

# **Removal of Heavy Metals Using Kenaf Fibers**

by

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Dissertation Report submitted in partial fulfillment of  
the requirements for the  
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**CERTIFICATION OF APPROVAL**

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**A project dissertation submitted to the  
Chemical Engineering Programme  
Universiti Teknologi PETRONAS  
in partial fulfilment of the requirement for the  
BACHELOR OF ENGINEERING (Hons)  
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Approved by,



**(Assoc Prof. Dr. Murugesan Thanabalan)**

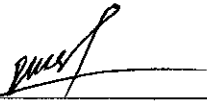
**UNIVERSITI TEKNOLOGI PETRONAS**

**TRONOH, PERAK**

**January 2009**

## CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained here in have not been undertaken or done by unspecified sources or persons.



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DINESH KUMAR VIJAYARAGAVAN

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## ABSTRACT

The feasibility of using natural fibers such as Kenaf to remove the heavy metals as a replacement for costly conventional methods of removing heavy metal ions has been reviewed. It is well known that the cellulose waste material can be obtained and is a cheap adsorbent. Some of the advantages of using Kenaf for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regenerations.

Two types of experiment were conducted. The first experiment was carried out by varying the concentration of the adsorbent and the solutions of heavy metals whilst another experiment was conducted by varying the amount of the kenaf fibres.

Several runs of both experiments were conducted and the results were analyzed in order to achieve the primary objective of this project. The results obtained were analyzed using Atomic Adsorption Spectroscopy method.

Kenaf fibres adsorbed more cadmium compared to nickel for both the individual solutions and mixed metal solution but the amount adsorbed in the mixed metal solution was comparably similar where as for individual solution, the adsorption of cadmium was higher compared to Nickel. Adsorption of metals also depends on the residence time. The longer the time, the more the metals are adsorbed.

## **TABLE OF CONTENT**

<b>ABSTRACT</b>		<b>i</b>
<b>CHAPTER 1:</b>	<b>INTRODUCTION</b>	<b>1</b>
	<b>1.1 Background of Study</b>	<b>1</b>
	<b>1.2 Problem Statement</b>	<b>7</b>
	<b>1.3 Objective and Scope of Study</b>	<b>7</b>
<b>CHAPTER 2</b>	<b>THEORY AND LITERATURE REVIEW</b>	<b>9</b>
	<b>2.1 Types of fibers</b>	<b>10</b>
	<b>2.2 Atomic Absorption</b>	<b>13</b>
	<b>2.3 Biodegradability of the fibers</b>	<b>15</b>
	<b>2.4 Factors which affect the adsorption capacity.</b>	<b>16</b>
<b>CHAPTER 3</b>	<b>METHODOLOGY</b>	<b>18</b>
	<b>3.1 Research Methodology</b>	<b>18</b>
	<b>3.2 Tools and Equipments</b>	<b>21</b>
<b>CHAPTER 4</b>	<b>RESULT AND DISCUSSION</b>	<b>22</b>
<b>CHAPTER 5</b>	<b>CONCLUSION AND RECOMMENDATION</b>	<b>33</b>
<b>REFERENCES</b>		<b>34</b>
<b>APPENDICES</b>		<b>36</b>

## LIST OF FIGURES

Figure 2.1	Schematic diagram of Atomic absorption spectroscopy	14
Figure 2.2	Idealized/ deviation response curve	14
Figure 3.1	Experimental procedure	20
Figure 4.1	Kenaf adsorption rate for 200 ppm Nickel in 400 ppm solution	23
Figure 4.2	Kenaf adsorption rate for 200 ppm cadmium in 400 ppm solution	23
Figure 4.3	Kenaf adsorption rate for 150 ppm Nickel in 300 ppm solution	24
Figure 4.4	Kenaf adsorption rate for 150 ppm Cadmium in 300 ppm solution	25
Figure 4.5	Kenaf adsorption rate for 100 ppm Nickel in 200 ppm solution	26
Figure 4.6	Kenaf adsorption rate for 100 ppm Cadmium in 200 ppm solution	26
Figure 4.7	Comparison between Cadmium and Nickel adsorption in 400 ppm solution	30
Figure 4.8	Comparison between Cadmium and Nickel adsorption in 300 ppm solution	30
Figure 4.9	Comparison between Cadmium and Nickel adsorption in 200 ppm solution	31
Figure 4.10	Percentage of individual ions removed	31
Figure 4.11	Amount of individual ions removed	32

## LIST OF TABLES

Table 2.1	Adsorption capacity	12
Table 4.1	Kenaf adsorption rate in 20 ppm of cadmium and 200 ppm nitrate solution	22
Table 4.2	Kenaf adsorption rate in 150 ppm of cadmium and 150 ppm nitrate solution	24
Table 4.3	Kenaf adsorption rate in 100 ppm of cadmium and 100 ppm nitrate solution	25



# CHAPTER 1

## INTRODUCTION

### 1.1. Background Studies

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate). Adsorption happens between solid-liquid or solid-gaseous phase. Adsorption is one the physico-chemical treatment processes found to be effective in removing heavy metals from aqueous solutions. The most common industrial adsorbents are activated carbon, silica gel, and alumina, because they present enormous surface areas per unit weight. Activated carbon is produced by roasting organic material to decompose it to granules of carbon, coconut shell, wood, and bone are common sources. Silica gel is a matrix of hydrated silicon dioxide. Alumina is mined or precipitated aluminum oxide and hydroxide. Although activated carbon is a magnificent material for adsorption, its black color persists and adds a grey tinge if even trace amounts are left after treatment; however filter materials with fine pores remove carbon quite well.

The application of low cost adsorbents from the plant wastes to remove heavy metals as a replacement of the conventional method that is being used now days. Natural fibres such as kenaf, roselle and tobacco show effective adsorption of heavy metals compare to other natural fibres. Cellulosic waste materials can be employed as cheap adsorbent and their good performance to remove heavy metal ions can be affected upon chemical treatment. Heavy metals are released excessively to the

environments through the rapid industrialization and created major concerns to the global. Heavy metals such as lead (Pb), mercury (Hg), copper (Cu), nickel (Ni) and zinc (Zn) are mostly harmful for living things and environment.

A heavy metal is a member of an ill-defined subset of elements that exhibit metallic properties, which would mainly include the transition metals, some metalloids, lanthanides, and actinides. There is a lot of different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. The term heavy metal has been called "meaningless and misleading" in an IUPAC technical report due to the contradictory definitions and its lack of a "coherent scientific basis". There is an alternative term *toxic metal*, for which no consensus of exact definition exists either. These metals are a cause of environmental pollution (heavy-metal pollution) from a number of sources, including lead in petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain.

Heavy metals are simply a certain class of metallic elements. Our bodies require trace amounts of some heavy metals, including copper, zinc, and others, but even these can be dangerous at high levels. Other heavy metals such as mercury, lead, arsenic, and cadmium have no known benefits, and their accumulation over time can cause serious illness and even premature death. The industrialization of our world has dramatically increased the overall environmental 'load' of heavy metal toxins. Today, heavy metals are abundant in our air, soil and even drinking water. They are present in virtually every area of modern life from construction materials to cosmetics, medicines, processed foods, fuel, appliances, and even personal care products. It is very difficult for anyone to avoid exposure.

Heavy metals can accumulate in the environment and cause damage to ecosystems and human health. Strategies to reduce these impacts have to be developed. However, it is difficult to tackle this problem because analysis and actions are usually addressed from separate areas, such as air, water or soil. In addition, long-term effects

are important. Hence, if only one environmental component is analysed for short periods, no consistent and effective strategy can be derived. A more holistic approach is required that will show how heavy metals are dispersed in world's environment, and their effects on ecological and human health. Unlike organic wastes, heavy metals are non biodegradable and they can accumulate in living tissues, causing various diseases and disorders.

Heavy metal toxins contribute to a variety of adverse health effects. There are over 20 different known heavy metal toxins that can impact human health. Accumulation within the body can lead to a decline in the mental, cognitive, and physical health of the individual. The following paragraphs discuss the most common and dangerous heavy metal toxins.

### 1.1.1 Heavy metals

#### 1.1.1.1 Arsenic

The use of this toxic element in numerous industrial processes has resulted in its presence in many biological and ecological systems. Ground, surface, and drinking water are susceptible to arsenic poisoning from the use of arsenic in smelting, refining, galvanizing, and power plants; environmental contaminants like pesticides, herbicides, insecticides, fungicides, desiccants, wood preservatives, and animal feed additives; and human made hazardous waste sites, chemical wastes, and antibiotics. After the absorption of arsenic compounds, the primary areas of distribution are the liver, kidneys, lung, spleen, aorta, and skin. Arsenic compounds are also readily deposited in the hair and nails.

