindigenous species in Florida. *Island Press*; 1997 [467 p].

Udaya Simha L, Panigrahy BK, Ramakrishna SV. Preliminary studies on fluoride adsorption by water hyacinth. Indian J Environ Prot 2002;22:506–11.

Van Assche, F. J., and Ciarletta, P., (1993). "Environmental exposure to cadmium in Belgium: Decreasing trends during the 1980s." Heavy Metals in the Environment Volume 1, pages 34-37. *Toronto-September* 1993.

Van Urk, G., and Marquenie, J. M., (1989). "Environmental Behaviour of Cadmium: WHO Are at Risk and Why," Heavy Metals in the Environment, Volume 11, *Geneva*, pages 456-459.

Vieira, R.H.S.F., Volesky, B., (2000). Biosorption: a solution to pollution. *Int. Microbiol.* 3, 17–24.

Wilson JR, Holst N, Rees M, (2005). Determinants and patterns of population growth in water hyacinth. *Aquat Bot*;81:51–67.

World Health Organisation (WHO) (1992). Environmental Health Criteria 134 - Cadmium International Programme on Chemical Safety (IPCS) Monograph.

Wolverton, B.C., , (1975).Water Hyacinth for Removal of Cadmium and Nickel from Polluted Waters, *NASA Technical Memorandum*, TM-X-72721.

Xiaomei Lu, Maleeya Kruatrachue, Prayad Pokethitiyook and Kunaporn Homyok (2004).. Removal of Cadmium and Zinc by Water Hyacinth, *Eichhornia crassipes. ScienceAsia.* 30 (2004): 93-103

Yuan, Y., Hall, K., Oldham, C., (2001). A preliminary model for predicting heavy metal contaminants loading from an urban catchment. Sci.*Total Environ*. 206, 299–307.

Zaranyika MF, Mutoko F, Murahwa H. Uptake of Zn, Co, Fe and Cr by water hyacinth (Eichhornia crassipes) in Lake Chivero, Zimbabwe. *Sci Total Environ* 1994;153:117–21.

Zhu YL, Zayed AM, Qian J-H, de Souza M, Terry M. Phytoaccumulation of trace elements by wetland plants: II. Water hyacinth. *J Environ Qual* 1999;28:339–44.

APPENDIX A

Calculation of stock solution and concentration

a) Stock solution of cadmium solution

Mass of $CdN_2O_6.4H_2O$ = x g

Volume = 1 liter (L)

Concentration need to prepared for stock solution = 1000 mg/L

Using formula (3.1),

Concentration = mass per volume
1000 mg/L = x g / 1 L
X g = 1000 mg
= 1 g

So, mass of $CdN_2O_6.4H_2O$ needed is 1 g.

b) Initial concentration from stock solution

From stock solution,

Initial concentration use for this experiment is 20 mg/L

Using formula (3.2),

$$M_iV_i = M_fV_f$$
$$1000 \text{ mg/L} \times V_i = 20 \text{ mg/L} \times 0.5 \text{ L}$$
$$V_i = 0.01 \text{ L}$$
$$= 10 \text{ mL}$$

Notes:
For volume, V_f it can changed depend on the volume of beaker or flask that is used for the experiment.

APPENDIX B

Atomic Adsorption Spectroscopy
Ref: Skoog *et. al*, Analytical Chemistry, 7th Edition, 1999

Terminology

Atomic absorption (AA) is the standard method for the analysis of specific metals. It is widely practiced in environmental analysis. The general aspects of the techniques are:

e) mg/L to µg/L detection is routine
f) analysis is generally very specific to a given element (although interferences are common)
g) some techniques offer multiple compound analysis for one injection
h) the techniques are fast and relatively inexpensive

Principle of Atomic Adsorption Spectroscopy

When metal cations enter a flame (or high T furnace or plasma), metal is quickly reduced to elemental (atomic) state.

For instance,

Fe2+ + 2e- ---> Fe0 **(2.1)**

Kinetic energy from gaseous collisions in a flame excites outer electrons to higher energy level. This excitation is a UV-visible transition. Light at a characteristic wavelength lA is absorbed. A diagram for the energy states of Thallium during AA is shown as an example in **Figure 2.4**.

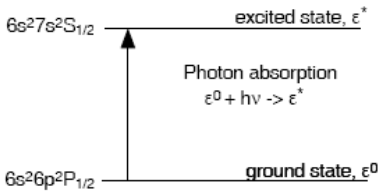


Figure 1: Thallium in flame ($\lambda_{A,\ max}$ = 378 nm)

Emission spectroscopy

As electrons "fall back" to ground state, photons are emitted for the transition to a metastable energy state (ξ*) and a portion of the deactivation is without radiation. Photons are emitted at characteristic wavelengths (λ_E) that are usually different than the wavelengths for absorption. Only 1% or so of the atoms are involved in the transition for a flame, and a more energetic source (such as argon plasma) is usually needed to take advantage of emission for chemical analysis. An example energy diagram for Thallium is shown in Figure 2.5.

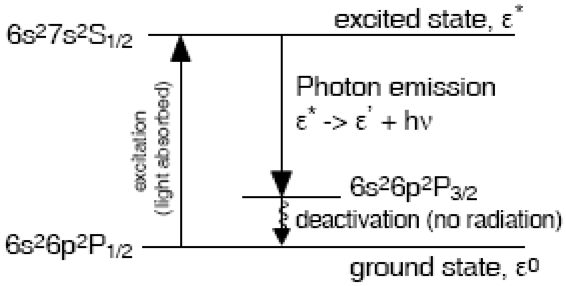


Figure 2: Thallium in flame with emission ($\lambda_{E,\ max}$ = 535 nm)

Flame Atomic Adsorption

A monochromatic beam of light is generated by a cathode ray tube. The lamp is selected from a set of available lamps in order to match the wavelength range with the characteristic wavelength (at maximum absorption) for the specific metal. A metal solution is aspirated into a flame by a nebulizer and burner assembly, shown in Figure 2.6. A variety of gas mixtures can be chosen to obtain the best flame temperature for the exitation of the metal. In order to promote the highest number of transitions (more light absorbed), the light should be aligned with the interconal region of the flame. A schematic of an air/acetylene flame is shown in Figure 2.6.

Following Beer's Law the absorbance A is directly proportional to concentration (A = ebC). The molar absorptivity e is a function of the wavelength and flame temperature. The other critical factor is the optical path length b. This corresponds to the length of the light beam segment that is within the flame. The burner head can be readjusted in order to get a different level of sensitivity.

