

Removal of Heavy Metals in Aqueous Solution Using Banana and Orange Peels

by

Zafira bt Abdul Rashid

(8554)

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

JANUARY 2009

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CERTIFICATION OF APPROVAL

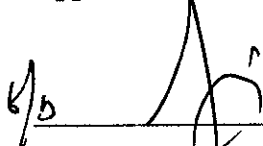
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Approved by,



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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 herein have not been undertaken or done by unspecified sources or persons.



ZAFIRA BT ABDUL RASHID

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ABSTRACT

This study compares the abilities of two low cost natural resources materials: banana and orange peel to remove Cadmium, Cd(II), Iron, Fe(III) and Nickel, Ni (II) simultaneously from aqueous solution. Kinetic studies and equilibrium sorption isotherm were measured in batch conditions. The results show that the Freundlich model gave a better fitting to the experimental data than Langmuir model within the concentration range studied. Two parameters were regulated throughout the experiment: adsorbent mass and initial solution concentration. The amount of metals uptake of both banana and orange peels was evaluated quantitatively. A high Fe(III) sorption was observed by both banana and orange peels followed by Ni(II) and Cd(II) metal ions. The adsorption capacity was found to be 3 mg/g (Fe^{3+}), 2.52 mg/g (Ni^{2+}), and 2.35 mg/g (Cd^{2+}) using banana peel sorbent and was 3 mg/g (Fe^{3+}), 2.58 mg/g (Ni^{2+}) and 2.37 mg/g (Cd^{2+}) using orange peel sorbent.

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ABBREVIATIONS AND NOMENCLATURES

Cd	= Cadmium
Fe	= Ferum/Iron
Ni	= Nickel
V	= Volume of metal-bearing solution contacted with the sorbent. [L]
C_i	= Initial concentration of the metal in the solution [mg/L]
C_f	= Equilibrium concentration of the metal in the solution [mg/L]
S	= Amount of added sorbent on dry basis. [g]
AAS	= Atomic Absorption Spectrometer
SEM	= Scanning Electron Microscopy
FT-IR	= Fourier Transform Infrared
EDX	= Energy Dispersive X-ray

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water pollution due to toxic heavy metals has been a major cause of concern for environmental engineers. The industrial and domestic wastewater is responsible for causing several damages to environment and adversely affecting people's health. There are several cases due to heavy metal contamination in aquatic environment, increase the awareness about the heavy metal toxicity such as "Minamata" tragedy due to mercury poisoning and "Itai-itai" disease in Japan due to cadmium toxicity.

Metals can be distinguished from other toxic pollutants since they are non-biodegradable and can accumulate in living tissues thus becoming concentrated throughout the food chain. A variety of industries are responsible for the release of heavy metals into the environment through their wastewater (Braukmann, 1990) which include iron and steel production, the non-ferrous metal industry, mining and mineral processing, pigment manufacture, the painting and photographic industries and metal working and finishing processes (electroplating). Moreover, considerable quantities of heavy metals can be released into the environment through the routes other than wastewater. For example, lead is widely used in metallic form and copper is used in electric equipment, water pipes, alloy as chemical catalyst and in anti fouling paints on ship hulls.

1.2 Problem Statement

1.2.1 Problem Identification

There are several methods that have been utilized to reduce the heavy metals ion content of effluent such as lime precipitation, ion exchange, Activated Carbon adsorption, membrane processing and electrolytic. However, these methods have been found to be limited due to high capital and operational costs and may be associated with the generation of secondary waste which present treatment problems such as the large

quantity of sludge generated by precipitation processes. On the other hand, ion exchange, reverse osmosis and adsorption are more attractive because the metal values can be recovered along with their removal from the effluents.

Reverse osmosis and ion exchange do not seem to be economically feasible due to their relatively high investment and operational cost. Adsorption has advantages over the other methods because of simple design with a free sludge environment and can involve low investment. Activated carbon has been recognized as a highly effective adsorbent for the removal of heavy metal ion from the concentrated and dilute metal bearing effluents (Netzer and Hughes, 1984; Reed and Arunachalam, 1994). The process however has not been used by small and medium scale industries for the treatment of their metal bearing effluents due to its high manufacturing cost.

For this reason, the use of low cost agricultural waste would be the most ideal as the alternative adsorbents since these materials are available in abundance in most countries. In this study, banana and orange peels are identified as the possible alternative adsorbents to activated carbon in order to remove traces of mixture of heavy metal ions from aqueous solution.

1.2.2 Significance of the Project

The search for new technologies involving the removal of toxic metals from wastewater 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). The major advantages of biosorption over conventional treatment methods are availability in abundant and low cost. With the completion of this project, it is hoped that it would offer another opportunity window to review the development of biosorption technology and for new discoveries toward the exploitation of this technology.

Despite the fact that there are numerous previous studies about the usage of banana and orange peels as the heavy metals adsorbents, few of them were practically done on the removal of mixture of heavy metals where in industrial scale, the presence of heavy metals in the wastewater is usually in the form of a mixture.

This study would be able to be used as the platform of a better understanding on using banana and orange peels to remove the mixture of heavy metals from the waste water. Ongoing research and development efforts are essential for improving and optimizing the effectiveness of mixture of heavy metals adsorption process by banana and orange peels.

1.3 Objectives and Scope of Study

1.3.1 Objectives

The objectives of this project are as follow:

1. To study the potential of natural adsorbent from agricultural by-product and/or domestic waste i.e. banana and orange peels in removing mixture of heavy metals from wastewater. Its performance as potential natural adsorbents will be determined from its capability of removing the heavy metals from the wastewater.
2. To conduct experimental batch tests, to determine the feasibility and characteristics of using banana and orange peels to adsorb mixture of heavy metals i.e. Cadmium-Cd(II), Iron-Fe(III) and Nickel-Ni(II) from aqueous solution. Adsorbent's mass and initial metal ion concentrations would be the variables in determining the metal uptakes by banana and orange peels in the adsorption process.
3. To prove the existence of heavy metals on the banana and orange peels adsorbents using the Scanning Electron Microscope imaging.
4. To examine the relationship between metals adsorbed and solution concentration at equilibrium using Langmuir and Freundlich isotherms.

1.3.2 Scope of Study

This project will cover the adsorption capacity of banana and orange peels towards three identified heavy metals i.e. Cadmium(Cd), Iron (Fe) and Nickel (Ni). The project would also determine the respective nature of adsorption of the metals in a competitive environment where there is a presence of another metal in the aqueous solution. This information would especially be important in the industrial scale as the presence of heavy metals in the wastewater are usually in the form of a mixture, thus creating the need to investigate the adsorption of metals in the competitive environment.

A batch adsorption test would be conducted to see if the adsorptive nature of banana and orange peels would be affected in the batch process. Moreover, the relationship between metals adsorbed and the metals ion concentration at equilibrium will be examined using most widely used sorption isotherm models of which the Langmuir and Freundlich equations.

Numerous studies have been conducted on the usage of banana and orange peels as the heavy metal adsorbents and it has been proved that both materials appeared to be useful in the removal of heavy metals in wastewater (G.Annadurai etc al.2003). However, there is lack of studies on the usage of banana and orange peels to remove the mixture of heavy metals. This is important as the presence of heavy metals in the wastewater is usually in the form of a mixture.

This study is not aimed to provide all the essential information in preparing the banana and orange peels to be the heavy metals adsorbent in the industrial scale. Instead, this study is hoped to serve as the starting platform in unlocking the potential of using banana and orange peels to remove the mixture of heavy metals in the industry. In the recommendation section that will follow later in this report, further steps that could be taken to study the adsorption capabilities of banana and orange peels in a greater detail would be presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Theory

2.1.1 Adsorption

An adsorption phenomenon is present in most natural physical, biological and chemical systems. This process of adsorption involves the separation of one substance, called adsorbate, from one phase to be accumulated or concentrated at the surface of another, called adsorbent. This is different from absorption where in the process of absorption, the solute would form a 'solution' with the absorbent.

The overall adsorption process consists of a series of steps. When the fluid is mixed together with the adsorbent particles, the solute first diffuses from the bulk fluid to the gross exterior surface of the particle. Then, the solute diffuses inside the pore to the surface of the pore. Finally, the solute is adsorbed on the surface of the adsorbent. The adsorption process would usually occur as a mono-layer on the surface of the fine pores. According to Weber (1989), four principal types of adsorption, that are exchange, physical, chemical and specific could be identified, depending upon the attractive force that exists between the adsorbate and the adsorbent. Exchange adsorption involves an electrostatic attachment of ionic species to sites of opposite charge at the surface of the adsorbent. Physical adsorption results from the effect of Van der Waals forces, which are made up from both London dispersion forces and the electrostatic forces.

Chemical adsorption involves a reaction that would occur between the adsorbate and adsorbent. This would result in a change in the chemical form of the adsorbate. The resulting chemical adsorption force is usually that derived from the physical Van der Waals forces. Lastly, the attachment of adsorbate molecules at functional groups on adsorbent surfaces can also result from specific interactions that do not result in adsorbate transformation. These specific adsorptions exhibit a range of binding energies ranging

from adsorbidity values commonly associated with physical adsorption to the higher energies associated with chemisorption.