Arsenic is a highly toxic element that has been used historically for purposes of suicide and homicide. Its health effects are well known and documented. Acute exposure to arsenic compounds can cause nausea, anorexia, vomiting, abdominal pain, muscle cramps, diarrhea, and burning of the mouth and throat. Garlic-like breath, malaise, and fatigue have also been seen while contact dermatitis, skin lesions, and skin irritation, are seen in individuals who come into direct tactile contact with arsenic compounds. Studies have shown close associations between both inhaled and ingested arsenic and cancer rates. Cancers

of the skin, liver, respiratory tract, and gastrointestinal tract are well documented in regards to arsenic exposure. Several arsenic compounds have been classified by the US Environmental Protection Agency as a Class A - Human Carcinogen (IARC 1987).

#### 1.1.1.2 Lead

Lead is the 5th most utilized metal in the U.S. Human exposure to lead occurs primarily through drinking water, airborne lead-containing particulates, and lead-based paints. The primary source of lead in drinking water is from lead-based plumbing materials. The corrosion of such materials will continue to increase concentrations of lead in municipal drinking water. The EPA actually allows small amounts of lead to be present in our tap water due to this insurmountable problem. Lead from water and airborne sources have been shown to accumulate in agricultural areas leading to increased concentrations in agricultural produce and farm animals. Cigarette smoke is also a significant source of lead exposure.

Lead is one of the most toxic elements naturally occurring on Earth. High concentrations of lead can cause irreversible brain damage, seizure, coma, and death if not treated immediately. Evidence suggests that lead may cause fatigue, irritability, memory problems, reduction in sensory and motor reaction times, decision making impairment, and lapses in concentration. In adults, lead is very detrimental to the cardiovascular system. Occupationally exposed individuals tend to have higher blood pressure and are at an increased risk for cardiovascular disease, myocardial infarction, and stroke. The kidneys are targets of lead toxicity and prone to impairment at moderate to high levels of lead concentrations. Other signs/symptoms of lead toxicity include gastrointestinal disturbances, abdominal pain, cramps, constipation, anorexia and weight loss, immunosuppressant, and some liver impairment.

Children absorb lead much more efficiently than adults do after exposure and are susceptible to the most damaging effects of lead toxicity. Lead not only appears to affect cognitive development of young children but also other areas of neuropsychological function. Young children exposed to lead may exhibit mental retardation, learning difficulties, shortened attention spans (ADHD), increased behavioral problems (aggressive behaviors) and reduced physical growth.

#### 1.1.1.3 Nickel

Small amounts of Nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Short-term overexposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. The EPA does not currently regulate nickel levels in drinking water. Nickel can accumulate in aquatic life, but its presence is not magnified along food chains.

#### 1.1.1.4 Cadmium

Cadmium derives its toxicological properties from its chemical similarity to zinc as essential micronutrient for plants, animals and humans. Cadmium is biopersistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted.

In humans, long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer, although data concerning the latter are difficult to interpret due to compounding factors. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals, although most human data do not support these findings.

The average daily intake for humans is estimated as 0.15 $\mu$ g from air and 1 $\mu$ g from water. Smoking a packet of 20 cigarettes can lead to the inhalation of around 2-4 $\mu$ g of cadmium, but levels may vary widely.

#### 1.1.1.5 Copper

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. People with Wilson's disease are at greater risk for health effects from overexposure to copper. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth.

Above explained metals are the most common heavy metals in the industry. The following paragraph will explained about the adsorbent which will be used in this project.

#### 1.1.2 Kenaf

Kenaf [Etymology: Persian], *Hibiscus cannabinus*, is a plant in the Malvaceae family. *Hibiscus cannabinus* is in the genus *Hibiscus* and is probably native to southern Asia, though its exact natural origin is unknown. The name also applies to the fibre obtained from this plant. Kenaf is one of the allied fibres of jute and shows similar characteristics. Other names include Bimli, Ambary, Ambari Hemp, Deccan Hemp, and *Bimlipatum Jute*.

It is an annual or biennial herbaceous plant (rarely a short-lived perennial) growing to 1.5-3.5 m tall with a woody base. The stems are 1-2 cm diameter, often but not always branched. The leaves are 10-15 cm long, variable in shape, with leaves near the base of the stems being deeply lobed with 3-7 lobes, while leaves near the top of the stem are shallowly lobed or unlobed lanceolate. The flowers are 8-15 cm diameter,

white, yellow, or purple; when white or yellow, the centre is still dark purple. The fruit is a capsule 2 cm diameter, containing several seeds as shown in appendix 1.1.

Kenaf get matured within 100 to 1000 days, which makes kenaf as an important plant as it grows very fast and requires minimum amount of fertilizers, pesticides and water. The stalk of the Kenaf plant consists of two distinct fibre types. The outer fibres are called as BAST and it's roughly about 40% of the stalk's dry weight. The inner fibres are called CORE and comprise about 60% of stalk's dry weight. The bast and core has got different heavy metals adsorption capacity. Large specific surface area, chemical and mechanical stability and layered structured makes the adsorption easier.

Some of the advantages of using Kenaf for wastewater treatment include simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regenerations.

## **1.2. Problem Statement**

Lead (Pb), mercury (Hg), copper (Cu), nickel (Ni), cadmium (Cd) and zinc (Zn) are classified as heavy metals in effluent. These metals are one of the causes of the environmental pollutions from a number of sources such as petrol emissions, industrial effluents or leaching of ions from soil into rivers and lakes by acid rain. It has created a major global concern. Unlike organic compounds, the heavy metals do not decay. Using the natural fibres like kenaf can lower the operating cost of using conventional adsorbents which is very expensive.

## **1.3. Objectives and scope of study**

The objective is to remove the heavy metals in the waste water using natural resources concerning the environment. To achieve this objective research and experiments will be carried out. The experiment is based on:-

- ✓ Using natural fibres to remove different heavy metals.

Using natural adsorbents such as kenaf to remove the heavy metals is the main purpose of this project. The concentration of the adsorbents and the heavy metals are varied so that an optimum concentration is achieved where the maximum level of heavy metals are adsorbed at the lowest cost.



## CHAPTER 2

### LITERATURE REVIEW

Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc., ([Kadirvelu et al., 2001a] and [Williams et al., 1998]). Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore they must be removed before discharge.

Currently, industries are conventional methods are used to remove the heavy metals such as lignite coal, kaolinite and montmorillonite, natural clinker and synthetic zeolites or activated carbon. Removal of heavy metals using this kind of methods is expensive and not feasible. The modification was predominantly done by pillaring with various polyoxy cations of  $Zr^{4+}$ ,  $Al^{3+}$ ,  $Si^{4+}$ ,  $Ti^{4+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  or  $Ga^{3+}$ , etc. Preparation of pillared clays with quaternary ammonium cations, namely, tetramethylammonium-, tetramethylphosphonium- and trimethyl-phenylammonium-,  $N'$ -didodecyl-N,  $N'$ -tetramethylethanediammonium, etc, are also common. Moreover, the acid treatment of clays often boosted their adsorption capacities.

The adsorption of toxic metals, viz., As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn, etc., have been studied predominantly. Montmorillonite and its modified forms have much higher metal adsorption capacity compared to that of kaolinite as well as modified-kaolinite. (Krishna Gopal Bhattacharyya<sup>a</sup> and Susmita Sen Gupta<sup>b</sup>) ([www.sciencedirect.com](http://www.sciencedirect.com)).

Adsorption capacities of clays and some other adsorbents for Ni(II) (units of Langmuir capacity and Freundlich capacity are  $\text{mg g}^{-1}$  and  $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$  respectively). ([www.scirus.com](http://www.scirus.com)).

## 2.1 Types of fibres

Fibre selection is the most important criteria before an experiment is conducted. Kenaf, alfalfa, pinyon juniper, and aspen fibres were used as model fibres for filtration. Digested alfalfa fibre represents a major potential source of fibre supply. About 23 millions tons of digested fibre could be recovered from the 45 million tons of alfalfa produced annually in the United States. Pinyon juniper is prolific on national lands in the southwest and adjacent states (2.8 million hectares) as well as in Mexico (>10 million hectares). Pinyon juniper, which has high extractives content and bark, has shown a fairly high sorption rate. Aspen fibres were used because of their high hemicellulose content.