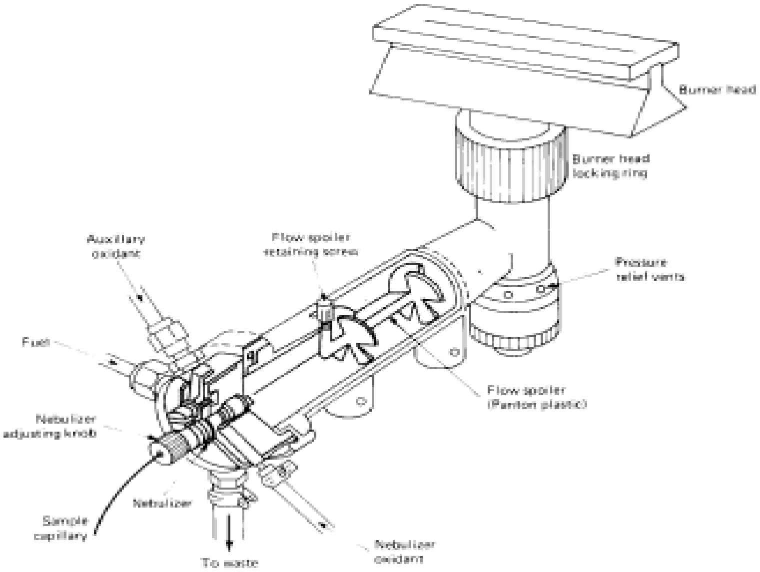


Figure 3: Nebulizer and burner assembly for flame atomic absorption. Adapted from Skoog (1984)

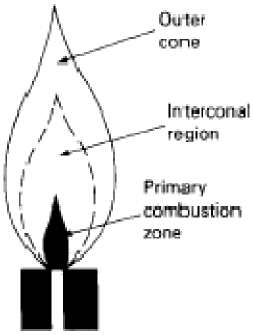


FIGURE 9–6 Schematic diagram of an acetylene/air flame.

Figure 2.7: Diagram of air/acetylene flame. Adapted from Skoog (1984)

Calibration techniques follow closely with those used for spectrophotometers. However, because the aspirator sometimes gets clogged, the rate of sample introduction into the flame can be uneven, and standards should be checked often. One common aspect of the methods (many times ignored by novice users) is filtering samples and keeping the solution acidic. All samples, standards, and rinsing solutions should contain a background acid concentration near 0.1 N (acid varies depending on the analysis). Also, the rinse solution should be aspirated during the periods between samples. This way, most metal ions are maintained in solution, rather than precipitating within the aspirator. Samples containing moderate turbidity can also clog an aspirator.

Most modern Flame AA's have automated optics controls and a computer interface. There are a variety of manual checks that should be done, however, to assure data quality. These steps include running external standards as samples, checking blanks often, running matrix spikes and checking the calibration curve. If a significant interference is found, it is usually recommended to try an alternate wavelength.

Furnace Atomic Absorption Spectroscopy

An electrothermal furnace may be used as the excitation source, and the optical methods can be based on either absorption spectroscopy (Standard Methods 3113) or emission spectroscopy. A furnace assembly is shown below in Figure 2.8. A small sample (μL) is placed on a hot furnace platform in a graphite tube (1200 - 3000°C). The atoms are excited and both absorption and emission are significant. There are two principle advantages of the furnace.

First, the residence time of the metals within the light path is much higher than the flame, and atomic absorption methods are about 20-1000 times more sensitive for furnace methods (*Standard Methods* 3113). The other advantage is that a small sample volume is needed. Two disadvantages of the furnace method are slower throughput and a higher level of interferences. Specialized instruments and methods are also available that use magnetic fields to greatly enhance selectivity and reduce interferences (Zeeman Effect).

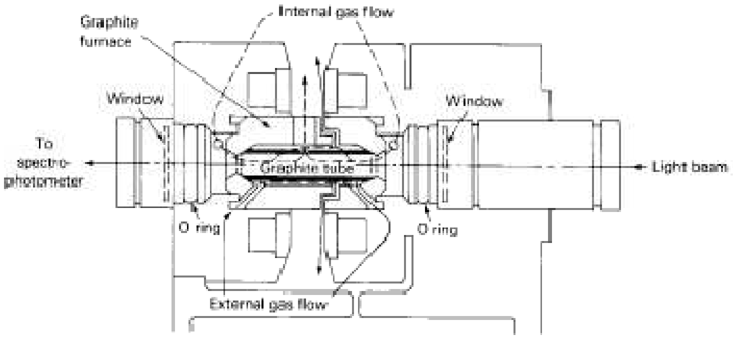


Figure 5. Schematic of Furnace (Electrothermal) Assembly. Adapted from Skoog (1984)

Figure 4: Schematic of furnace (Electrothermal) Assembly. Adapted from Skoog(1984)

Element data for uses Atomic Adsorption Spectroscope

Cadmium

1. Analytical conditions

Lamp current : 9 mA
Wavelength : 228.8 nm
Slit : 1.3 nm
Burner head : Standard type
Burner height : 5.0 mm
Flame : Air-acetylene
Oxidant gas pressure : 160 kPa
Fuel gas flow rate : 2.0 L/min

2. Notes

(1) Measurable Condition Range

Upper measurable concentration limit lies at approx. 6 mg/L.

(2) Standard Solution

By diluting the stock solution with pure water, prepare a standard solution for analysis. At this stage, make sure solution acidic by adding a small volume of HCL or HNO_s to the stock solution.

The diluted solution cannot be stored for a long time and must be prepared just before each analysis.

(3) Examination of Analytical Conditions

Burner height and fuel gas flow rate as conditions optimum for analysis should be set up while atomizing a solution at 0.2 to 0.4 mg/L.

Cd can be dissociated into free atoms sufficiently with an air-acetylene flame. The free atoms are distributed relatively uniformly in a flame. Therefore, atomic absorption sensitivity for Cd is not changed remarkably and is apt to cause self-absorption of the resonance emission spectrum in the hollow cathode lamp. It should therefore be used at a low current.

(4) Remarks on Analysis

When Cd solution is prepared at a low acidic concentration, hydroxide is produced and degrades atomic absorption sensitivity. Is it therefore required to keep the acidic concentration constant.

Analysis of Cd is affected by coexisting Si.

APPENDIX C

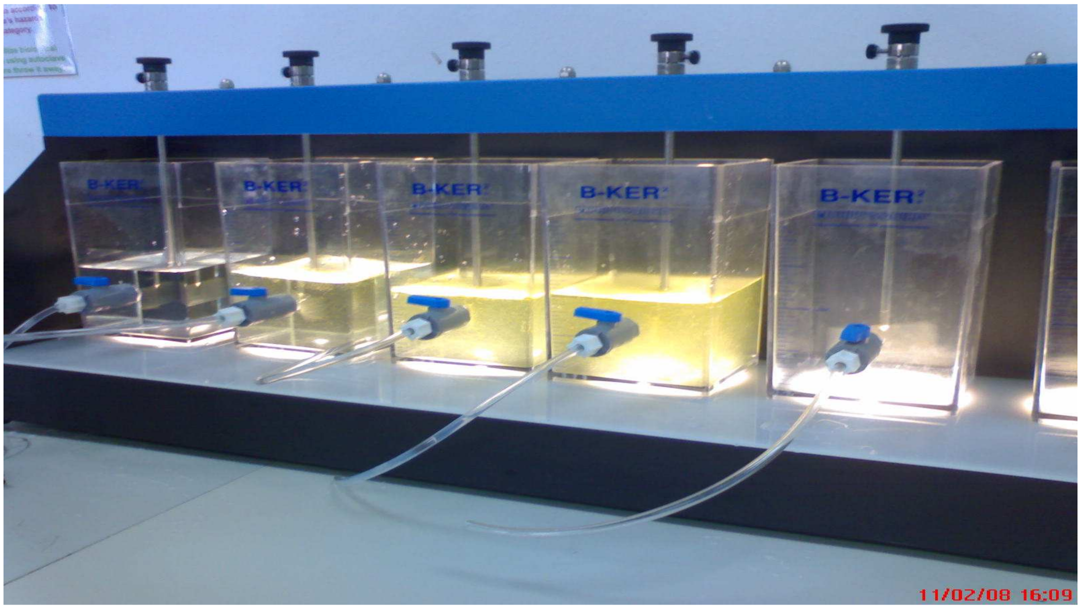


Figure 1: Jar Test is used to mixed up between cadmium solution and dried water hyacinth