The extent of adsorption would depend heavily by the solvophobicity or lyophobicity of the compound, that is its “dislike” for, or insolubility in the solvent phase. The greater is the insolubility of the adsorbate in the solvent, the greater is the tendency for the adsorbate to be adsorbed from the solvent onto the adsorbent. Bonding between the adsorbate and the solvent must firstly be broken in order for the adsorption process to be continued. The greater the solubility of the compound, the stronger is the bond, and hence the lower is the extent of adsorption.

Another factor that would also influence the extent of adsorption is the affinity of the adsorbate for the surface of the adsorbent. If the affinity of adsorbate to the adsorbent is stronger than the bond that exists between adsorbate and its solvent, the adsorption process would occur.

A number of parameters specific to the adsorption system will affect the adsorption process. For the adsorbate, they include concentration, molecular weight, molecular size, molecular structure, molecular polarity, steric form or configuration and the nature of background or competitive adsorbates. For the adsorbent, the most important factors that would determine the extent of adsorption process would include surface area, the physicochemical nature of the surface, the availability of that surface to adsorbate molecules and the physical size and form of the adsorbent particles. System parameters such as temperature and pH can also influence the adsorption process to the extent that they effect changes in any one or more of the parameters mentioned above (Weber, 1989, p.1-9).

2.1.2 Biosorption

It has long been recognised that many biological materials would accumulate metals. Much of the past researches emphasis have been on the investigation of the utilisation of various microorganism for metal adsorption. However, there is a growing indication that

various plant and animal materials can also be used to accumulate metals. The utilization of microorganisms as the adsorbent is generally attractive, due to the fact that it grows rapidly, is relatively inexpensive to generate and has been demonstrated to have adsorption capacities that are comparable to or can exceed various other adsorbents.

Although microbial biomass appears to be a rather inexpensive medium for the adsorption of heavy metal ions, it is also possible to utilize the specialized structures contained in higher life forms to develop selective bioadsorbents that may have even higher capacities for some metal ions. In this aspect, much attention has been given lately to the development of plant and animal tissues to be used as the adsorbent for heavy metal ions. In animal tissues, it has been recognised that certain metals would accumulate naturally into a particular animal tissue structure. For example, Strontium (Sr) tends to replace Calcium (Ca) in bones. These same types of biological materials can be used in a controlled system to selectively isolate dissolved metal ions in wastewater or other water sources (Scott and Petersen, 1996, p.85).

Biosorption have similar applications to conventional water treatment processes such as ion exchange or activated carbon. The advantages offered by biosorbents compared to other methods are the higher loading capacity at low-metal-contaminant levels. So, the biological materials could effectively treat lower concentration influents and reach a lower level of effluent concentration. Biosorbents are also more selective for transition and heavy metals, thus making it a better alternative to other adsorbents currently available to the market (Smith *et al*, 1993, p.5).

As the biomass is relatively inexpensive, it is also an option to simply dehydrate the loaded bioadsorbent and use it to isolate the metals for disposal, instead for looking for a method to perform desorption effectively. Furthermore, the volume could be reduced further via incineration, as the adsorbents are made up of organic materials. The resulting ash from the incineration process will even have higher concentrations of metal. This would bring added cost benefits for the cases where biomass is used for the adsorption process.

2.1.3 Biosorbents

The effectiveness of biosorbents depends to a large extent on their biochemical composition, particularly on functional groups available in cell wall polysaccharides. Carboxyl groups can play an important role in metal biosorption by algal biosorbents (T.A.Davis *et al*, 2003, p.4311). Pectin, a cell wall polysaccharide of higher plants, is based mainly on galacturonic acid, features a large number of carboxyl groups, and has a known ability to bind divalent cations (G.T.Grant *et al*, 1973, p.195). Therefore, pectin-rich materials such as citrus peels, from which pectin is commercially extracted, have a high potential for metal binding. A number of pectin-rich byproducts have been studied for their metal-binding abilities including apple waste (S.H.Lee *et al*, 1997), sugar beet pulp (V.M. Dronnet *et al*, 1996), orange peels (M. Ajmal *et al*, 2000), orange and banana peels (G. Annadurai *et al*, 2003), citrus peels and coffee husks (R. Jumle *et al*, 2002), and different fruit materials, such as several types of citrus peel (S. Schiewer *et al*, 2008).

2.1.4 Heavy Metals Identified for the Study

Three heavy metals have been identified as the adsorbates for the adsorption process. These metals have been selected due to their identification as heavy metals and also priority pollutants. Furthermore, these materials are also available abundantly in a typical industrial effluent. In this section, the general information of each heavy metal is discussed briefly. Furthermore, Table 2.1 shows the sources and effects of these selected heavy metals.

- **Cadmium**

Cadmium is a component of some of the lowest melting alloys; it is used in bearing alloys with low coefficients of friction and great resistance to fatigue; it is used extensively in electroplating, which accounts for about 60% of its use. It is also used in many types of solder, for standard E.M.F. cells, for Ni-Cd batteries, and as a barrier to control nuclear fission. Cadmium compounds are used in black and white television phosphors and in blue and green phosphors for color TV tubes. It forms a number of

salts, of which the sulfate is most common; the sulfide is used as a yellow pigment. Cadmium and solutions of its compounds are toxic.

- Iron

Iron is a relatively abundant element in the universe. It is found in the sun and many types of stars in considerable quantity. Its nuclei are very stable. Iron is a vital constituent of plant and animal life and works as an oxygen carrier in hemoglobin. Taconite is becoming increasingly important as a commercial ore. The pure metal is not often encountered in commerce, but is usually alloyed with carbon or other metals.

- Nickel

It is extensively used for making stainless steel and other corrosion-resistant alloys such as Invar(R), Monel(R), Inconel(R), and the Hastelloys(R). Tubing made of copper-nickel alloy is extensively used in making desalination plants for converting sea water into fresh water. Nickel is used extensively to make coins and nickel steel for armor plates and burglar-proof vaults, and is also a component in Nichrome(R), Permalloy(R), and constantan. Nickel gives glass a greenish color. Nickel plating is often used to provide a protective coating for other metals, and finely divided nickel is a catalyst for hydrogenating vegetable oils. It is also used in ceramics, in the manufacture of Alnico magnets, and in the Edison(R) storage battery.

Table 2.1: Heavy metals sources and effects

Heavy Metal	Sources	Effects
Iron	Iron pipes, welding, drinking water, iron cookware	Cancer, birth defects, constipation, heart damage, heart failure, liver disease, hepatitis, insomnia, pancreas damage, shortness of breath, bleeding gums

Nickel	Fertilizer, food processing, fuel oil combustion, industrial waste	Kidney dysfunction, anorexia, heart attack, oral cancer, nausea, hormone disruption, muscle tremors, vomiting, low blood pressure
Cadmium	Pigments and batteries manufacturing, metal-plating, plastic industries	Kidney disease, lung irritation, affect nervous and immune system

(source: http://www.alternative-doctor.com/anti-ageing/heavy_metal.html)

According to Malaysia's Environmental Quality (Sewage and Industrial Effluents) Regulation, 1979, each heavy metal need to meet certain concentration to be released into the environment. *See Appendix A.*

2.1.5 Characteristics of Banana Peel

Jamil R. Memon *et al*, (2008) have studied the characterization of banana peel by scanning electron microscopy (SEM) and FT-IR spectroscopy and its use for Cadmium removal. From the studies, the surface area of the dried banana peel was measured using the BET method and was found to be 13 m²/g. The analysis of banana peel for the determination of protein, fiber, dry matter and ash was carried out and the results are presented in Table 2.2.

Table 2.2: Composition of banana peel

Proximate Analysis	Percentage (%)
Dry Matter	90.36
Moisture	9.64

Fat	5.02
Crude Fiber	11.04
Crude Protein	10.14
Ash	18.98

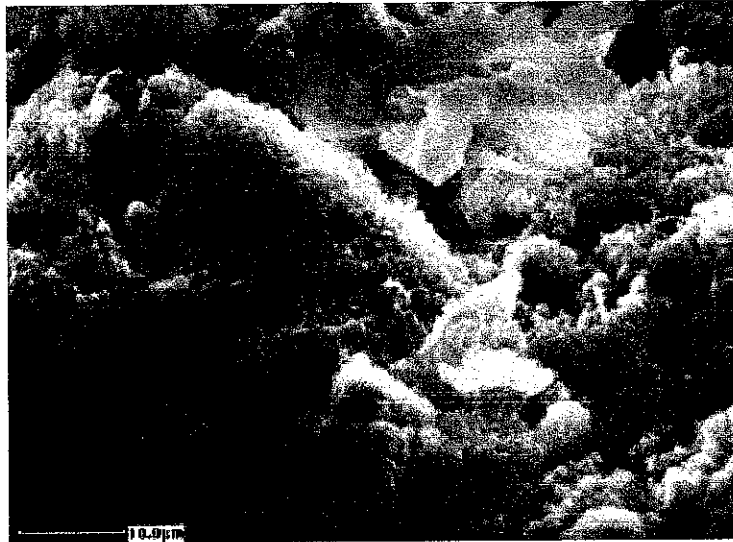


Figure 2.1: Scanning electron microscopic (SEM) analysis of banana peel
(source: <http://lib.bioinfo.pl/pmid:18760572>)

The surface morphology of banana peel was studied with the use of SEM. Figure 2.1 shows a microporous structure of banana peel at a resolution of 1500X with a particle size of 10µm. Elemental analysis was done using energy dispersive X-ray (EDX) analysis to identify the composition of banana peel.