Most lignocellulosic raw materials need to be reduced in size before they can be used for filtration. One method is pulverization through chipping followed by Wiley, ball- or hammer-milling, or by sawing. Pulverization ignores the integrity of anatomical structure. The Wiley mill used for screening had two stationary blades and a rotor with four cutting edges that revolve at a high speed; the resultant shearing action minimized moisture loss.

The other method, fiberization through refining or mechanical pulping, preserves fibre integrity and the final product is a collection of fibres. Like wood fibres, agro-based or nonwood fibres need to be reduced before they can be used for filtration. The usual process used in our laboratory is refining, which allows the fibre to be made into a web or mat and also washes the substrates. Refining can be tailored by varying steam pressure, duration, and types of plates.

Table 2.1 shows the types of the adsorbents researched so far and their adsorption capacity.

	<b>Adsorbents</b>	<b>Equilibrium time (min)</b>	<b>Langmuir capacity</b>	<b>Freundlich capacity</b>	
<b>Clay adsorbents</b>	Raw kaolinite	120	2.8	–	
	Ca-bentonite	120	6.3	–	
	Na-bentonite		24.2	–	
	Kaolinite	180	10.4	1.1	
	ZrO-kaolinite		8.8	0.8	
	TBA-kaolinite		8.4	0.5	
	Montmorillonite		28.4	4.5	
	ZrO-montmorillonite		22.0	1.3	
	TBA-montmorillonite		19.7	1.2	
	Acid-activated kaolinite	180	11.9	1.5	
	Acid-activated montmorillonite		29.5	6.0	
	<b>Other adsorbents</b>	Bagasse fly ash	80	1.1	0.9
		Peat	–	28.3	5.3
Granular activated carbon		200	6.5	–	
Modified granular activated carbon			7.0	–	

	<b>Adsorbents</b>	<b>Equilibrium time (min)</b>	<b>Langmuir capacity</b>	<b>Freundlich capacity</b>
	<b>Protonated yeast (<i>Saccharomyces cerevisiae</i>)</b>	60	11.4	–

Table 2.1: Adsorption capacity

Many researches has been done to improve the adsorption capacity and to find a replacement for the conventional methods, which is used in the industries. The following section will explain the researched which has been carried out using plant waste to improve and replace the conventional methods.

#### 2.1.1. Rice husks/ rice hulls

Rice husk is insoluble in water, has good chemical stability, has high mechanical strength and possesses a granular structure, which makes it is a good adsorbent. Pre-treatment removes lignin, hemicelluloses and increase porosity and surface area which increases reaction rates and improve cellulose hydrolysis.

#### 2.1.2. Spent grain

Spent grain obtained from brewery can be used to treat Pb(II) and Cd(II) ions. The best pH range for metal adsorption is 4 to 6. The adsorption capacity enhanced after is it treated with NaOH. The adsorption rate is twice higher for the Pb compared to Cd.

#### 2.1.3. Sugarcane bagasse/ fly ash

Sugarcane bagasse consists of cellulose (50%), polyoses (27%) and lignin (23%). These three biological polymers cause sugarcane bagasse rich in hydroxyl and phenolic groups. Triethylenetetramine modified sugarcane bagasse was the best adsorbent material to remove Cd and Pb.

#### 2.1.4. Saw dust

It is obtained from wood industry and is an abundant by product which is easily available in country sides with negligible price. Three possible reasons for increase in adsorption capacities of heavy metal ions:-

- 2.1.4.1. Changes on wood surface-increased in surface area, average pore volume and pore diameter after alkaline treatment. The surface area and average pore diameter increase about 1.5-2 times after modification.
- 2.1.4.2. Improvement in ion exchange process especially with  $\text{Na}^+$  ions.
- 2.1.4.3. Microprecipitation of metal hydroxides- $\text{Cu}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$  in pores saw dust.

## 2.2 Atomic Absorption

In analytical chemistry, atomic absorption spectroscopy is a technique for determining the concentration of a particular metal element in a sample. Atomic absorption spectroscopy can be used to analyze the concentration of over 62 different metals in a solution. Although atomic absorption spectroscopy dates to the nineteenth century, the modern form was largely developed during the 1950s by a team of Australian chemists. They were led by Alan Walsh and worked at the CSIRO (Commonwealth Science and Industry Research Organization) Division of Chemical Physics in Melbourne, Australia. The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample.

Atomic-absorption (AA) spectroscopy uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame or graphite furnace (Appendix 2). The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. Applying the Beer-Lambert law directly in AA spectroscopy is difficult due to

variations in the atomization efficiency from the sample matrix, and nonuniformity of concentration and path length of analyte atoms (in graphite furnace AA). Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.

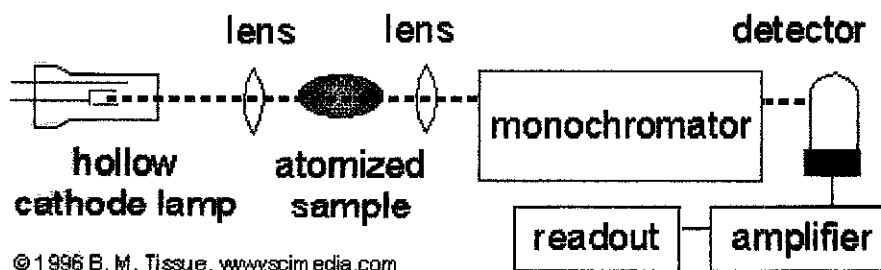


Figure 2.1: schematic diagram of Atomic absorption spectroscopy

All the atoms has its own pattern wave length at which it will absorb energy, due to its unique electron configurations in the outer most orbits. In order to tell how much of a known element is present in a sample, one must first establish a basis for comparison using known quantities. It can be done producing a calibration curve. For this process, a known wavelength is selected, and the detector will measure only the energy emitted at that wavelength.

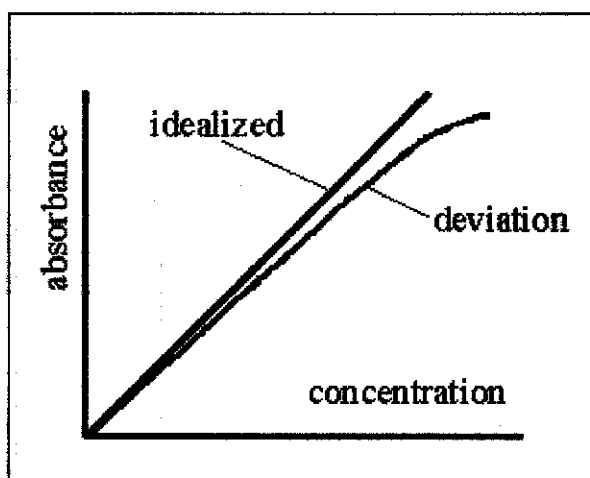


Figure 2.2: idealized/ deviation response curve.

However, as the concentration of the target atom in the sample increases, absorption will also increase proportionally. Thus, one runs a series of known concentrations of some compound, and records the corresponding degree of absorbance, which is an inverse percentage of light transmitted. A straight line can then be drawn between all of the known points. From this line, one can then extrapolate the concentration of the substance under investigation from its absorbance. The use of special light sources and specific wavelength selection allows the quantitative determination of individual components of a multi element mixture. The more concentrated is the solution, the more is the energy is absorbed.

The light beam is generated by lamp that is specific for a target metal. The lamp must be perfectly aligned so the beam crosses the hottest part of the flame. The light passed through the flame is received by the monochromator, which is set to accept and transmit radiation at the specified wavelength and travels into the detector. The detector measures the intensity of the beam of light. When some of the light is absorbed by metal, the beam's intensity is reduced. The detector records that reduction as absorption. That absorption is shown on output device by the data system.

### **2.3 Biodegradability of the fibres**

One of the advantages of using the lignocellulosic materials for the filtrations is that their ability to biodegradable after disposed. Most lignocellulosic materials, especially agricultural fibres, will degrade in contact with moisture or water; some lignocellulosic materials, such as flax and straw, will degrade within days or weeks. The extent of biodegradability can be predicted based on chemical composition, physical properties, and preservative activities.