Figure 2: pH meter to adjust pH concentration of Cadmium Solution

Figure 3: Hybridization Incubator

Figure 4: Atomic Adsorption Spectroscopy,AAS

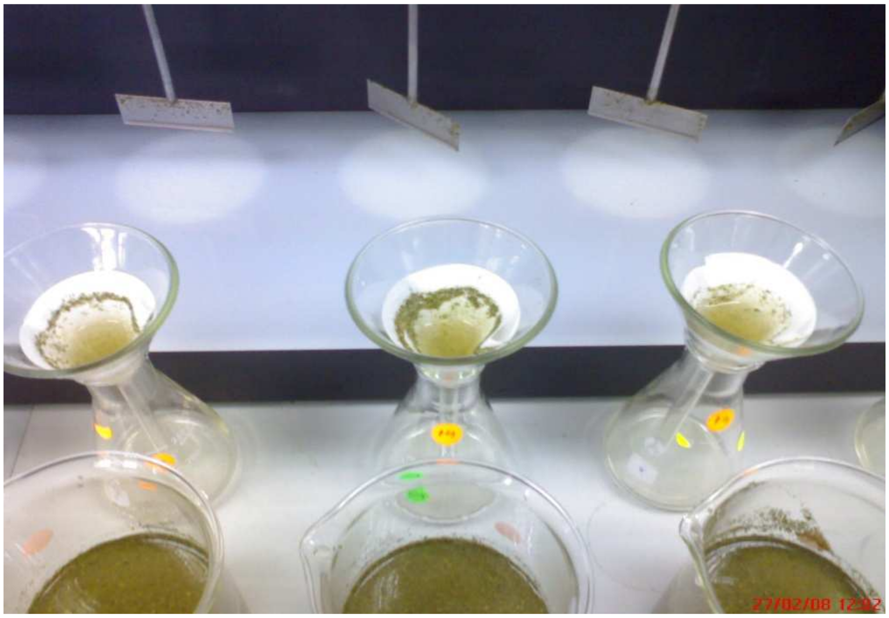


Figure 5: Filtration using filter paper

APPENDIX D

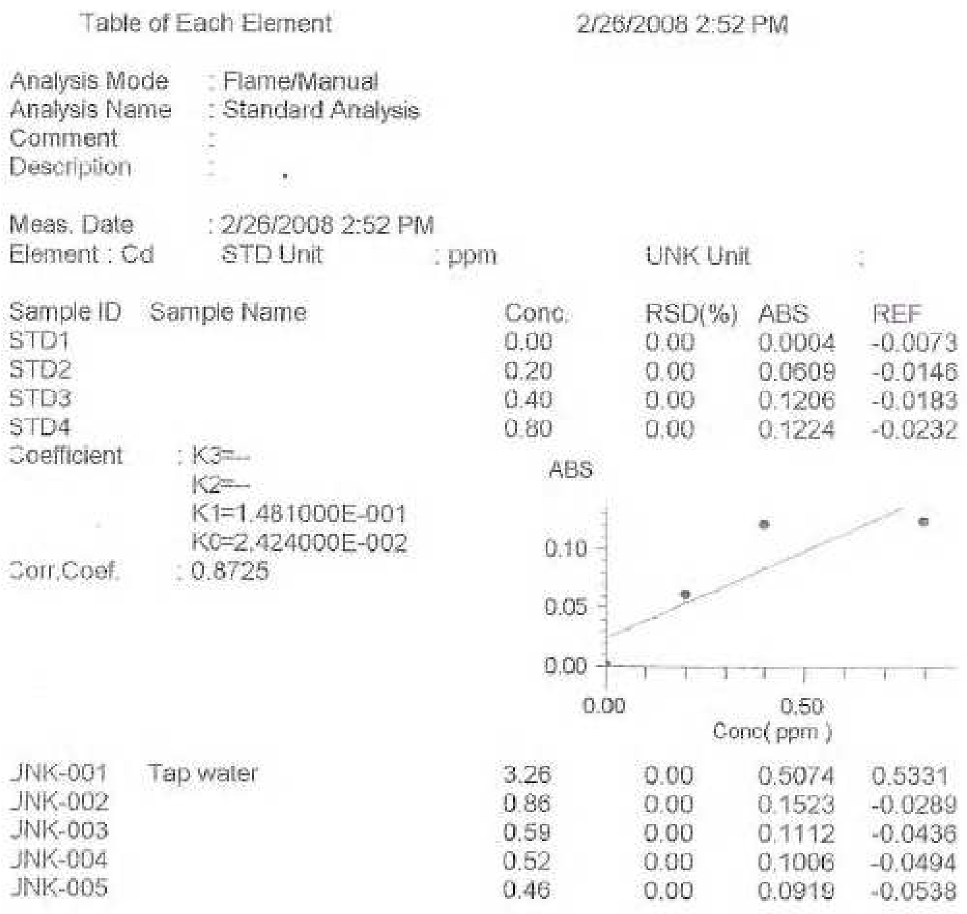


Table of Each Element 2/26/2008 2:52 PM

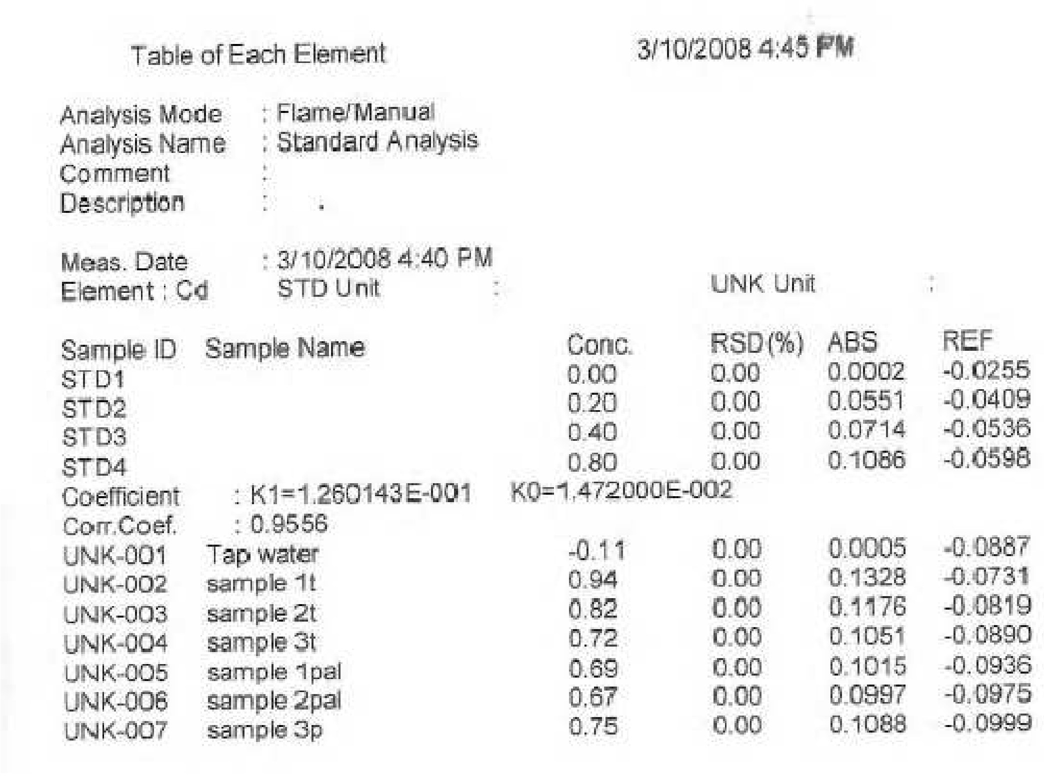
Analysis Mode : Flame/Manual
Analysis Name : Standard Analysis
Comment :
Description :

Meas. Date : 2/26/2008 2:52 PM
Element : Cd STD Unit : ppm UNK Unit :

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.00	0.00	0.0004	-0.0073
STD2		0.20	0.00	0.0609	-0.0146
STD3		0.40	0.00	0.1206	-0.0183
STD4		0.80	0.00	0.1224	-0.0232

Coefficient : K3=--
K2=--
K1=1.481000E-001
K0=2.424000E-002
Corr.Coef. : 0.8725

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
UNK-001	Tap water	3.26	0.00	0.5074	0.5331
UNK-002		0.86	0.00	0.1523	-0.0289
UNK-003		0.59	0.00	0.1112	-0.0436
UNK-004		0.52	0.00	0.1006	-0.0494
UNK-005		0.46	0.00	0.0919	-0.0538



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Analysis Mode    : Flame/Manual
Analysis Name    : Standard Analysis
Comment          :
Description      :    .

Meas. Date       : 3/10/2008 4:40 PM
Element : Cd      STD Unit          :             UNK Unit          :