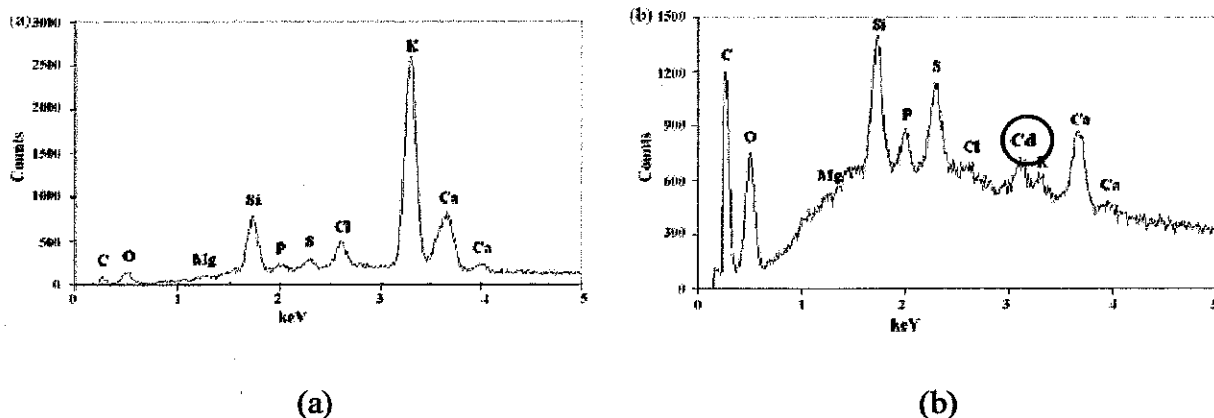


Figure 2.2: Energy dispersive X-ray (EDX) analysis of (a) unadsorbed and (b) Cd adsorbed banana peel

Figure 2.2(a) shows the EDX analysis of unadsorbed banana peel where there are presence of various elements along with a high amount of potassium(K). On the other hand, figure 2.2(b) shows EDX analysis of Cd adsorbed banana peel where there is an additional peak confirming the sorption of Cd onto the surface of the banana peel.

This study shows the potential of using banana peel as the bio-sorbent for the removal of heavy metal ions from wastewater.

2.1.6 Characteristics of Orange Peel

Orange peel is one of biomass wastes. It makes up 75% of the world total citrus fruit production. Orange peel principally consists of cellulose, hemi-cellulose, pectin, chlorophyll pigments and other low molecular weight compounds like limonene and so on. (Xiaomin Li et. al., 2006)

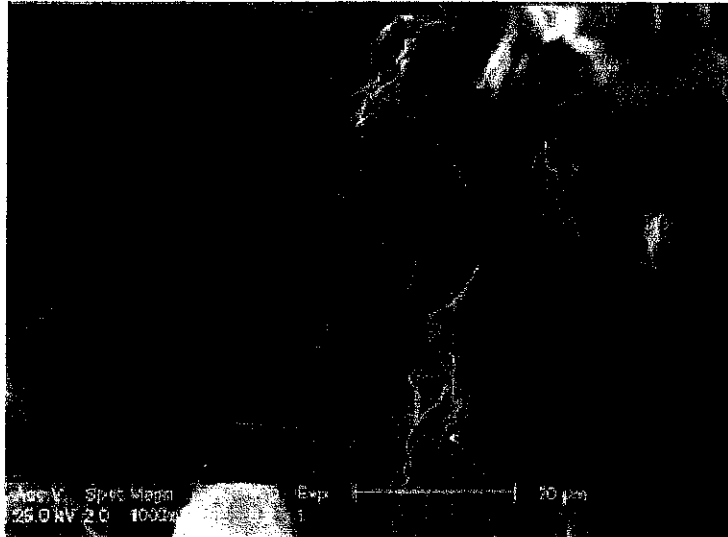


Figure 2.3: Scanning electron microscopic (SEM) analysis of orange peel

Figure 2.3 shows SEM images for orange peel from previous study. Based on the analysis, it was observed that there are highly heterogeneous pores within orange peel which has potential as bio-sorbent for the removal of heavy metals ions from wastewater.

Previous studies show that the residue of banana and orange peels can be processed and converted to be adsorbents because they have large surface areas, high swelling capacities, excellent mechanical strengths and are convenient to use and have great potential to adsorb harmful contaminants such as heavy metals.

2.2 Literature Reviews

There were many literatures found about the utilization of agricultural waste materials as the adsorbents for heavy metals. *See Appendix B for a list of adsorption capacity of agricultural waste as heavy metals adsorbents.* Some previous studies also have been done on banana and orange peels as the heavy metals adsorbent.

H. Benaïssa (2008) compares the abilities of four low-cost materials: eucalyptus bark, maize leaves, grape bunch and banana peel to remove cadmium from synthetic aqueous solutions. This study measures the kinetic data and equilibrium sorption isotherms in batch conditions. The kinetics of cadmium sorption was contact time, initial cadmium concentration and sorbent type dependent. The results showed that the kinetics of cadmium sorption was described by a pseudo-second order rate model. The cadmium uptake of these low-cost materials was quantitatively evaluated using sorption isotherms. The results indicated that the Langmuir model gave a better/an acceptable fit to the experimental data than the Freundlich equation within the concentration range studied. A high cadmium sorption was observed by these materials. From the results, they have concluded that eucalyptus bark was the most effective to remove cadmium ions with a maximum sorption capacity about 99.50 mg/g followed by grape bunch (75.59 mg/g), banana peel (69.44 mg/g) and maize leaves (57.84 mg/g).

N.A. Adesola *et al* (2008) studied the Isotherm and Thermodynamic of the Biosorption of Zinc (II) from Solution by Maize Leaf. They investigated the removal of Zn(II) ions from dilute aqueous solution using maize (*Zea mays*) leaf as the adsorbent. The effects of pH, contact time, and initial metal ion concentrations were studied at 27°C. The analysis of residual metal ions was determined using atomic absorption spectrophotometer. The optimum pH obtained was in the range pH 4-7. Kinetic studies show that the uptake of zinc ions increases with time and that maximum adsorption was obtained within the first 40 minutes of the biosorption process. The adsorption isotherms obtained at 27°C and optimum pH fitted well into both the Freundlich and Langmuir isotherms. The Freundlich and Langmuir equations are $\log \Gamma = 1.7833 \log C_e + 0.1316$ and $1/\Gamma = 0.0423/C_e - 0.3565$, respectively. The correlation factors are 0.9964 and 0.9974, respectively. The free energy change for the biosorption of Zn(II) at 27°C, initial concentration of 100 mg/L and pH 4-7 is $-5.4525 \text{ kJ mol}^{-1}$. From the studies, they have concluded that maize leaf has potential for the removal of zinc ions from industrial wastewater.

G. Annadurai *et al* (2002) have investigated the adsorption capacity of Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Pb^{2+} separately using banana and orange peels. The liquid phase adsorption removal was done in the concentration range of 5-25ppm at 30°C. They have determined that under comparable conditions, the amount of adsorption decreased in the order $\text{Pb}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+}$ for both adsorbents. From the studies, they have also determined the adsorption isotherm could be better described by the Freundlich equation and the amount of adsorption increased with increasing pH and reached plateau at $\text{pH} > 7$. Their studies results in metal uptake up to 7.97 mg/g of Pb^{2+} of banana peel at $\text{pH} 5.5$.

Apart from these researchers, there were many more that have investigated on the utilisation of various agricultural waste materials for the adsorption of heavy metals from wastewater or aqueous solution. For example, Xiaomin Li *et al.*, 2007, Donghee Park *et al.*, 2008 and Saifuddin M. Nomanbhay *et al.*, 2005, have all shown that numerous agricultural wastes has the ability to adsorb heavy metals from aqueous solution.

CHAPTER 3

METHODOLOGY

3.1 Materials Preparation

3.1.1 Banana and Orange Peels Adsorbents

1. The banana and orange peels were collected from self consumption. The collected materials were processed separately but follow the same procedure.
2. The banana and orange peels were cut into small pieces (1-5 mm), dried and washed thoroughly with double distilled water to remove the adhering dirt.
3. The materials were then air dried in an oven at 100°C for 24 hours.
4. Dried banana and orange peels then were grounded using blender.
5. The peels then were sieved (250 μm) using vibratory sieve shaker before being stored separately in plastic bottle for further use.

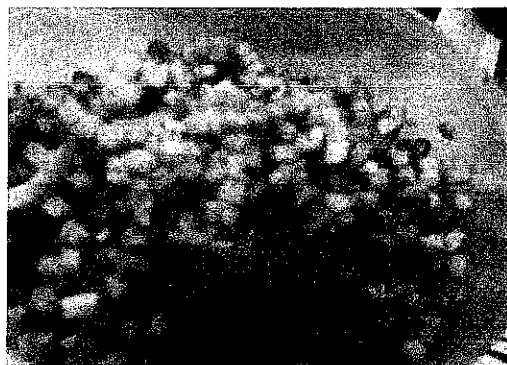
The process is illustrated in Figure 3.1.