## 2.4 Factors which affect the adsorption capacity

### 2.4.1 Fibre chemistry

The possible explanation for why lignocellulosic materials have some degree of heavy metal ion sorption capacity can be explained in terms of cellulose, lignin, hemicelluloses, and extractives. Cellulose, a homopolysaccharide of glucose units, is the most abundant lignocellulosic material and a stable compound. Cotton with high cellulose content shows very low sorption capacity. The generally high sorption capacity of nonwoods can be attributed to syringyl lignin. Guaiacyl lignin is found in softwoods and a mixture of syringyl and guaiacyl lignin in hardwoods. The general order of sorption capacity for nonwoods, hardwood, and softwood is nonwood (3%–10%) > hardwood (20%–25%) > softwoods (26%–32%). Two assumptions can be made about the relationship of lignin to sorption capacity: (1) the lower the lignin contents, the higher the sorption capacity or (2) low lignin content represents low density and easy accessibility of ions to active sites.

Cellulose and lignin make minimum contributions to ion exchange and hemicellulose and extractives are the major players. Chelation is another possible chemical reaction in the presence of flavonoids. The sorption capacity of lignocellulosics for metal ions is generally described as adsorption. The cations are attracted to negatively charged active sites throughout the lignocellulosic materials. These groups are abundant in lignocellulosics, yet they are tightly bonded to each other in cellulose and lignin and thus are not available unless hydrogen bonding is broken through chemical modification

### 2.4.2 Chemical modification

Sulfonation is a pulping procedure that acts on lignin. Sulfonated lignin becomes soluble in water and delignification occurs at 170°C. Our sulfonation procedure was a mild process. Our intention was not to remove all the lignin but to sulfonate some lignin to increase ion exchange capacity.



### 2.4.3 Shape of the filtration medium

Substrates used as filtration media need to be formed into a shape that maximizes surface area. One possibility is pellets. We recommend formation of the material into nonwoven mats or webs. Mats or webs can be formed by either the Rando Webber or Dan Webber methods. Both methods work in a similar manner; Rando Webber is based on a needle-laying process and Dan Webber on an air-laying process. Substrate fibres need to be at least 1 mm long for such mats. Binding chemicals are usually added<sup>[4]</sup>.

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Research methodology**

Kenaf is a natural fibre which grows vigorously in Malaysia. The plant is good adsorbent of heavy metals if the metals are treated individually <sup>[4]</sup>. The kenaf samples were reduced in size before it is used as an adsorbent in this project. This is because it will increase the contact surface areas of the adsorbents so that more of the heavy metals can be adsorbed. Experiment is done by varying the concentration of the heavy metals in the prepared solutions to get the optimum concentration and decrease the usage of kenaf.

##### **3.1.1. Adsorbent preparations**

1. Kenaf bast fibres were grounded to pass 0.18-mm (30-mesh) screen; any fines less than 0.18 mm (80 mesh) were removed.
2. Fibres were oven dried for 24 h at 40°C (Appendix 1.2).

##### **3.1.2. Adsorbate preparations**

1. Nickel Sulfate and Cadmium Sulfate was weighted to 100mg each.
2. 1000 ml of distilled water was mixed with the weighed sulfates to make 100 ppm of solutions.

##### **3.1.3. Experiment procedure**

1. The grinded Kenaf fibres were weighed 1 gram.
2. 100 ml of metal solution was mixed with the measured Kenaf fibres.

3. The solution was stirred and samples are taken for every 2 hours.
4. 10 ml of sample is pipette from the stirred solution.
5. The sample was then filtered using filtered paper.
6. The samples were kept inside vials until it been analyzed.
7. The step 1 until step 6 is repeated using 2 gram and 3 gram of kenaf fibres.
8. The experiment is repeated with 150 ppm and 200 ppm of metal solution.

Note: The solution has to be filtered with fine filter papers to avoid the growth of fungus in the solution and acid Nitric must be added in the filtered solutions for the same purpose.

#### 3.1.4. Product analysis

1. The filtered samples were analyzed for Ni and Cd concentration using AAS-flame methods.
2. The results were plotted and the adsorption capacity was analyzed.

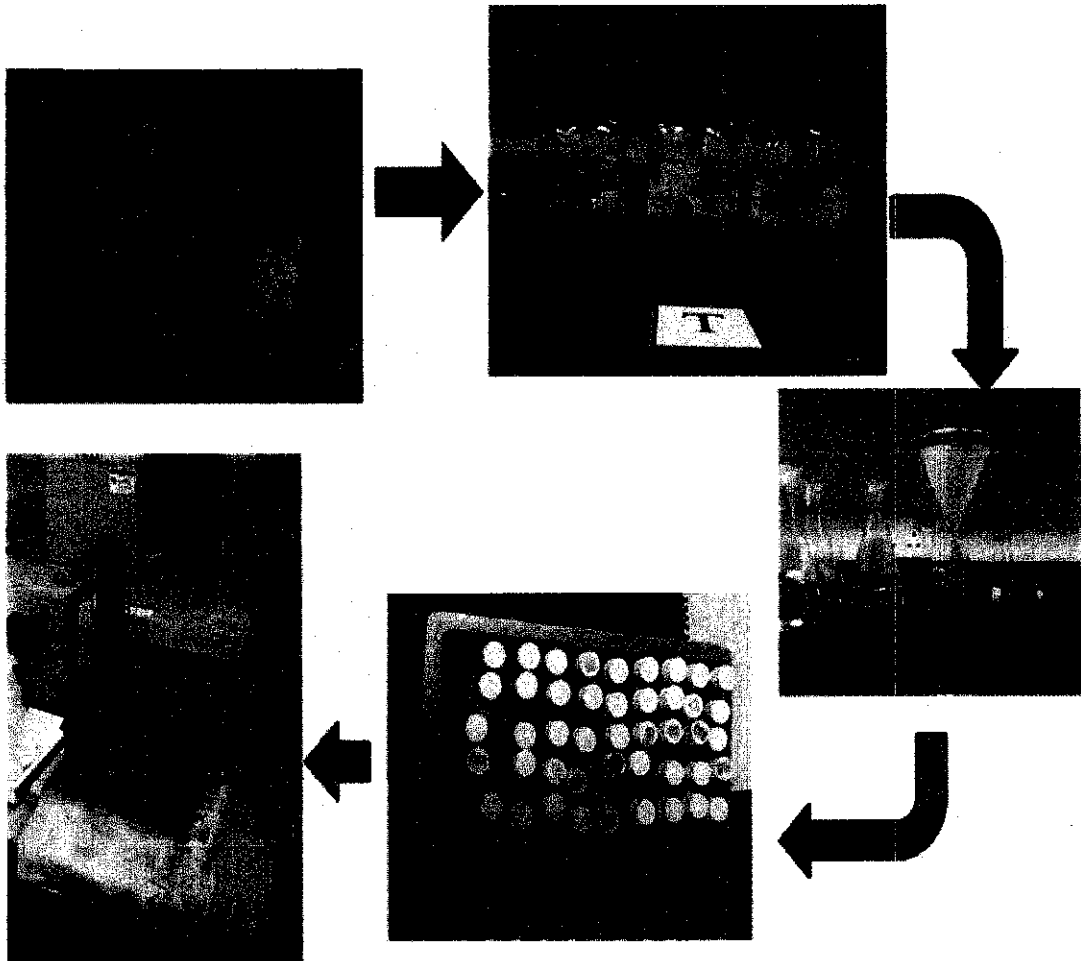


Figure 3.1: Experimental procedure

Experiment is done for different concentration of adsorbent in the different concentration of adsorbate (Ni + Cd solution). Nine different types of experiment are carried out in this project. The result is tabulated and graph is drawn to compare it.

### 3.1.5. Chemical modification

Chemical modification is to be done to improve the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favour metal uptake. According to the literature review done it is more favourable to use chemically treated adsorbents compared to untreated ones <sup>[5]</sup>.

Therefore sulfonation conducted by dissolving 168 g sodium sulfite and 19 g of sodium bicarbonate in 1 L water (stock solution); 10 mL of this mixture was added to 100 g of fibre, stirred, and heated to 70°C for 2 h. Sulfonation in combination with refining was performed by mixing the sample with equivalent volume of stock solution and enough water to soak the sample. Refining was conducted after 1 week.

### 3.1.6. Reagents and Analysis

Standard AAS reference was purchased or 1000-mg/L standard stock solutions were prepared from nickel (II) sulfate, zinc sulfate, copper metal and cadmium sulfate, dissolved in equivalent of 2% nitric acid. Sodium sulfite and bicarbonate were of reagent grade. Samples were analyzed by atomic absorption spectrophotometry (AAS).

## 3.2 Tools and equipments

The experiment requires the lab tools and equipments for storing solutions and for data collections. Researches have to be done about the Kenaf and catalyst that can be used for enhancing the reaction to the better extend.