Sample ID   Sample Name                 Conc.     RSD(%)   ABS      REF
STD1                                    0.00      0.00     0.0002   -0.0255
STD2                                    0.20      0.00     0.0551   -0.0409
STD3                                    0.40      0.00     0.0714   -0.0536
STD4                                    0.80      0.00     0.1086   -0.0598
Coefficient      : K1=1.260143E-001   K0=1.472000E-002
Corr.Coef.       : 0.9556
UNK-001     Tap water                   -0.11     0.00     0.0005   -0.0887
UNK-002     sample 1t                   0.94      0.00     0.1328   -0.0731
UNK-003     sample 2t                   0.82      0.00     0.1176   -0.0819
UNK-004     sample 3t                   0.72      0.00     0.1051   -0.0890
UNK-005     sample 1pal                 0.69      0.00     0.1015   -0.0936
UNK-006     sample 2pal                 0.67      0.00     0.0997   -0.0975
UNK-007     sample 3p                   0.75      0.00     0.1088   -0.0999
```

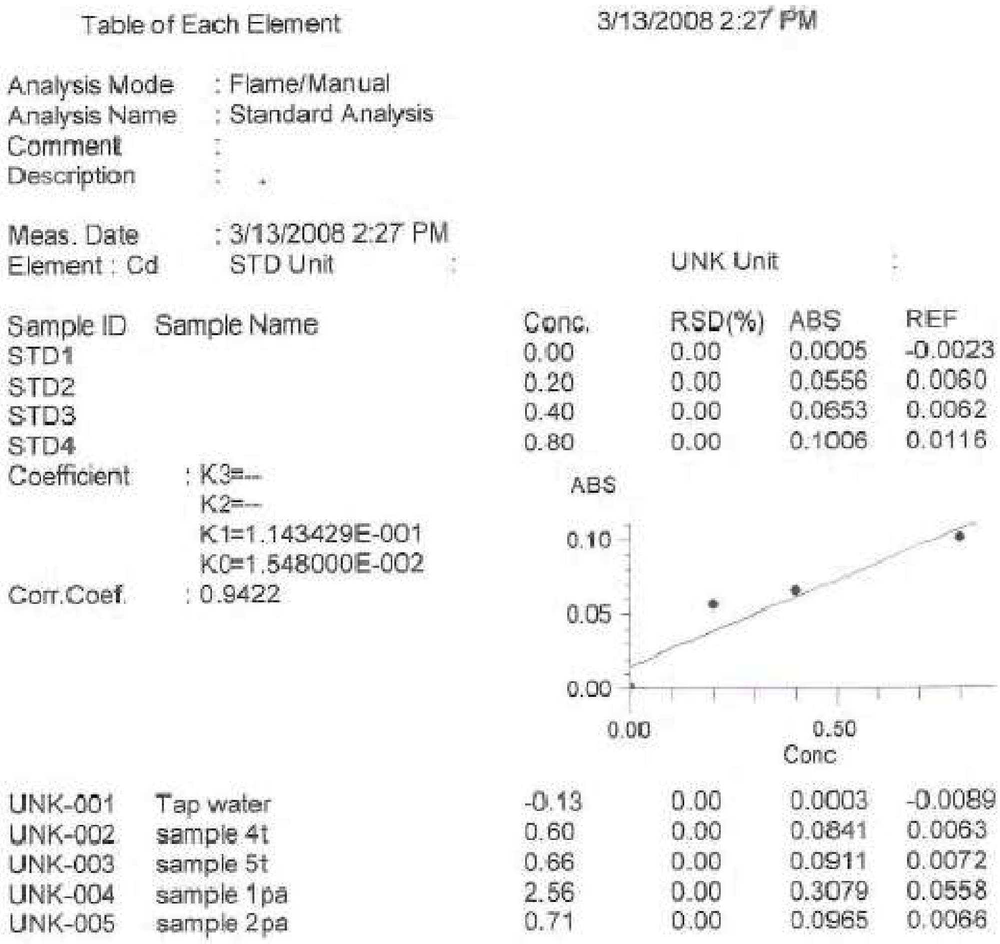

Table of Each Element　　3/13/2008 2:27 PM

Analysis Mode : Flame/Manual
Analysis Name : Standard Analysis
Comment :
Description :

Meas. Date : 3/13/2008 2:27 PM
Element : Cd　STD Unit :　　UNK Unit :

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.00	0.00	0.0005	-0.0023
STD2		0.20	0.00	0.0556	0.0060
STD3		0.40	0.00	0.0653	0.0062
STD4		0.80	0.00	0.1006	0.0116

Coefficient : K3=--
K2=--
K1=1.143429E-001
K0=1.548000E-002
Corr.Coef. : 0.9422

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
UNK-001	Tap water	-0.13	0.00	0.0003	-0.0089