3.1.2 Heavy Metals Solution

1. The heavy metal solutions were prepared separately from 1000 ppm standard solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ respectively.
2. Each metal solutions were prepared according to the concentration required (50, 40, 30, 20 and 10 ppm) and mixed together to get the mixture of heavy metals solution.



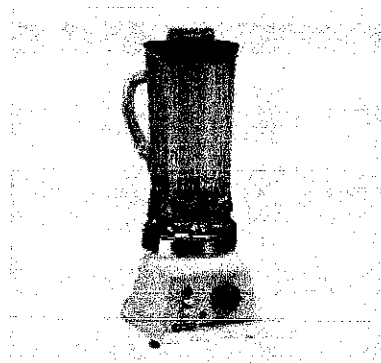
(a) Cut adsorbents into small pieces.



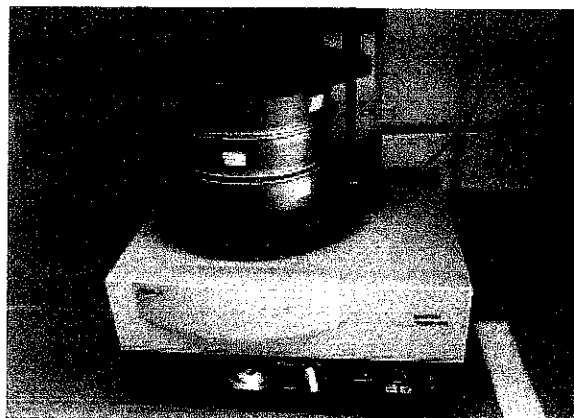
(b) Banana Peel (1-5mm)



(c) Dry adsorbents in the oven at 100°C for 24h.

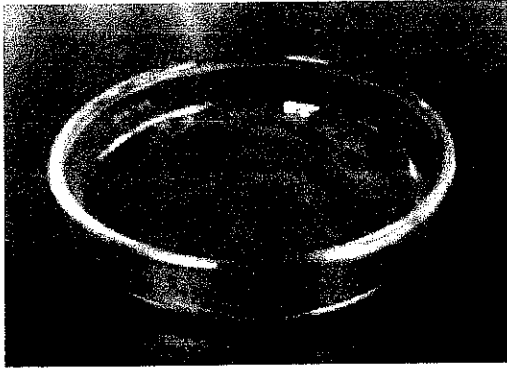


(d) Grind the adsorbents



(e) Sieve adsorbents using Vibratory Sieve Shaker

Figure 3.1: Preparation of Adsorbents



(a)



(b)

Figure 3.2: Sieved Adsorbents (250 μ m) (a) Banana Peel and (b) Orange Peel

3.2 Experimental Procedure

3.2.1 Metal Uptake Capacity

The metal uptake capacity of banana and orange peels can be evaluated using the formula (Volesky, 1999, p.136):

$$\text{Metal uptake, } q = V[L] \times \frac{(C_i - C_f)[\text{mg} / L]}{S[\text{g}]} \quad (1)$$

Where,

- V = Volume of metal-bearing solution contacted with the sorbent.
- C_i & C_f = Initial and equilibrium concentration of the metal in the solution.
- S = Amount of added sorbent on dry basis.

The metal uptake could also be analysed by calculating the metal uptake rate as defined by the equation,

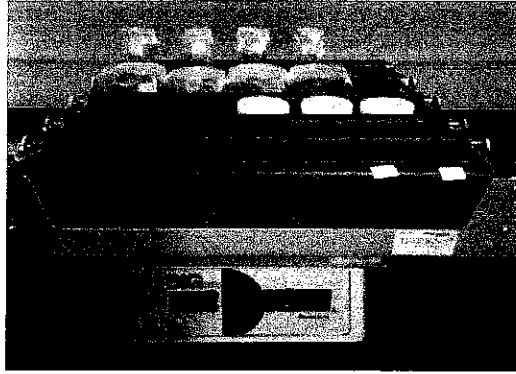
$$\text{Percentage adsorbed} = \frac{C_i - C_f}{C_i} \times 100\% \quad (2)$$

3.2.2 Uptake Kinetics

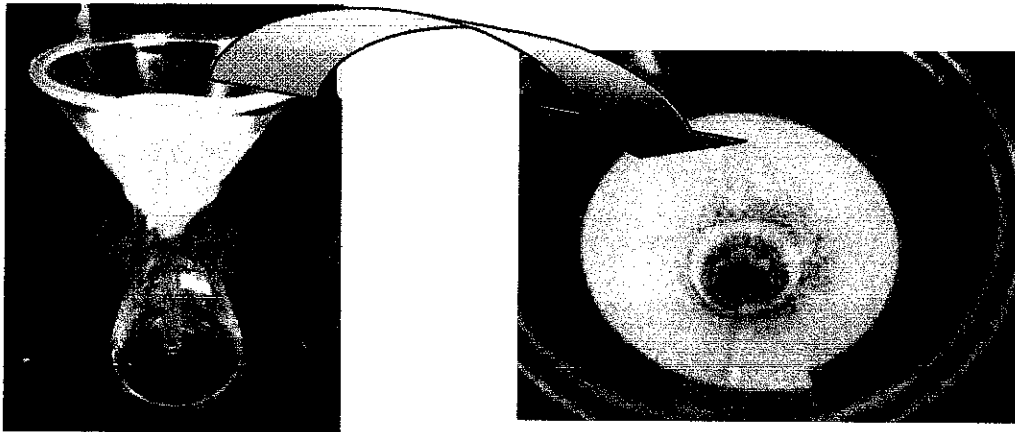
There are two variable parameters for metals removal kinetic studies: Adsorbent Mass and Initial Solution Concentration. The metal uptakes q (mg metal ion/g dried sorbent) was determined as the difference between the initial and time concentrations of metals in aqueous solution.

3.2.2.1 Effects of Adsorbents Mass

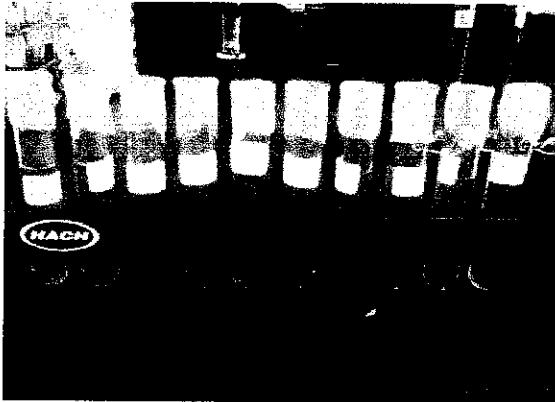
1. 50ppm of 150ml heavy metals ion solutions were poured into each of a series of Erlenmeyer flasks containing 2g, 1g, 0.5g and 0.1g of banana peel adsorbents. An additional flask was used as a control solution, where the solution did not contain any adsorbent.
2. The flasks then were agitated using the rotary shaker at 160rpm for 7 hr.
3. After 1hr, the shaker was stopped for a while to let the adsorbents settled at the bottom of the flasks. Then, 10ml of solution sample was taken from each flask and filtered using filter paper to remove the remaining adsorbents which then were placed back into the flasks. This is to maintain the amount of adsorbents throughout the experiment. The adsorption process was then continued.
4. Step 3 was repeated after 3hr, 5hr and 7hr.
5. The metal ions concentrations in the filtered samples were determined using Atomic Absorption Spectrometry (AAS).
6. From the concentration data obtained from AAS, the plots of metal uptake (calculated using Equation 1 and 2) against time for each of the adsorbent mass were prepared.
7. Throughout the experiment, the pH of the solution was maintained at 6 and temperature at $25 \pm 1^\circ\text{C}$.
8. The experiment was repeated using orange peel adsorbent.



(a) Adsorption Process using Rotary Shaker



(b) Filtration Process



(c) Samples Taken



(d) Analyzing Sample using AAS

Figure 3.3: Experimental Procedure

3.2.2.2 Effects of Metal Ions Concentrations

1. 40ppm, 30ppm, 20ppm and 10ppm of heavy metals ion solutions were poured into a series of Erlenmeyer flasks containing 2g of banana peel adsorbent respectively.
2. The flasks then were agitated using the rotary shaker at 160rpm for 7 hr.
3. After 1hr, the shaker was stopped for a while to let the adsorbents settled at the bottom of the flasks. Then, 10ml of solution sample was taken from each flask and filtered using filter paper to remove the remaining adsorbents which then were placed back into the flasks. This is to maintain the amount of adsorbents throughout the experiment. The adsorption process then continued.
4. Step 3 was repeated after 3hr, 5hr and 7hr.
5. The metal ions concentrations in the samples were determined using Atomic Absorption Spectrometry (AAS).
6. From the concentration data obtained from AAS, the plots of metal uptake (calculated using Equation 1 and 2) against time for each of the adsorbent mass were prepared.
7. Throughout the experiment, the pH of the solution was maintained at 6 and temperature at $25\pm 1^{\circ}\text{C}$.
8. The experiment was repeated using orange peel adsorbent.