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 Mixed metal

Results from the experiment are tabulated in the Table 4.1, 4.2 and 4.3 while the adsorption rates for Ni and Cd are illustrated in Figure 4.1 to 4.6. The experiment is only conducted for the mixed metals because there is a study on the individual metal adsorption has been done by James b Hans.

	TIME (HOUR)	NICKEL CONCENTRATION	CADMIUM CONCENTRATION
1 gram Kenaf	0	199.71	200.25
	1	197.96	198.2
	3	197.66	198.09
	5	197.59	197.93
	7	197.41	198.01
2 gram Kenaf	0	199.76	200.21
	1	196.07	195.85
	3	195.87	195.84
	5	193.84	193.82
	7	193.73	193.74
3 gram Kenaf	0	199.69	200.21
	1	194.97	194.8
	3	194.82	194.72
	5	189.64	189.75
	7	187.68	187.61

Table 4.1: Kenaf adsorption rate in 20 ppm of cadmium and 200 ppm nitrate solution

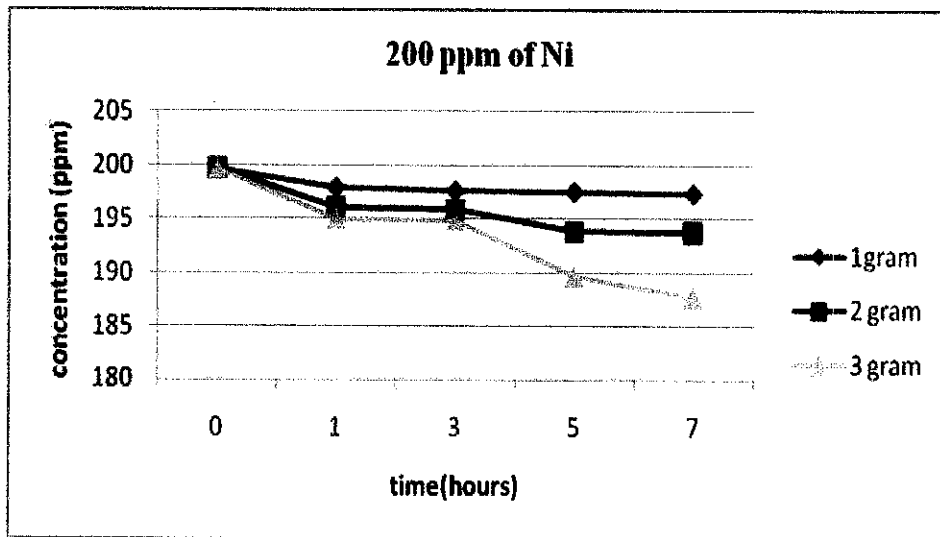


Figure 4.1: Kenaf adsorption rate for 200 ppm Nickel in 400 ppm solution

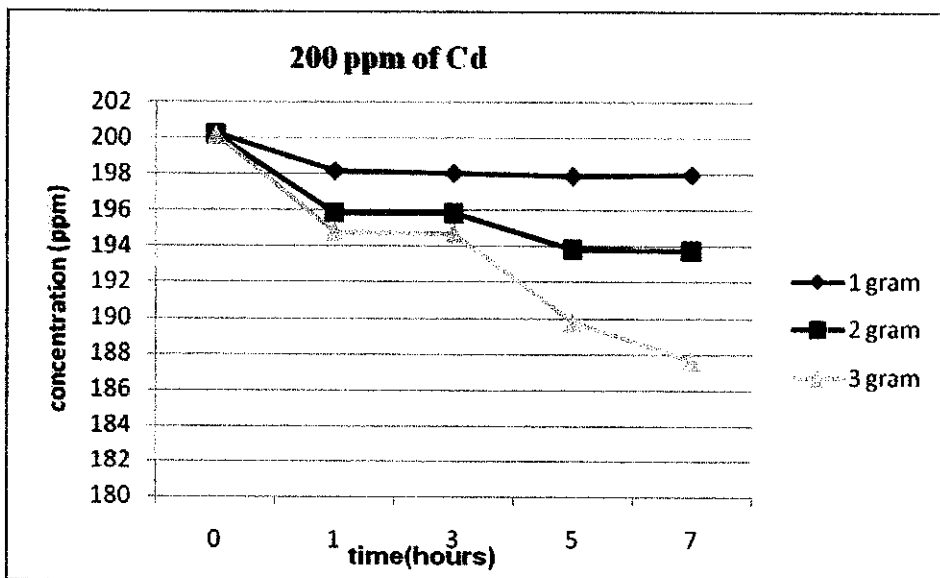


Figure 4.2: Kenaf adsorption rate for 200 ppm cadmium in 400 ppm solution

	TIME (HOUR)	NICKEL CONCENTRATION	CADMIUM CONCENTRATION
1 gram Kenaf	0	150.44	150.32
	1	145.09	144.89
	3	145.08	144.89
	5	144.58	144.87
	7	145.01	144.85
2 gram Kenaf	0	150.67	150.12
	1	143.53	143.5
	3	143.15	143.47
	5	143.43	143.17
	7	143.02	143.18
3 gram Kenaf	0	150.56	150.09
	1	142.65	140.21
	3	142.19	140.1
	5	138.79	136.96
	7	137.4	136.95

Table 4.2: Kenaf adsorption rate in 150 ppm of cadmium and 150 ppm nitrate solution