UNK-002	sample 4t	0.60	0.00	0.0841	0.0063
UNK-003	sample 5t	0.66	0.00	0.0911	0.0072
UNK-004	sample 1pa	2.56	0.00	0.3079	0.0558
UNK-005	sample 2pa	0.71	0.00	0.0965	0.0066

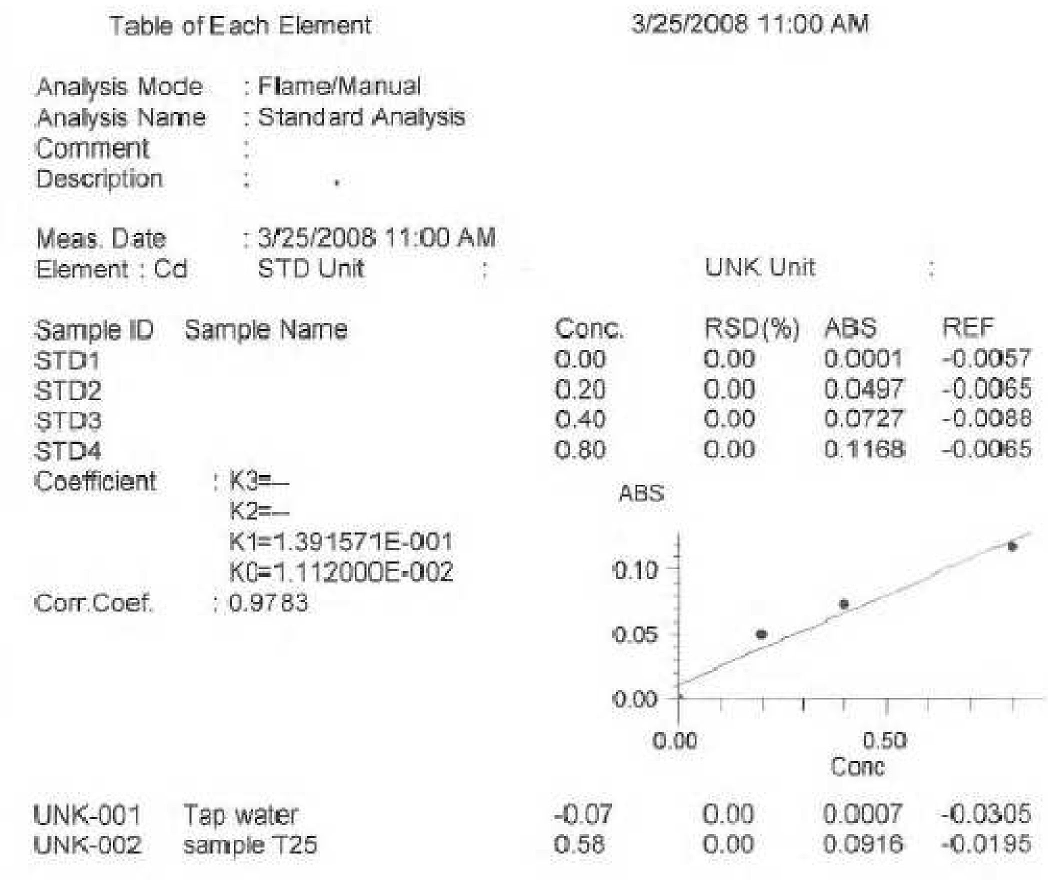

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        Table of Each Element                          3/25/2008 11:00 AM

Analysis Mode     : Flame/Manual
Analysis Name     : Standard Analysis
Comment           :
Description       :

Meas. Date        : 3/25/2008 11:00 AM
Element : Cd        STD Unit          :                  UNK Unit          :

Sample ID   Sample Name                        Conc.       RSD(%)   ABS      REF
STD1                                           0.00        0.00     0.0001   -0.0057
STD2                                           0.20        0.00     0.0497   -0.0065
STD3                                           0.40        0.00     0.0727   -0.0088
STD4                                           0.80        0.00     0.1168   -0.0065
Coefficient      : K3=--
                   K2=--                           ABS
                   K1=1.391571E-001
                   K0=1.112000E-002               0.10
Corr.Coef.       : 0.9783
                                                  0.05

                                                  0.00
                                                        0.00         0.50
                                                                Conc

UNK-001     Tap water                          -0.07       0.00     0.0007   -0.0305
UNK-002     sample T25                         0.58        0.00     0.0916   -0.0195