3.2.3 Uptake Isotherms

The equilibrium isotherms were determined by contacting a constant mass 2g of sorbent material with a range of different concentrations of heavy metals solution: 10-50 ppm. The mixtures were agitated in a series of beakers with equal volumes of solution 50ml for a period of 24 hours at room temperature $25\pm 1^{\circ}\text{C}$. The reaction pH was not controlled through out the experiments. The equilibrium concentration of each metal was obtained using AAS and the metals loading by sorbent materials were calculated.

3.3 Tools

3.3.1 Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometry (AAS) is the main equipment used in this study. It is used to determine the concentration of the identified metal ion in a particular solution. The AAS can be used to analyze the concentration of over 62 different metals in a solution. The AAS instrument measures the concentration of metals in the sample at typical concentration range in the low mg/L range.

In their elemental form, metals will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular metal by focusing a beam of UV light at a specific wavelength through a flame and into a detector. The sample of interest is aspirated into the flame. If that metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity. A computer data system converts the change in intensity into an absorbance.

In this study, the AAS will determine the concentration of the Nickel (Ni), Iron (Fe) and Cadmium (Cd) remained in the solution. The solution samples were collected after 1hr, 3hr, 5hr and 7hr of the adsorption process. Apart from AAS, other experimental apparatus are also required for this study. They are mainly the normal apparatus needed for jar tests such as Erlenmeyer flask, beaker, measuring cylinder, shaker and others.



Figure 3.4: Atomic Absorption Spectrometry (AAS)

3.3.2 Scanning Electron Microscope (SEM)

The scanning electron Microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

SEM can produce very high resolution images of a sample surface, revealing details about 1 to 5 nm in size. Due to the way these images are created, SEM micrographs have a very large depth of field yielding a characteristic three dimensional appearance useful for understanding the surface structure of a sample.

In this research, the SEM was used to produce a high resolution image of the banana and orange peels before and after the heavy metals adsorption process in order to prove the existence of heavy metals on the peels surface.

CHAPTER 4

RESULTS AND DISCUSSION

All the results obtained from the experiments are tabulated in Appendices C and D. After the calculations using Equations 1 and 2, all the results are illustrated in Figure 4.1 to 4.10.

In this section, the findings are explained generally based on the trends that can be observed. The findings are also arranged according to the type of experiments done, i.e. the effects of adsorbent mass, the effects of initial solution concentration and equilibrium sorption. These trends are explained in greater details, offering the possible reasons and explanations to the trends observed. It is important to note that the banana and orange peels adsorbents were not prepared in any special way and the results found from this study could be used as the base performance of banana and orange peels in adsorbing heavy metals mixture.

4.1 Uptake Kinetic of Metals

4.1.1 Effects of Adsorbent Mass

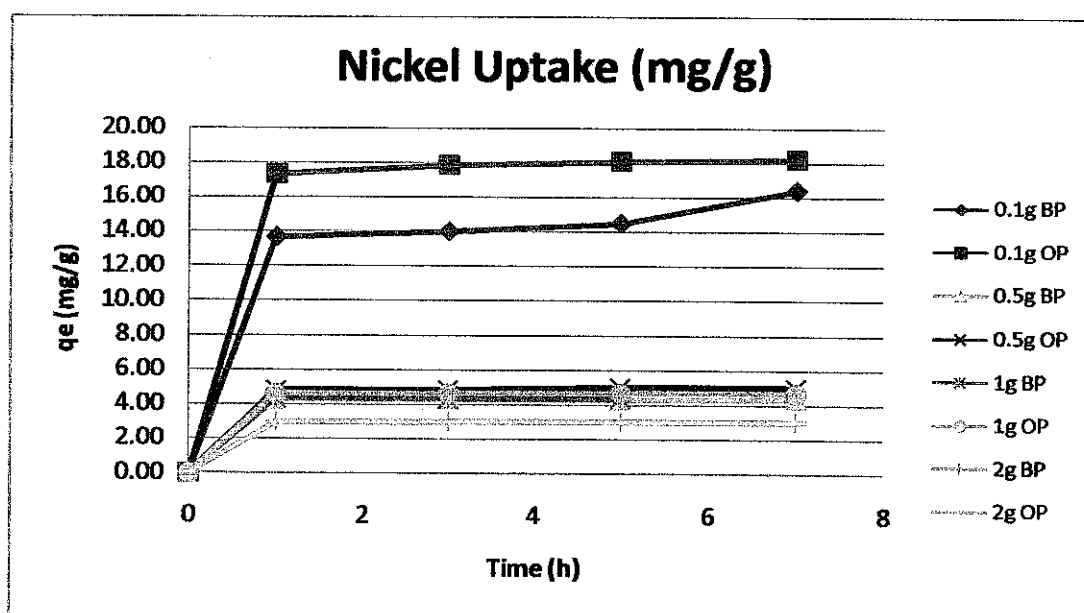


Figure 4.1: Metal Uptake vs. Time for Ni(II)

Figure 4.1 shows the Ni(II) metal uptake by both banana and orange peels. The trend shows that metal uptake is increasing with adsorption time and amount of sorbents. The highest Ni(II) uptake was 18.23mg/g using 0.1g orange peel sorbent. The least was 3.01mg/g adsorbed by 2g of banana peel sorbent.

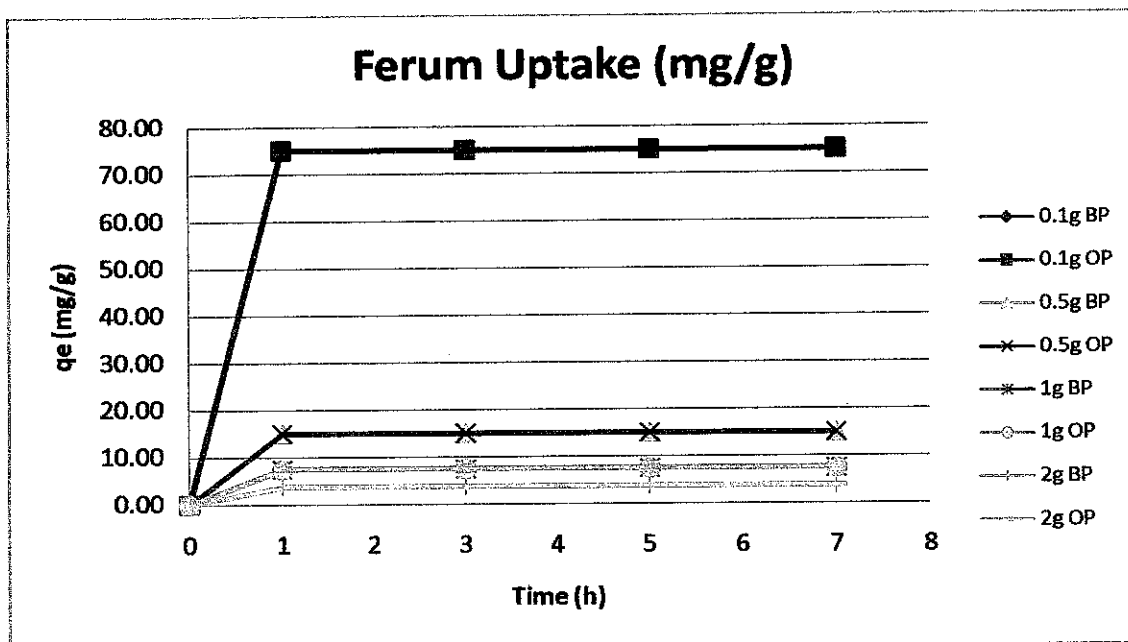


Figure 4.2: Metal Uptake vs. Time for Fe(III)

Figure 4.2 shows the Fe(III) metal uptake by both banana and orange peels. The trend shows that metal uptake is increasing with adsorption time and amount of adsorbent used. Both banana and orange sorbents show the same amount of Fe(III) uptake by each adsorbent mass (75mg/g using 0.1g sorbent; 15mg/g using 0.5g sorbent; 7.5mg/g using 1g sorbent; 3.75mg/g using 2g sorbent) This is due to 100 percent of Fe(III) ion was removed/adsorbed by both sorbents.