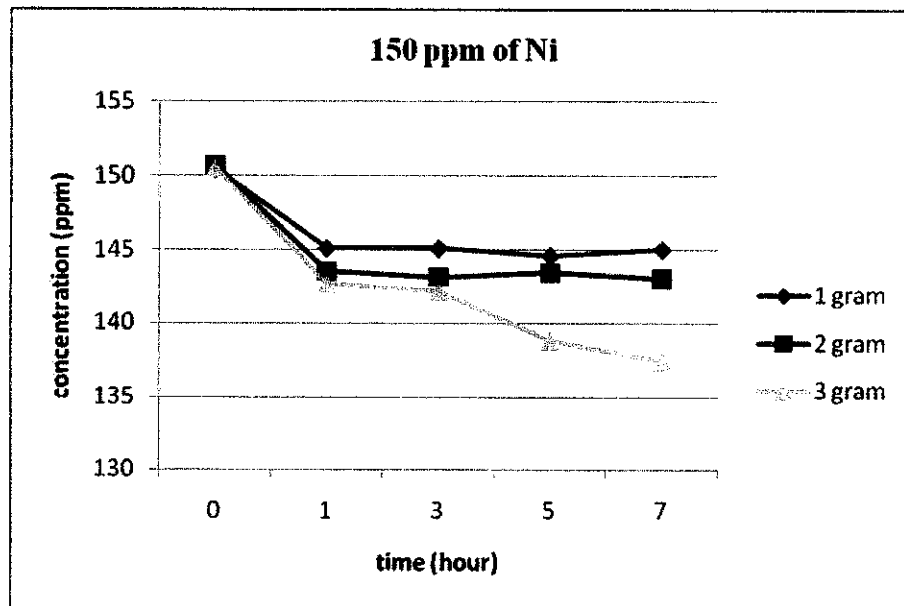


Figure 4.3: Kenaf adsorption rate for 150 ppm Nickel in 300 ppm solution



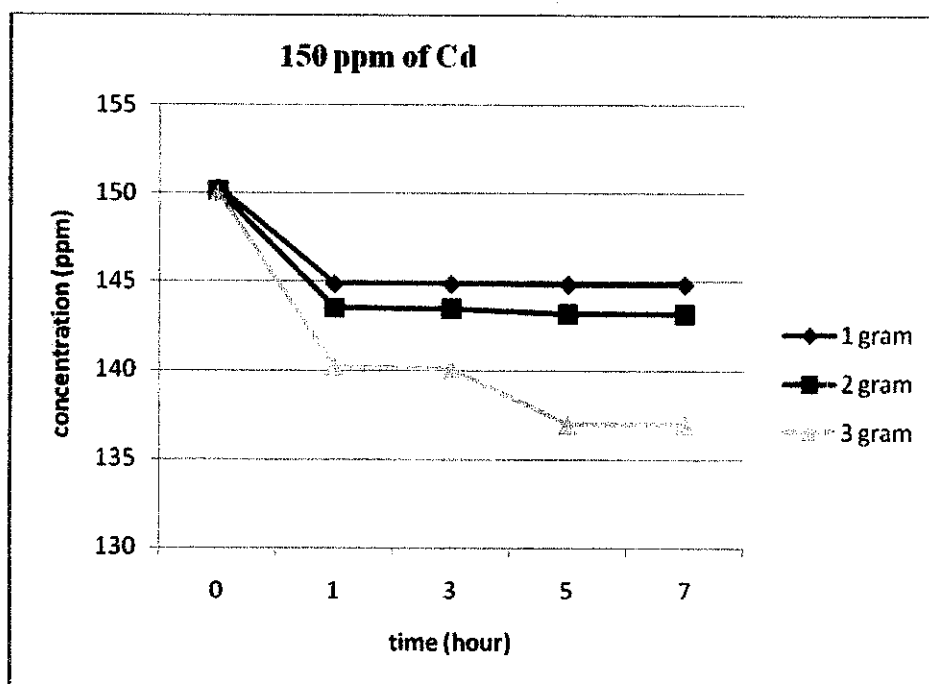


Figure 4.4: Kenaf adsorption rate for 150 ppm Cadmium in 300 ppm solution

	TIME (HOUR)	NICKEL CONCENTRATION	CADMIUM CONCENTRATION
<b>1 gram Kenaf</b>	0	100.25	100.36
	1	94.49	94.07
	3	94.16	93.55
	5	94.15	93.26
	7	94.07	93.3
<b>2 gram Kenaf</b>	0	100.38	96.46
	1	94.27	93.38
	3	94.04	92.35
	5	92.86	91.84
	7	92.98	91.48
<b>3 gram Kenaf</b>	0	100.4	96.5
	1	93.8	92.94
	3	93.8	91.61
	5	90.55	88.86
	7	90.39	88.73

Table 4.3: Kenaf adsorption rate in 100 ppm of cadmium and 100 ppm nitrate solution

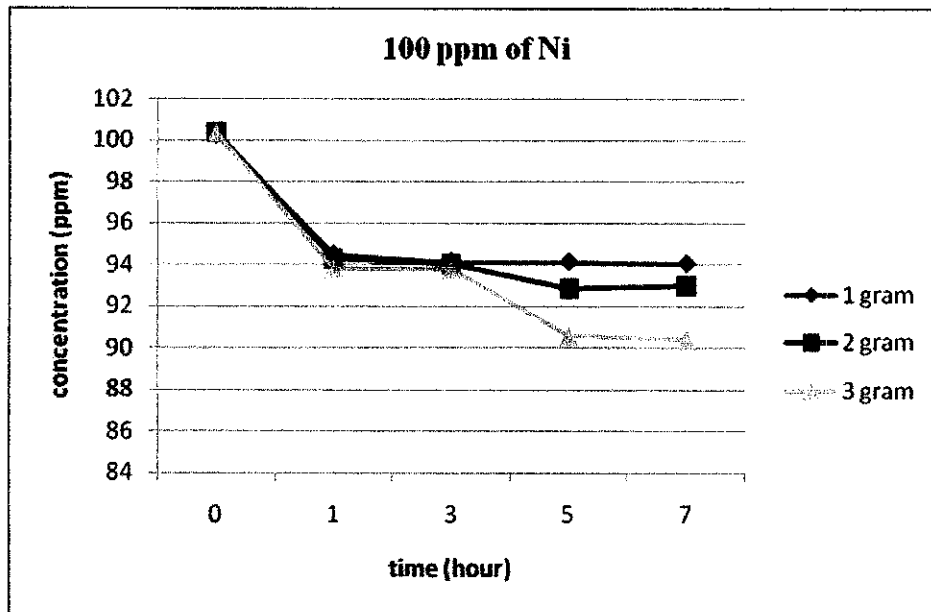


Figure 4.5: Kenaf adsorption rate for 100 ppm Nickel in 200 ppm solution

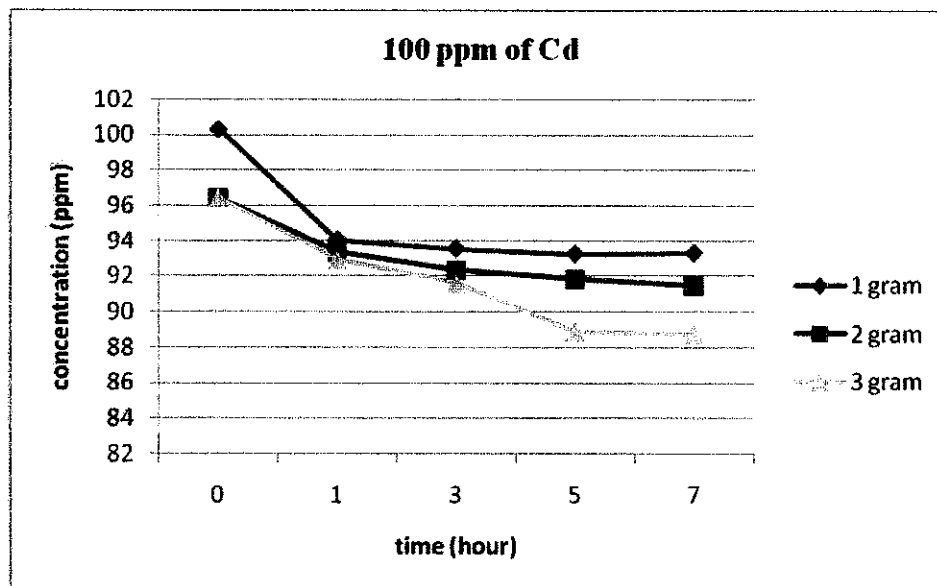


Figure 4.6: Kenaf adsorption rate for 100 ppm Cadmium in 200 ppm solution

From Figure 4.1 until Figure 4.6, it is known that as the amount of Kenaf fibres increased the adsorption rate or the amount of Nickel ion and Cadmium ion adsorbed increases. When 1 gram of Kenaf fibres was used, the amount of Ni and Cd adsorbed was very much less compared to 2 grams or 3 grams of Kenaf. The increase of the

amount of ions adsorbed was because as the amount of Kenaf fibres increased, more effective contact surface area was available for the ions to be adsorbed.

The size of the adsorbent is also a major contributor for the efficiency of adsorption rate. Bigger size of the adsorbent will have less contact surface area compared to the smaller size of adsorbent. As the contact surface area increases, more metal ions are adsorbed because more of metal ions have the chance to have effective collision with the Kenaf fibre. In addition, the adsorbent must not smaller than 0.18 mm because a smaller size than 0.18mm adsorbent would be difficult to be filtered.

The result further shows that the adsorption rate for the first hour is very steep compared to the subsequent hours. It shows the same trend for all the nine experiment that has been carried out. The adsorption rate is high at the first hour because there are more of active sites of Kenaf fibres during the initial hours. As the time goes on more metals are adsorbed but in a slower rate because the number of active sites reduces with the time. When active sites is more, the metal ions are easily get adsorbed by the Kenaf fibre. At the 7<sup>th</sup> hour the graph flatten horizontally where the adsorption rate is the lowest. The adsorption rate decreases maybe because there is very less or no active sites of Kenaf fibres where the adsorption would took place.

The rate of removal decreases with the length of the residence time. The result shows that the rate of adsorption decreases as the residence time increases. It can be seen that the overall adsorption at 7<sup>th</sup> hour is more compare to the adsorption of Ni and Cd ions at the 1<sup>st</sup> hour but at a slower rate. The more the residence time, the more is the adsorption or effective contact to the Kenaf. The solution is stirred so that the Kenaf won't sediment because sedimentation of Kenaf below of the conical flask will lessen the contact surface area for the adsorption to take place.

As the concentration of the solution is decrease, the adsorption rate or the amount of the metals adsorbed increases. This again can be explained using the contact surface area of the Kenaf fibres. The adsorption also increases as we increase the amount of the Kenaf fibres from 1 gram to 3 grams. When 3 grams of Kenaf fibres used

in the lower concentration of the metal solution, the concentration of the metal solution decreases less compared to higher concentration.

Comparison between the Nickel and Cadmium adsorption as illustrated in Figure 4.7 to 4.9, Cadmium is adsorbed more compared to the Nickel. This finding is inline with the results for individual metals as reported by James b Hans in his journal shown in the Figure 4.10 and 4.11. The same trend is followed for the mixed metals in this project where Kenaf is more effective in removing Cadmium metals compare to other heavy metals for all the metal concentration.

The experiment result shows reduction in the amount of heavy metals in the solution. According the literature reviews, it is known that a better adsorbent adsorb heavy metals more than 10% of heavy metals in the solution in shorter time. Both experiments will give different adsorption capability and amount of metal ions adsorbed. It depends on which method gives a better adsorption compared to the other.