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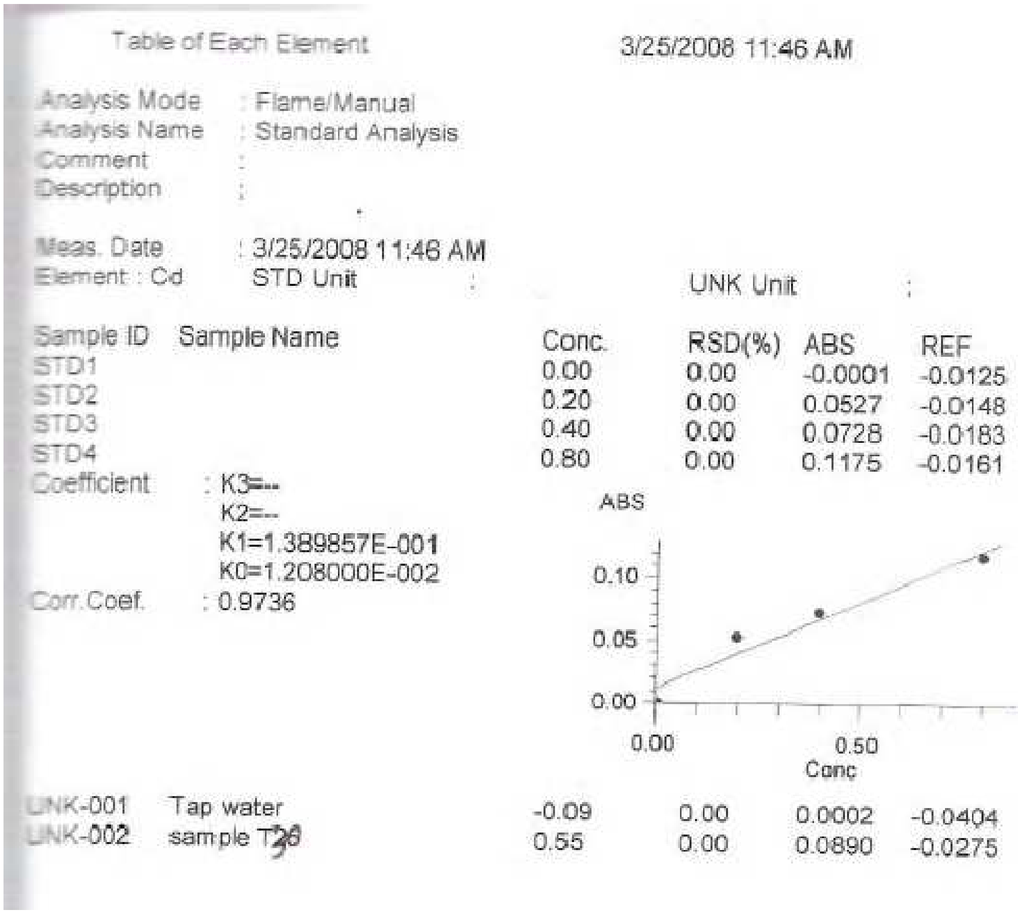


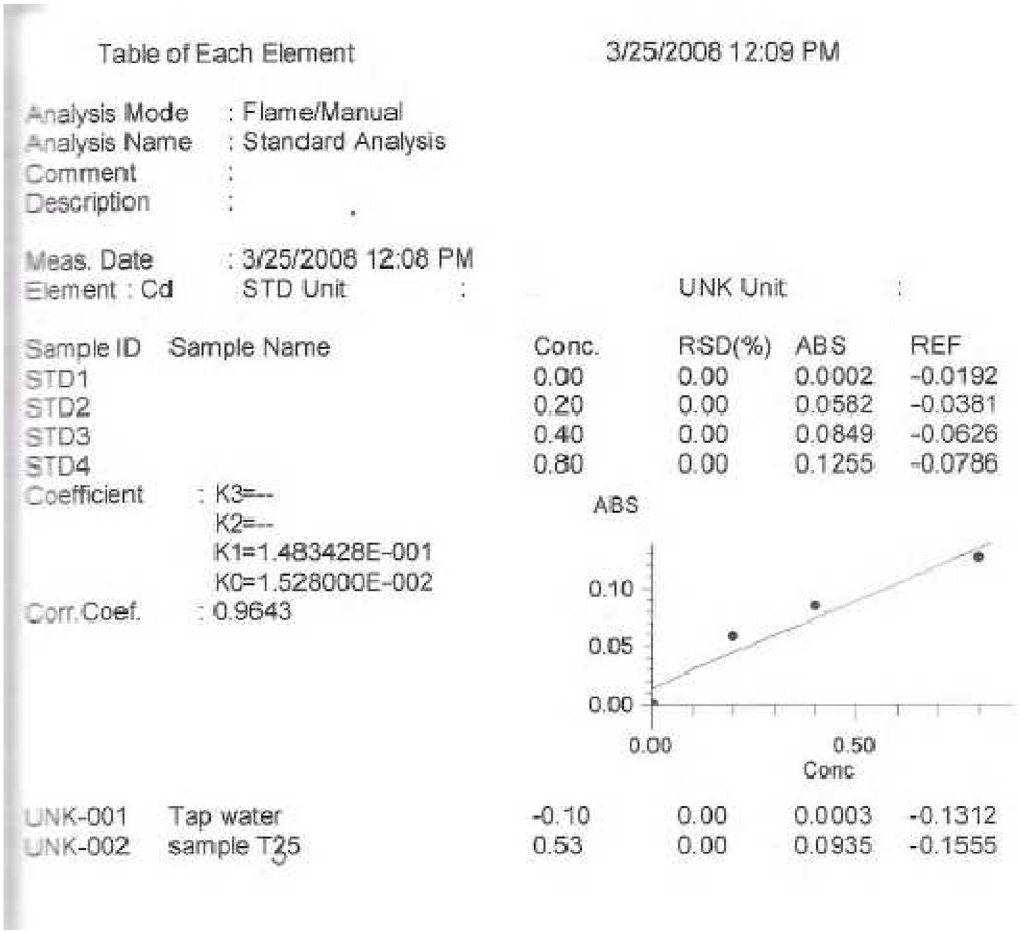
Table of Each Element 3/25/2008 11:46 AM

Analysis Mode : Flame/Manual
Analysis Name : Standard Analysis
Comment :
Description :

Meas. Date : 3/25/2008 11:46 AM
Element : Cd STD Unit : UNK Unit :

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.00	0.00	-0.0001	-0.0125
STD2		0.20	0.00	0.0527	-0.0148
STD3		0.40	0.00	0.0728	-0.0183
STD4		0.80	0.00	0.1175	-0.0161
UNK-001	Tap water	-0.09	0.00	0.0002	-0.0404
UNK-002	sample T26 3	0.55	0.00	0.0890	-0.0275

Coefficient : K3=--
K2=--
K1=1.389857E-001
K0=1.208000E-002
Corr.Coef. : 0.9736



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Analysis Name    : Standard Analysis
Comment          :
Description      :

Meas. Date       : 3/25/2008 12:08 PM
Element : Cd       STD Unit          :              UNK Unit         :

Sample ID  Sample Name                     Conc.     RSD(%)  ABS      REF
STD1                                       0.00      0.00    0.0002   -0.0192
STD2                                       0.20      0.00    0.0582   -0.0381
STD3                                       0.40      0.00    0.0849   -0.0626
STD4                                       0.80      0.00    0.1255   -0.0786
Coefficient    : K3=--
                 K2=--
                 K1=1.483428E-001
                 K0=1.528000E-002
Corr.Coef.     : 0.9643

UNK-001    Tap water                       -0.10     0.00    0.0003   -0.1312
UNK-002    sample T25                      0.53      0.00    0.0935   -0.1555
```