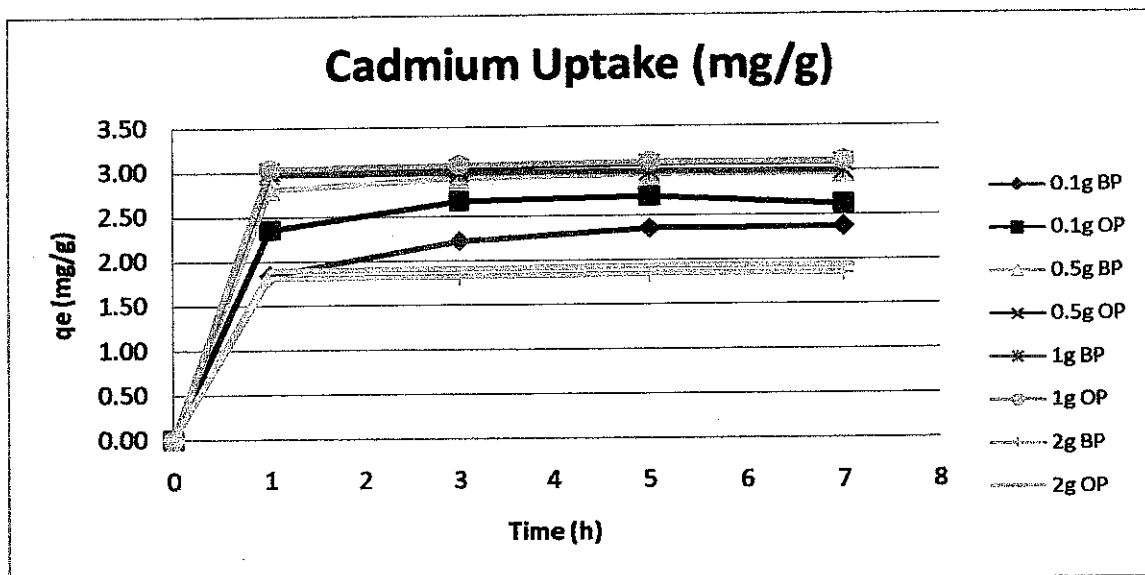


Figure 4.3: Metal Uptake vs. Time for Cd(II)

Figure 4.3 shows the Cd(II) metal uptake by both banana and orange peels. The trend shows that metal uptake is increasing with adsorption time and the amount of adsorbent used. The highest Cd(II) uptake was recorded by 1g of orange peel sorbent which is 3.11mg/g. The least was 1.85mg/g adsorbed by 2g of banana peel.

According to Figures 4.1, 4.2 and 4.3, the kinetics of heavy metals removal by both sorbent materials used present a similar shape characterized by a strong increase in metals sorption initially followed by a slow increase until equilibrium is reached. Overall, the necessary time to reach this equilibrium is about 1h for both sorbents. Furthermore, an increase of removal time to 7h does not show notable affects.

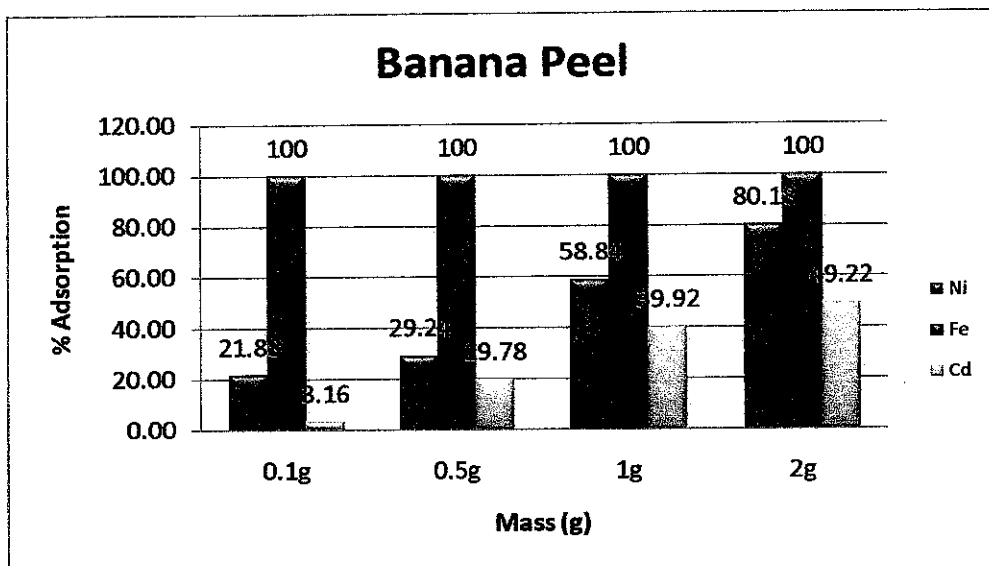


Figure 4.4: Percentage Adsorption vs. Adsorbent Mass for Banana Peel

Figure 4.4 shows the percentage adsorption against adsorbent mass for banana peel. The amount of percentage adsorption is increasing with the adsorbent mass with the highest was 100% for Fe(III) followed by Cd(II) with 80.18% and Ni(II) with 49.22%. On the other hand, the least percentage adsorption can be seen for the lowest amount of sorbent, 0.1g for each metal, except for Fe(III).

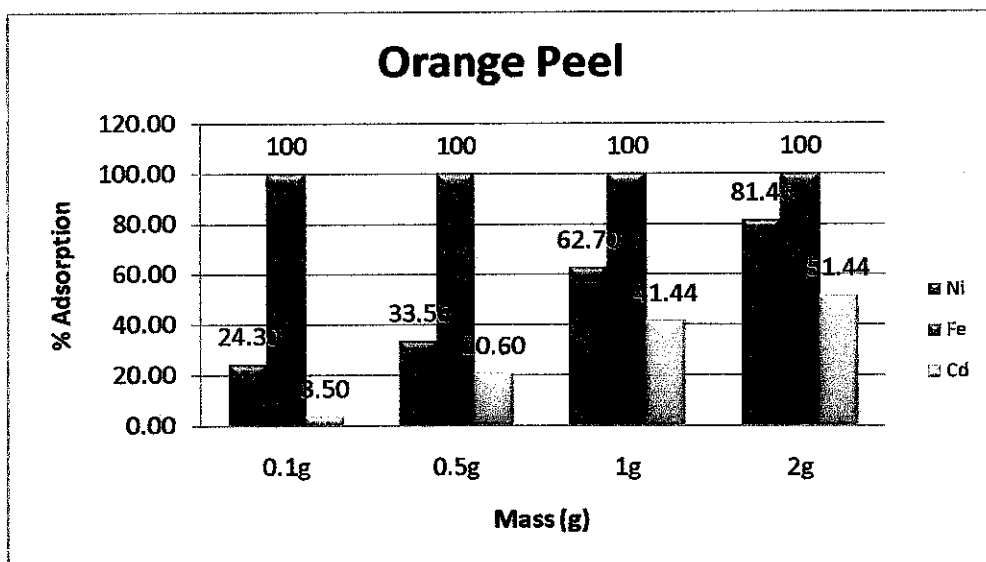


Figure 4.5: Percentage Adsorption vs. Adsorbent Mass for Orange Peel

Figure 4.5 shows the percentage adsorption against adsorbent mass for orange peel. The amount of percentage adsorption is increasing with the adsorbent mass with the highest was 100% for Fe(III) followed by Ni(II) with 81.46% and Cd(II) with 51.44% using 2g of sorbent. Same goes with banana peel sorbent, the least percentage adsorption obtained using the least amount of sorbent, 0.1 g for each metal.

From the trends observed from the plots at Figures 4.1 to 4.5, it can be seen that for each of the metals, that by increasing the amount of adsorbent mass, the metal uptake were decrease and percentage of ions adsorbed were increased. This is due to the larger surface area provided for the metal ions to be bounded. As the amount of adsorbent increased, the amount of metal ions that surround a particular unit of adsorbent would also increase. Thus, this would result in a greater extent of adsorption.

4.1.2 Effects of Initial Solution Concentration

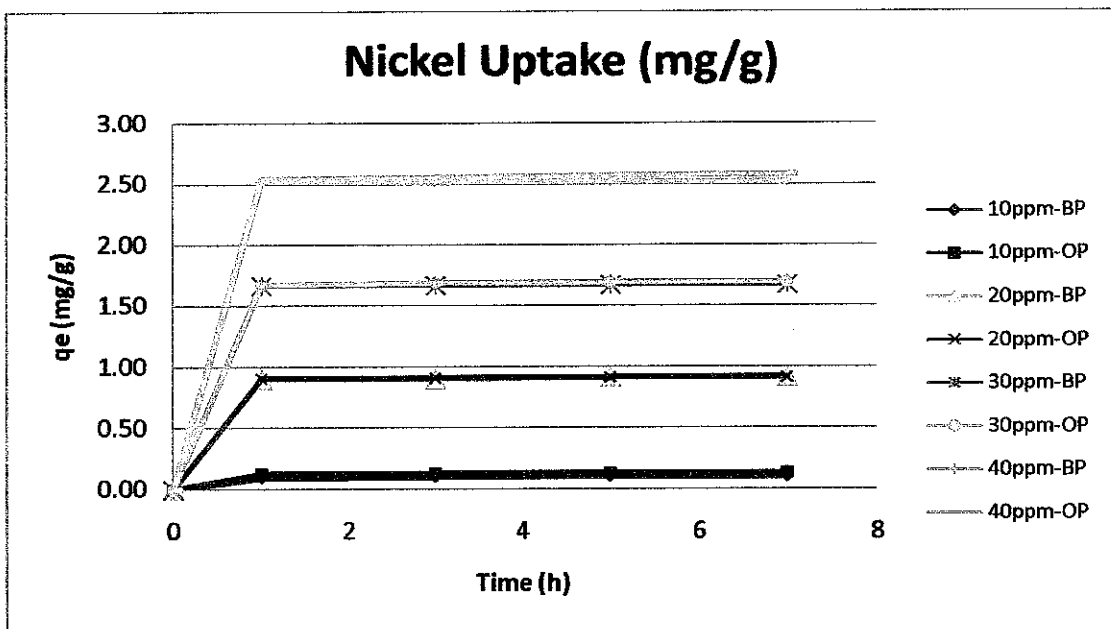


Figure 4.6: Metal Uptake vs. Time for Ni(II) at Different Concentrations

Figure 4.6 shows the fraction of Ni(II) adsorbed against time at different initial solution concentration. The amount of Ni(II) adsorbed was highest on orange peel sorbent (2.58mg/g) followed by banana peel sorbent (2.52mg/g) at 40ppm. The least metal uptakes were obtained by both sorbents at 10ppm initial solution concentration.