The overall adsorption process consists of a series of steps. When the fluid is passing through the Kenaf fibers, the adsorbate first will diffuses from the bulk fluid to the gross exterior surface of the Kenaf. Then the solute diffuses inside the pore to the surface of the pore. Finally the solute ( $\text{Ni}^+$  or  $\text{Cd}^{2+}$ ) is adsorbed on the surface.

The possible explanation for why lignocellulosic materials have some degree of heavy metal ion sorption capacity can be explained in terms of cellulose, lignin, hemicellulose, and extractives. Two assumptions can be made about the relationship of lignin to sorption capacity: (1) the lower the lignin contents, the higher the sorption capacity or (2) low lignin content represents low density and easy accessibility of ions to active sites.

The adsorption capacity of lignocellulosics for metal ions is generally described as adsorption. The cations are attracted to negatively charged active sites throughout the lignocellulosic materials. The exact location of the active sites has yet to be determined, but it is believed that hydroxyl and carbonyl groups are the main suppliers of active sites. These groups are abundant in lignocellulosics, yet they are tightly bonded to each

other in cellulose and lignin and thus are not available unless hydrogen bonding is broken through chemical modification.

Almost all adsorption systems show that as temperature is increased, the amount adsorbed by the adsorbent decreases strongly. This is useful since adsorption have to be done at room temperatures and to avoid desorption. To regenerate the Kenaf, temperature has to be raised.

Atomic absorption spectroscopy method is used to identify the adsorption rate of heavy metals in the solutions. The calibration curve drawn and the reduced in the amount of heavy metals were noted (analyzed by the AAS spectroscopy). It is a faster method compared to the manually calculating the amount of heavy metals using concentration or colour changes.

For the mixed metals (nickel and cadmium mixed in one solution) the amount adsorbed is nearly same for both the heavy metals but when the experiment done for individual metal solution, Cadmium is adsorbed a lot more compared to Nickel. It shows similar trend as the concentration increased the amount adsorbed increases.

The above Figure 4.1 to 4.6 is summarized into Figure 4.7 to 4.9 to make the comparison easier with the literature.