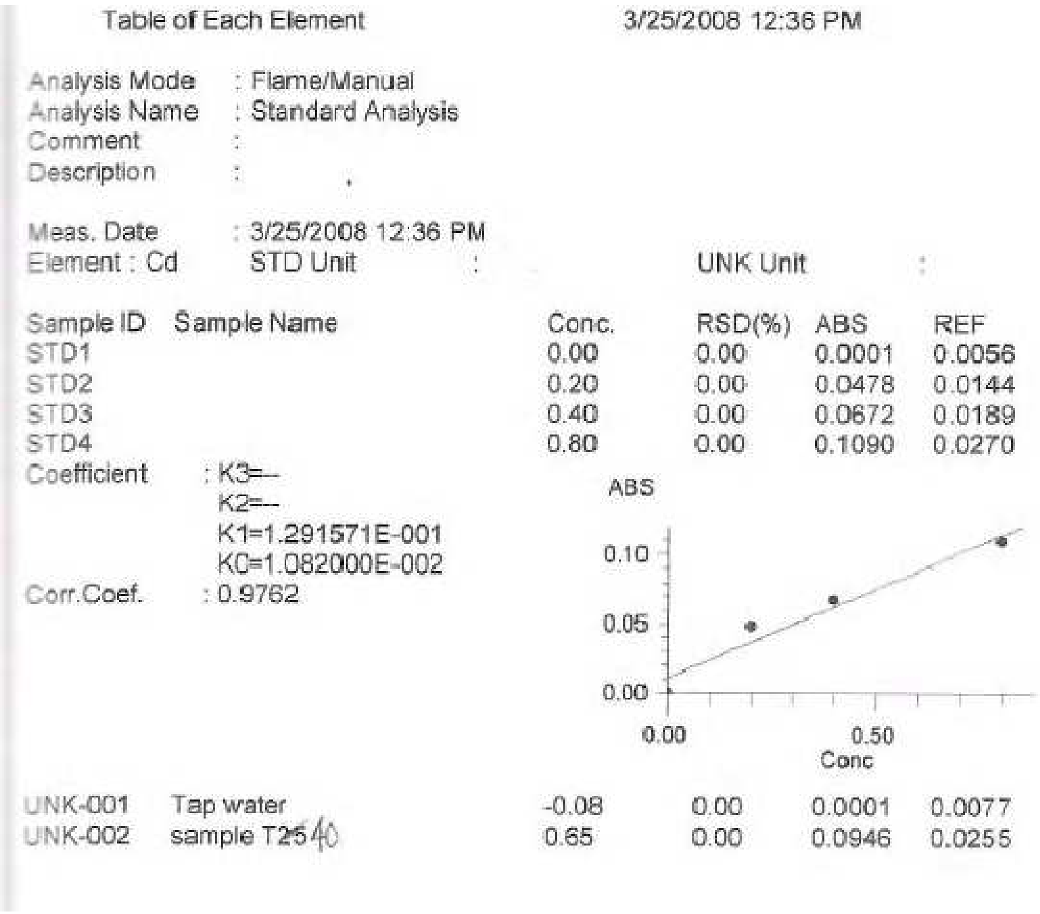

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        Table of Each Element                    3/25/2008 12:36 PM

Analysis Mode    : Flame/Manual
Analysis Name    : Standard Analysis
Comment          :
Description      :

Meas. Date       : 3/25/2008 12:36 PM
Element : Cd       STD Unit        :                UNK Unit        :

Sample ID  Sample Name                    Conc.     RSD(%)  ABS      REF
STD1                                      0.00      0.00    0.0001   0.0056
STD2                                      0.20      0.00    0.0478   0.0144
STD3                                      0.40      0.00    0.0672   0.0189
STD4                                      0.80      0.00    0.1090   0.0270
Coefficient    : K3=--
                 K2=--
                 K1=1.291571E-001
                 K0=1.082000E-002
Corr.Coef.     : 0.9762

UNK-001   Tap water                       -0.08     0.00    0.0001   0.0077
UNK-002   sample T~~25~~40                0.65      0.00    0.0946   0.0255
```

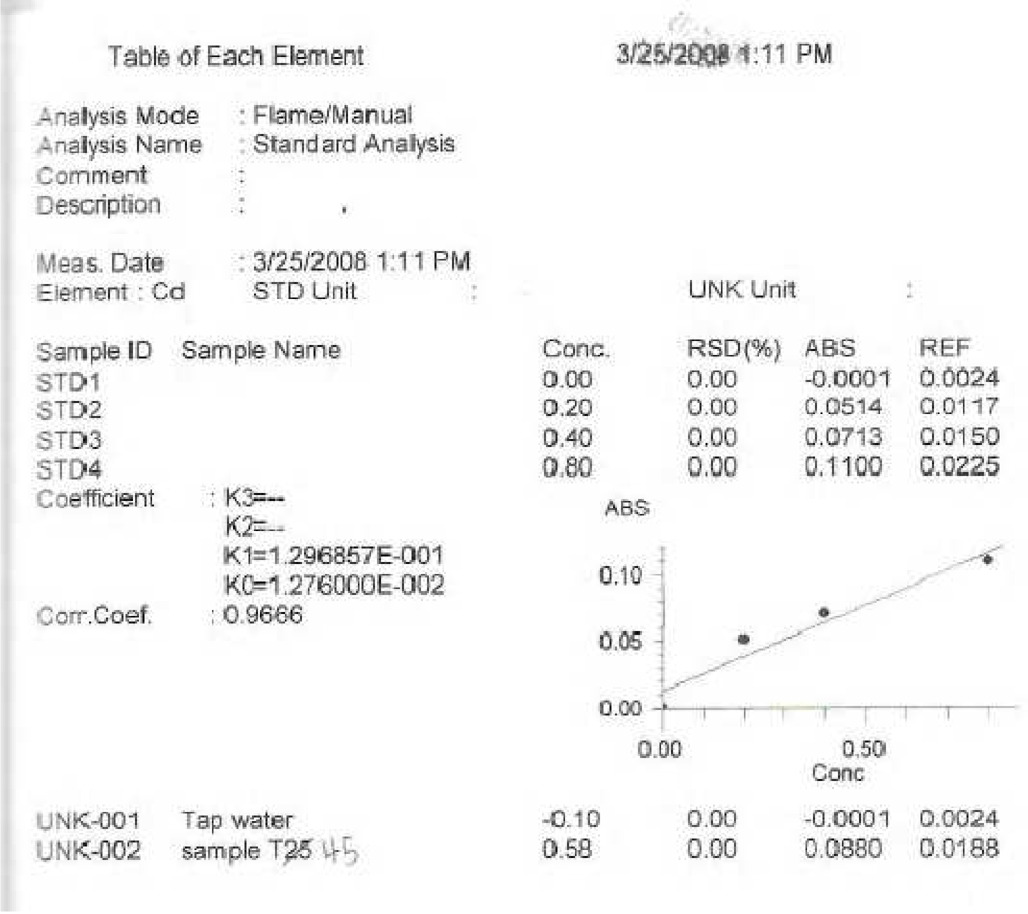

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     Table of Each Element                         3/25/2008 1:11 PM

Analysis Mode      : Flame/Manual
Analysis Name      : Standard Analysis
Comment            :
Description        :

Meas. Date         : 3/25/2008 1:11 PM
Element : Cd        STD Unit           :           UNK Unit          :

Sample ID   Sample Name              Conc.     RSD(%)   ABS       REF
STD1                                 0.00      0.00     -0.0001   0.0024
STD2                                 0.20      0.00     0.0514    0.0117
STD3                                 0.40      0.00     0.0713    0.0150
STD4                                 0.80      0.00     0.1100    0.0225
Coefficient      : K3=--
                   K2=--
                   K1=1.296857E-001
                   K0=1.276000E-002
Corr.Coef.       : 0.9666

UNK-001     Tap water                -0.10     0.00     -0.0001   0.0024
UNK-002     sample T25 45            0.58      0.00     0.0880    0.0188
```