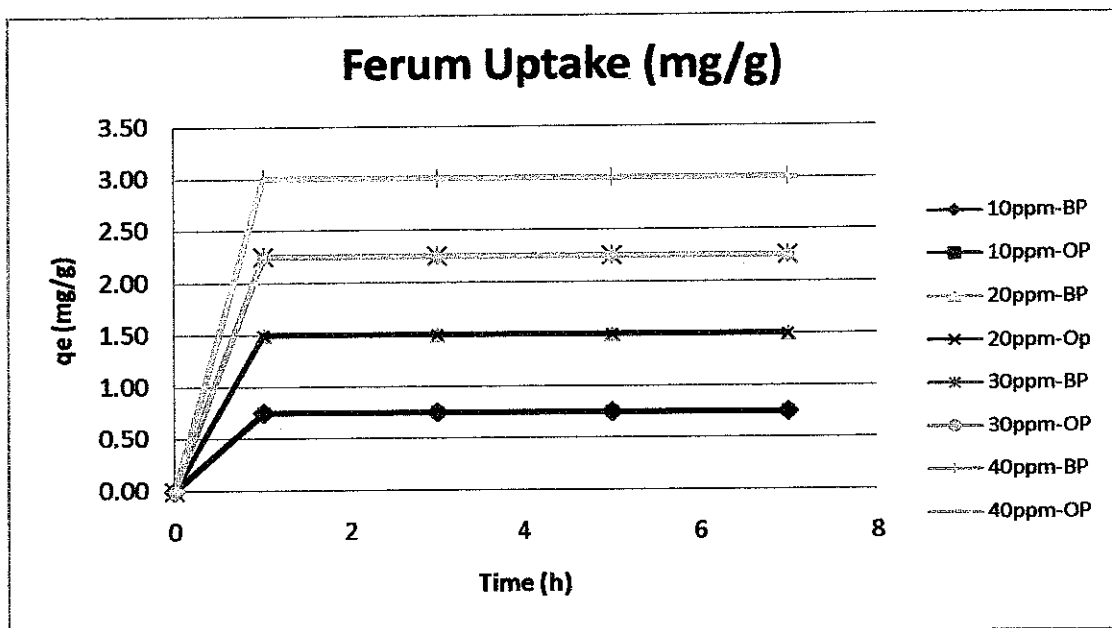


Figure 4.7: Metal Uptake vs. Time for Fe(III) at Different Concentrations

Figure 4.6 shows the fraction of Fe(III) adsorbed against time at different initial solution concentrations. Both banana and orange sorbents show the same amount of Fe(III) ion adsorbed at each initial solution concentration (3mg/g at 40ppm; 2.25mg/g at 30ppm; 1.5mg/g at 20ppm; 0.75mg/g at 10ppm). This is due to 100 percent of Fe(III) ion was removed/adsorbed by both sorbents.

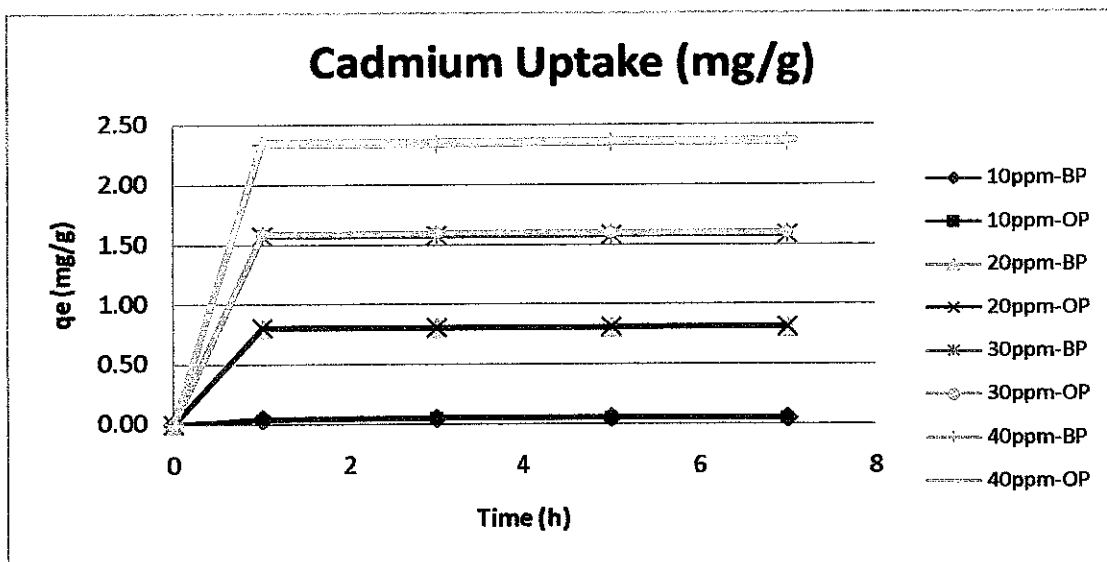


Figure 4.8: Metal Uptake vs. Time for Cd(II) at Different Concentrations

Figure 4.8 shows the fraction of Cd(II) adsorbed against time at different initial solution concentration. The amount of Cd(II) adsorbed on both sorbents was almost similar with the highest amount at 40ppm: 2.35 mg/g by banana peel and 2.37 mg/g by orange peel. The same trend can be seen at each initial solution concentration.

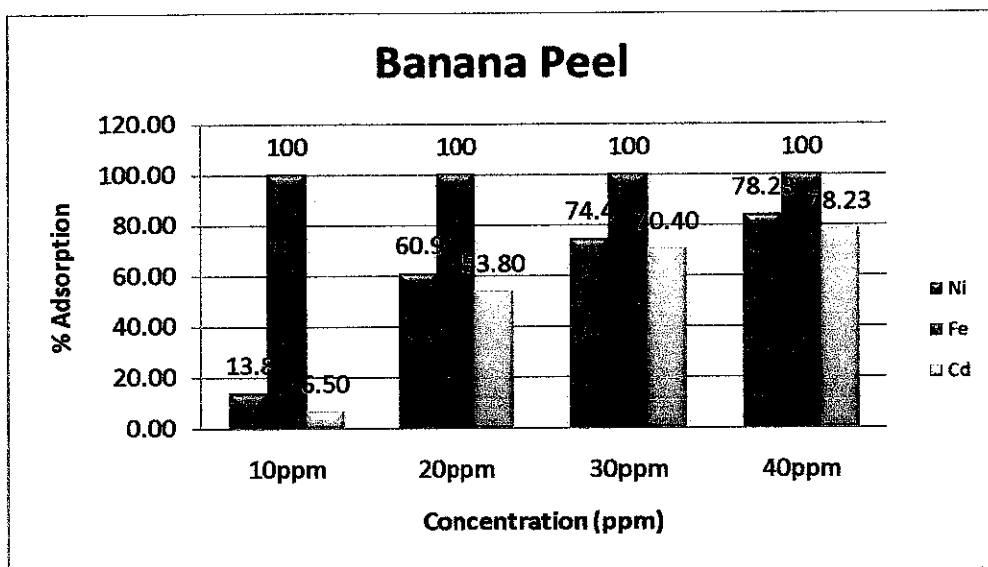


Figure 4.9: Percentage Adsorption vs. Concentration for Banana Peel

Figure 4.9 shows the percentage adsorption against initial solution concentration for banana peel. The amount of percentage adsorption is the highest (100%) for Fe(III) ion at each initial solution concentration. Ni(II) was absorbed the most at 40ppm with 78.23%. It also can be seen that the amount of Cd(II) ion adsorbed was the highest at 40ppm with 78.23%.

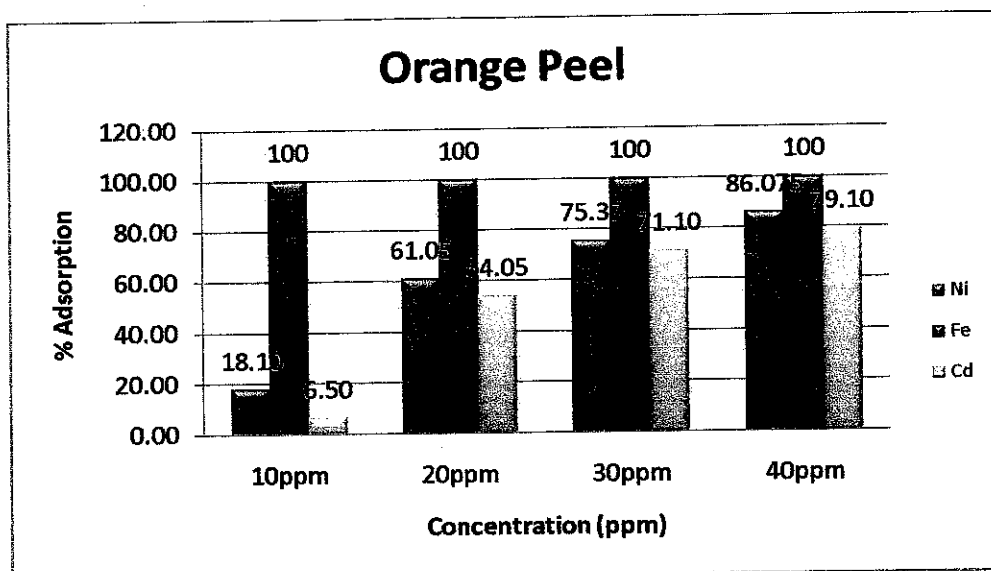


Figure 4.10: Percentage Adsorption vs. Concentration for Orange Peel

Figure 4.10 shows the percentage adsorption against initial solution concentration for orange peel. Again, the amount of percentage adsorption is the highest (100%) for Fe(III) ion at each initial solution concentration. The amount of Ni(II) ion adsorbed was increasing with initial solution concentration with the highest was 84% at 40ppm. Same goes with Cd(II) ion which was adsorbed the most at 40ppm with 79.10%.