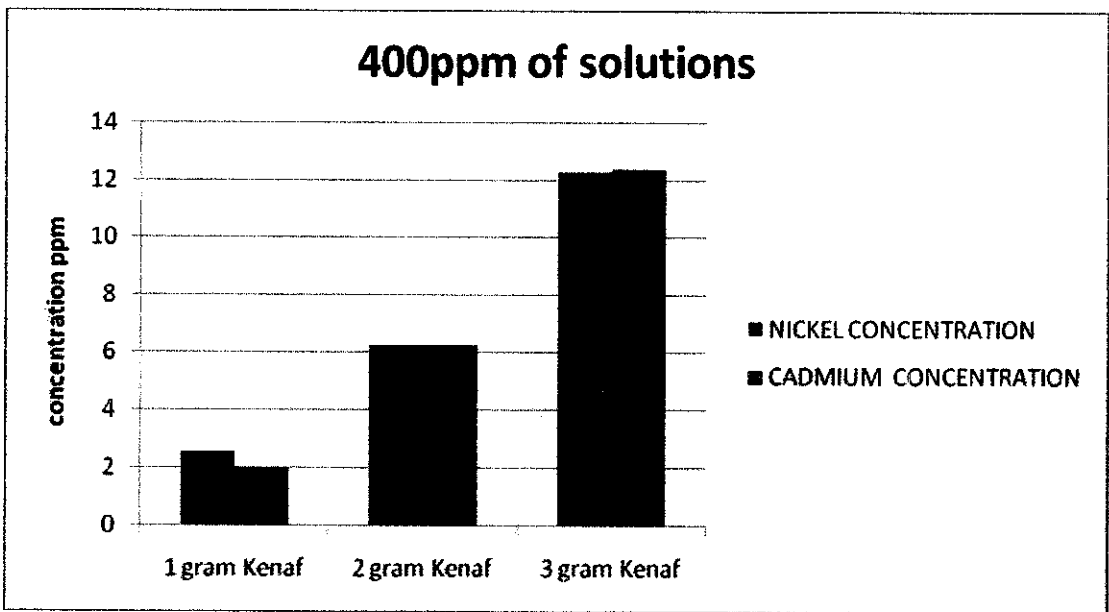


Figure 4.7: comparison between Cadmium and Nickel adsorption in 400ppm solution

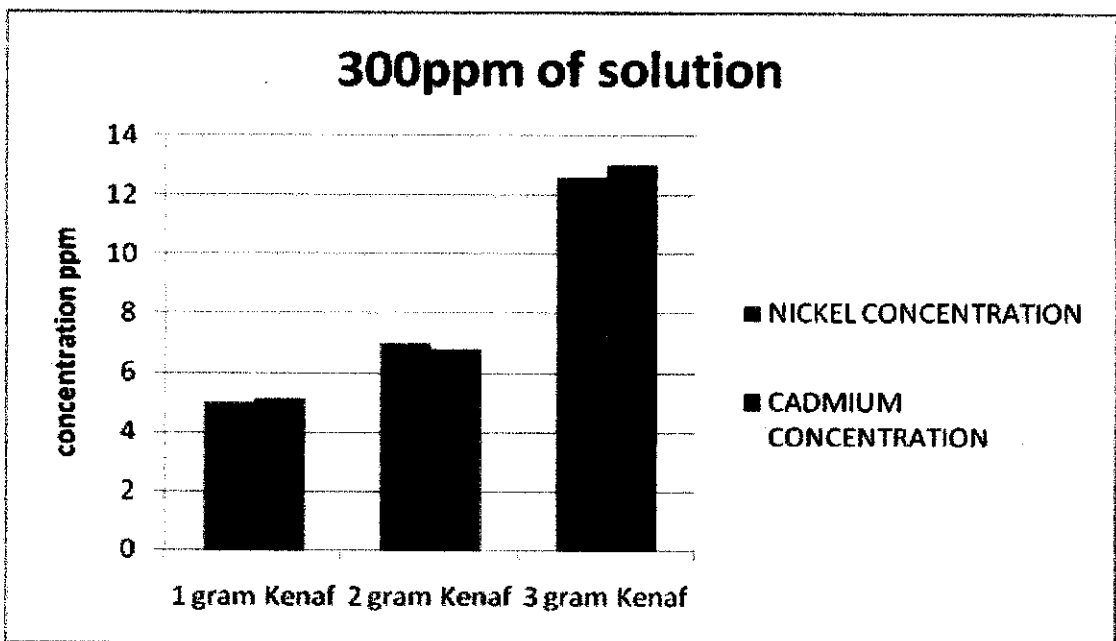


Figure 4.8: comparison between Cadmium and Nickel adsorption in 300ppm solution

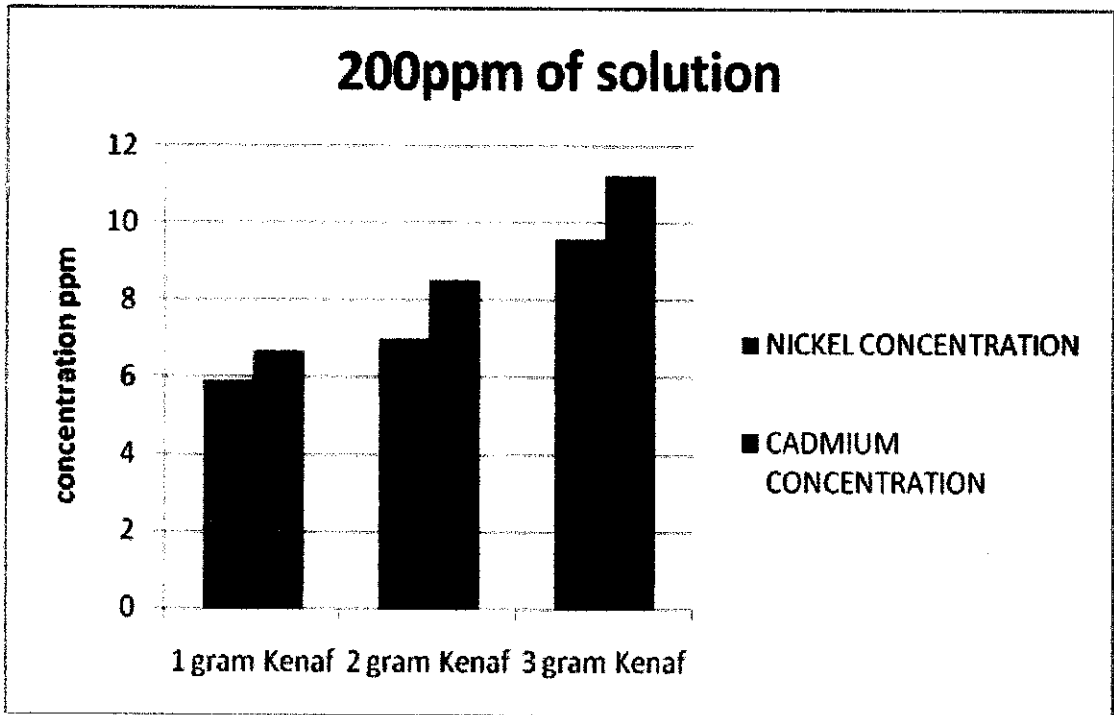


Figure 4.9: comparison between Cadmium and Nickel adsorption in 200ppm solution

#### 4.2 Previous study on Kenaf adsorption

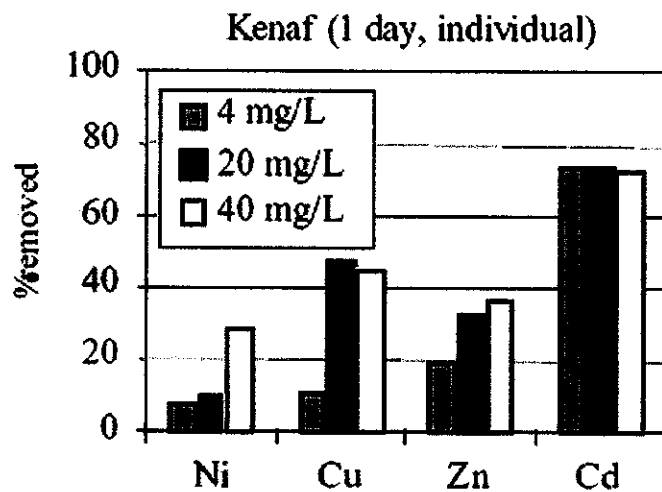


Figure 4.10: Percentage of individual ions removed.

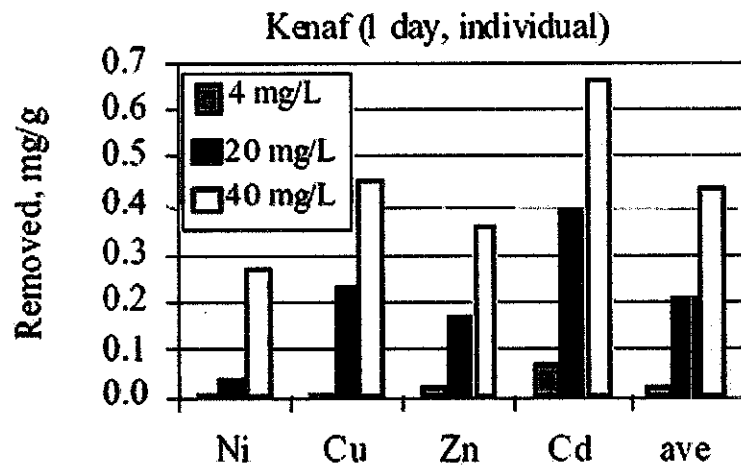


Figure 4.11: Amount of individual ions removed.



## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATION**

The adsorption of metals was analysed using AAS method. From the results obtained, it can be concluded that Kenaf fibres is a potential good adsorbent of nickel and cadmium. As the concentration of Kenaf fibres increased the more Ni and Cd ions were adsorbed and the more concentrated is the solution, the more metal ions are adsorbed. Kenaf fibres also adsorb more Cadmium ions compared to Nickel ions. Furthermore, the higher the concentration of metals, the higher the metals were adsorbed.

Various types of fibres can be used to adsorb heavy metals. Chemical modification such as acidification or sulfonation experiments on the Kenaf fibres are recommended to be carried out because from the literature review it is known that **chemical modified fibre will adsorb more heavy metals compared to untreated fibres**. In addition, regeneration of the Kenaf fibres has to be taken into consideration to lower down the operating cost and for environmental purposes.

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## APPENDICES

### Appendix 1

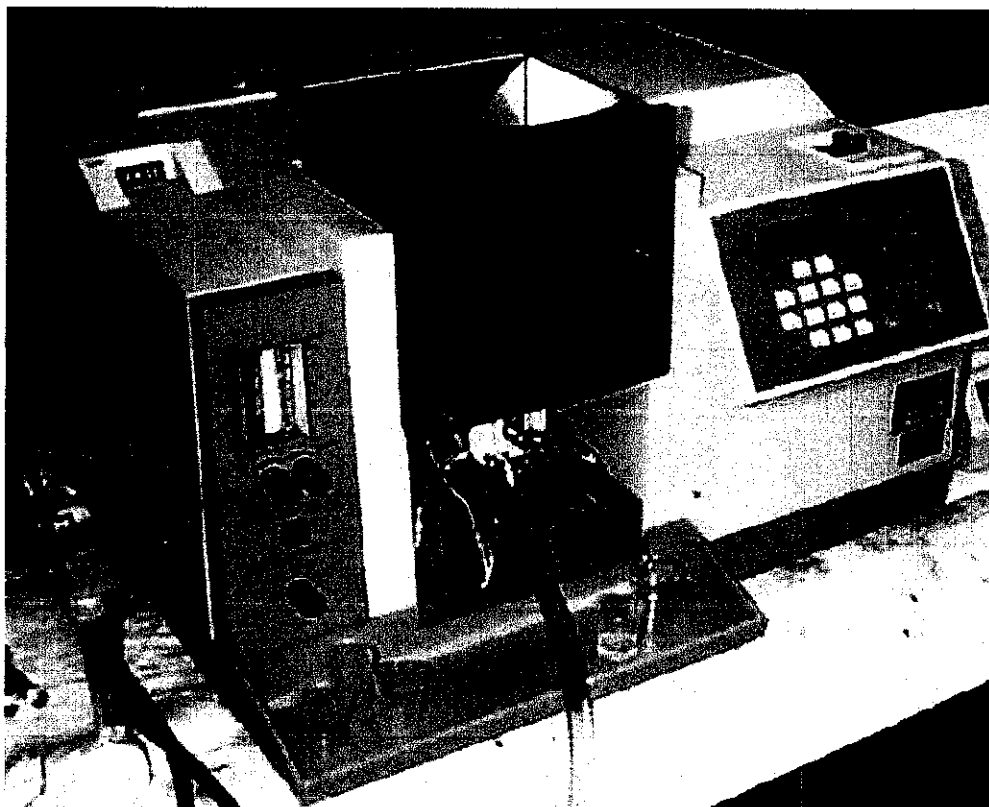


Appendix 1.1: Kenaf tree

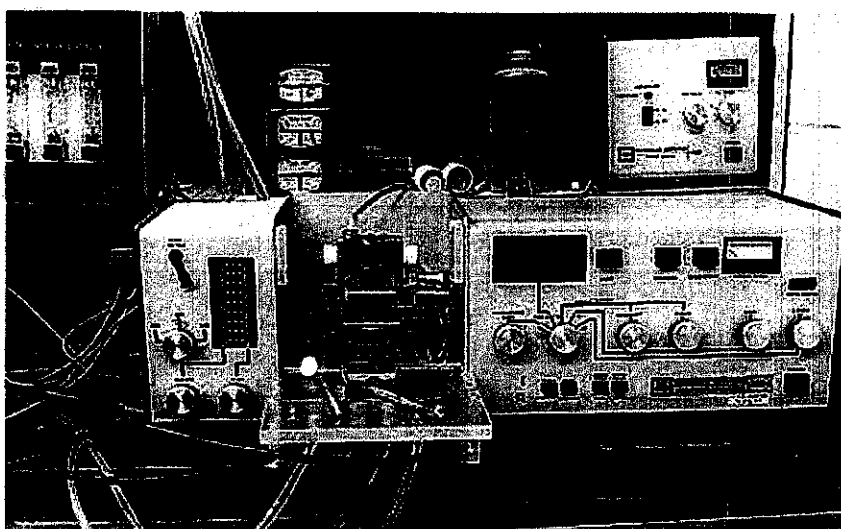


Appendix 1.2: Dried Kenaf stem

Appendix 2



Appendix 2.1: flame atomic-absorption spectrometer



Appendix 2.2: graphite-furnace atomic-absorption spectrometer