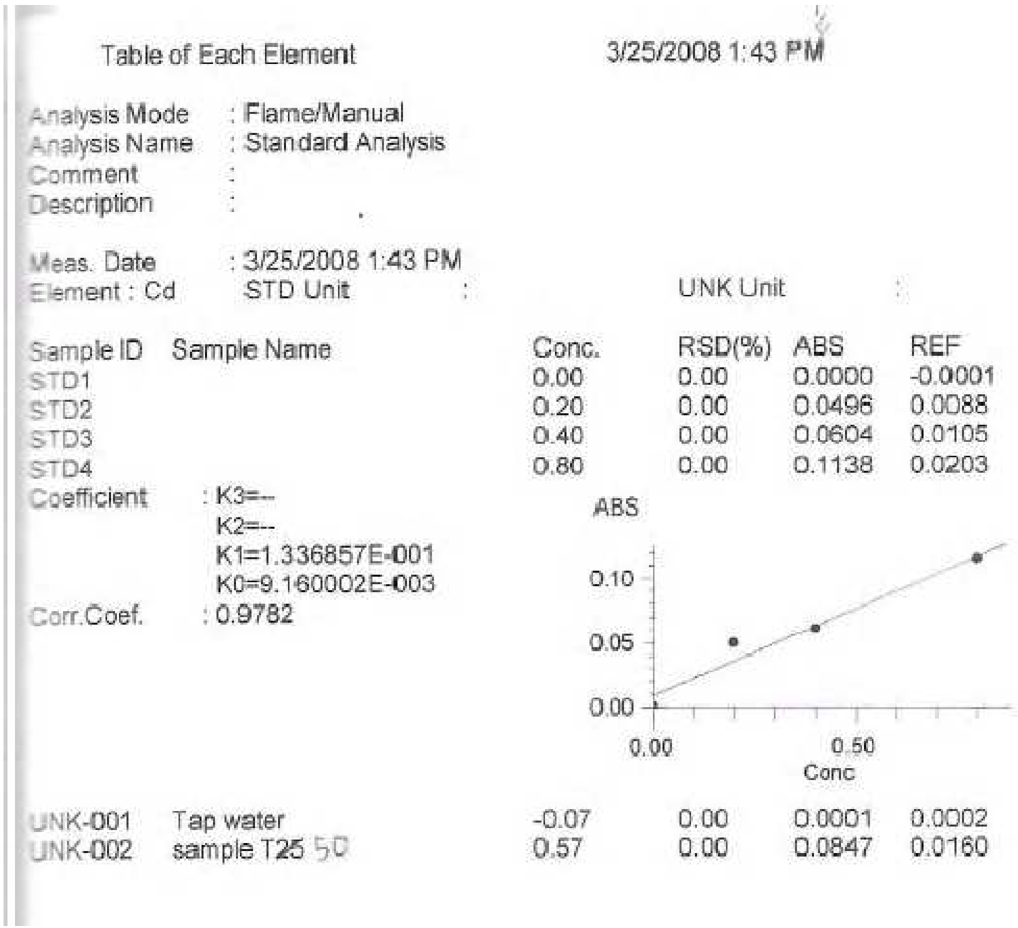

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     Table of Each Element                      3/25/2008 1:43 PM

Analysis Mode    : Flame/Manual
Analysis Name    : Standard Analysis
Comment          :
Description      :

Meas. Date       : 3/25/2008 1:43 PM
Element : Cd       STD Unit        :              UNK Unit          :

Sample ID  Sample Name                   Conc.     RSD(%)  ABS      REF
STD1                                     0.00      0.00    0.0000   -0.0001
STD2                                     0.20      0.00    0.0496   0.0088
STD3                                     0.40      0.00    0.0604   0.0105
STD4                                     0.80      0.00    0.1138   0.0203
Coefficient    : K3=--
                 K2=--
                 K1=1.336857E-001
                 K0=9.160002E-003
Corr.Coef.     : 0.9782

UNK-001    Tap water                     -0.07     0.00    0.0001   0.0002
UNK-002    sample T25 50                 0.57      0.00    0.0847   0.0160
```

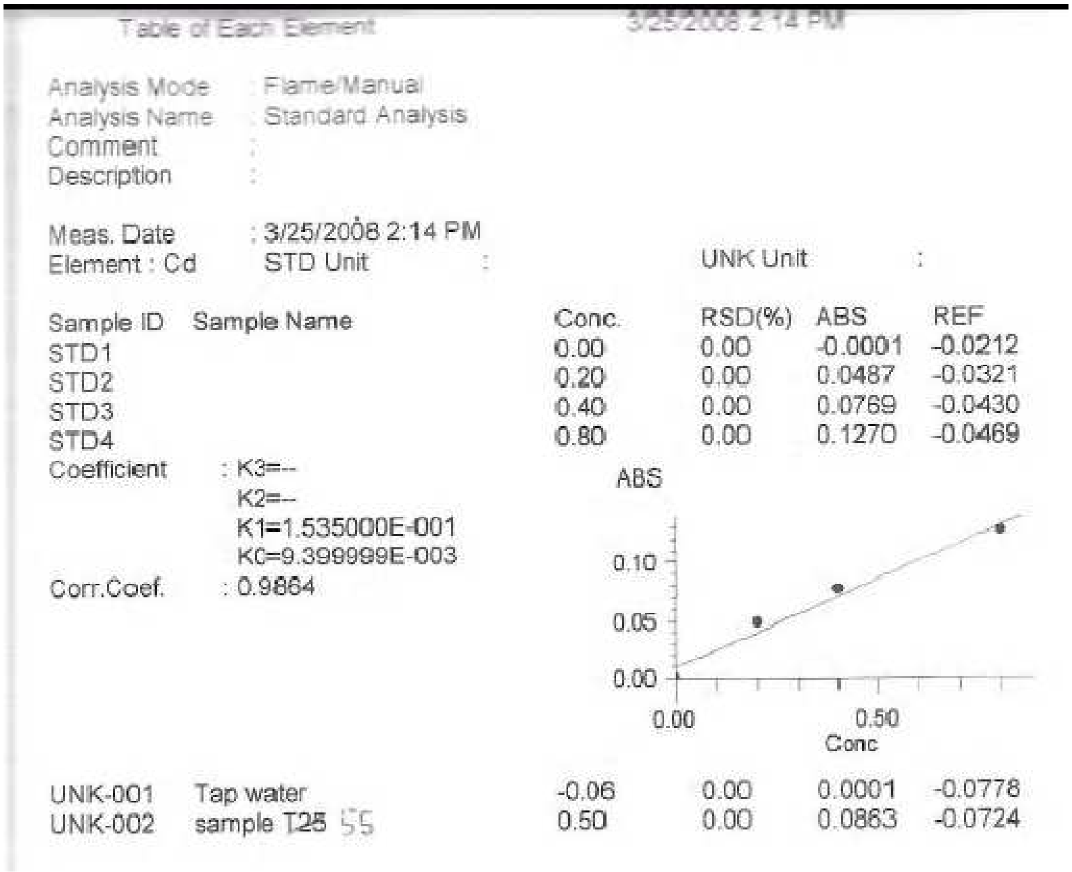

Table of Each Element 3/25/2008 2:14 PM

Analysis Mode : Flame/Manual
Analysis Name : Standard Analysis
Comment :
Description :

Meas. Date : 3/25/2008 2:14 PM
Element : Cd STD Unit : UNK Unit :

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.00	0.00	-0.0001	-0.0212
STD2		0.20	0.00	0.0487	-0.0321
STD3		0.40	0.00	0.0769	-0.0430
STD4		0.80	0.00	0.1270	-0.0469

Coefficient : K3=--
K2=--
K1=1.535000E-001
K0=9.399999E-003
Corr.Coef. : 0.9864

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
UNK-001	Tap water	-0.06	0.00	0.0001	-0.0778
UNK-002	sample T25 55	0.50	0.00	0.0863	-0.0724