From the trends observed from the plots at Figures 4.6, 4.7 and 4.8, it can be seen that for each of the metals, that by increasing the initial metal concentration, the metal uptakes and percentage of ions adsorbed would increase. This is a result of the increase in the driving force of the concentration gradient, as an increase in the initial metal ions concentrations (Ozer, A *et al*, 2004). As the initial solution concentration is increased, the amount of metal ions that surround a particular unit of adsorbent would also increase. Hence, this would result in a greater extent of adsorption.

In all three metals, orange peel gave the highest adsorption capacity for both Cd(II) and Ni(II) metal ions compared to banana peel as illustrated in Figures 4.9 and 4.10. On the other hand, both sorbents gave 100 percent adsorption capacity for Fe(III) metal ion. It means generally, the trend of the sorption is $Fe^{3+} > Ni^{2+} > Cd^{2+}$.

The trend could be explained based on the modes of adsorption on cellulosic materials. The adsorption of metal ions on cellulosic materials could be attributed to two main terms; intrinsic adsorption and columbic interaction (Sun and Shi, 1998). The columbic term results from the electrostatic energy between the adsorbents and the adsorbates. The charges on both substrates as well as softness and hardness of charge on both sides are mostly responsible for the intensity of the interaction. Columbic interaction can be observed from adsorption of cationic species versus anionic species on adsorbents (Sun and Shi, 1998).

According to Igwe, and Abia, 2007, the intrinsic adsorption of the materials is determined by their surface areas, which can be observed by the effect of different sizes of adsorbents. Both factors also could interact that is the micro porous adsorption and surface adsorption takes place at the same time.

All these results show that the amounts of the metal ions bound by the banana and orange peel sorbents depend on the metal ion type, amount of adsorbent used and the initial concentration of the metal ion solution.

The differences in the uptake level of the metal ions also can be explained in terms of difference in the ionic sizes of the metal ions (Igwe and Abia, 2003).

The ionic radii of the metal ions are:

- Cd^{2+} (0.97Å)
- Ni^{2+} (0.83 Å)
- Fe^{3+} (0.738 Å)

The smaller the ionic diameters, the higher the adsorption rate (*Uzun and Guzel, 2000*). From this study, Fe(III) ion which has the smallest ionic radius had the highest adsorption capacity. This is followed by Ni(II) and then Cd(II), against the trend of ionic radius.

4.2 Uptake Isotherms

There are few models available to describe sorption isotherms of ions from metal solutions. The utilization of a model has value in comparing different biomaterials under different operating conditions and rests solely on the adequacy between the observed experimental tendencies and the shape of the mathematical laws associated to this model (H.Benaissa, 2008). Among the models, the Langmuir and Freundlich sorption models are commonly used to fit experimental data when solute uptake occurs by monolayer sorption. They can provide information on metal uptake capacities and differences in metal uptake between various species. These models were tested in this study.

4.2.1 Langmuir Isotherm

The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir model takes the form:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

which may be linearized as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$$

where:

q_e = the amount of metal ion adsorbed at equilibrium per g of sorbent (mg/g)

C_e = equilibrium concentration of metal ion in the solution (mg/L)

K_L = Langmuir model constant (related to affinity of binding sites)

q_m = Langmuir model constant

Therefore, a plot of (C_e/q_e) versus C_e gives a straight line of slope $1/q_m$ and intercept $1/K_L q_m$. The q_m values provide a measure of maximum sorption capacity, q_{max} in such a system. The maximum sorption capacity is a useful criterion in assessing which of the two peels adsorbent materials has the greatest uptake. Figures 4.11 and 4.12 show the Langmuir isotherms for both banana and orange peel sorbents.

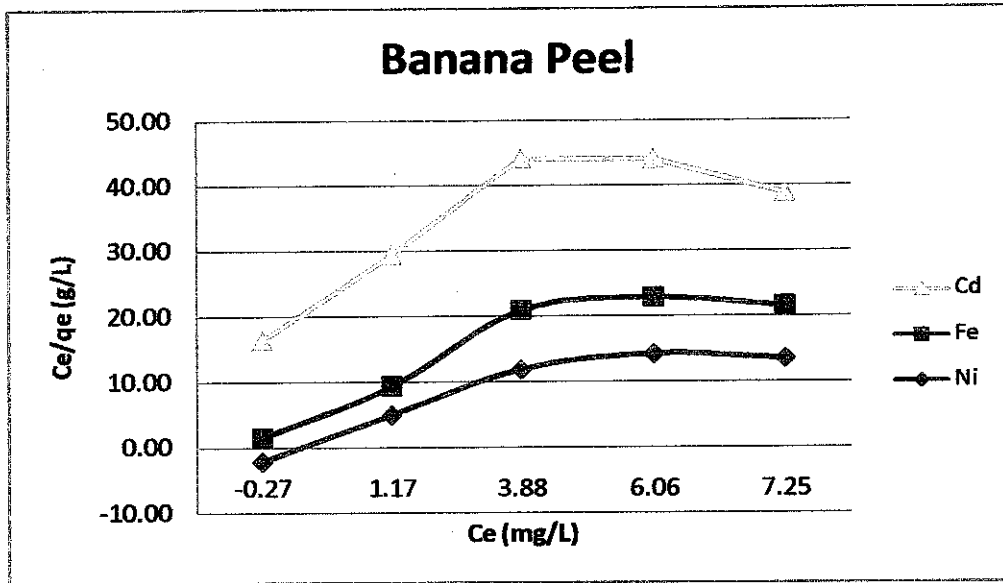


Figure 4.11: Langmuir Isotherm of Cd(II), Fe(III) and Ni(II) by banana peel sorbent.

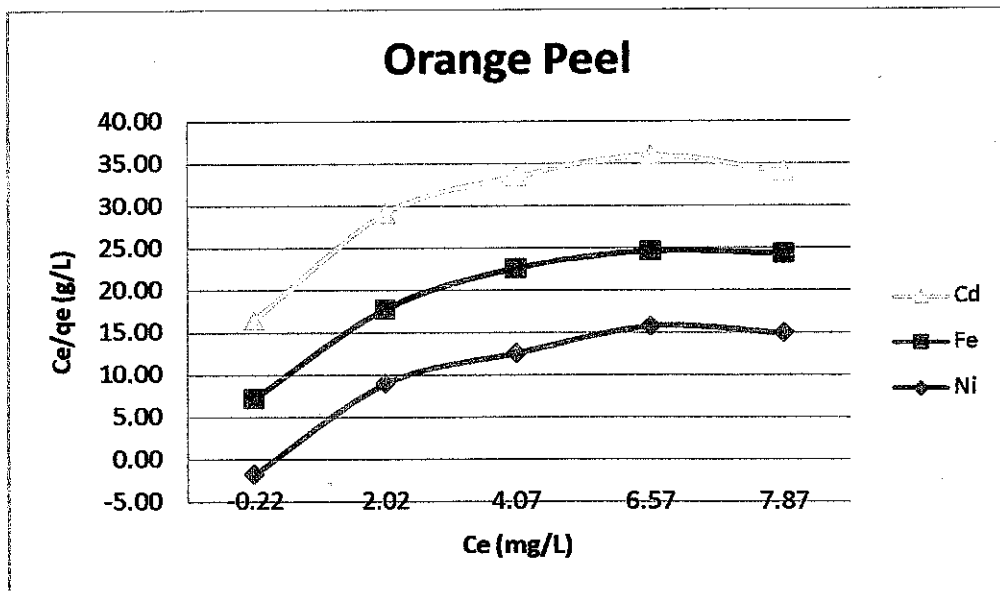


Figure 4.12: Langmuir Isotherm of Cd(II), Fe(III) and Ni(II) by orange peel sorbent.

4.2.2 Freundlich Isotherm

The Freundlich model is an empirical equation based on adsorption on a heterogenous surface. The equation is commonly represented by:

$$q_e = K_F C_e^n$$

which may be linearized as follow:

$$\ln q_e = \ln K_F + n \ln C_e$$

which:

q_e = the amount of metal ion adsorbed at equilibrium per g of sorbent (mg/g)

K_F = Freundlich model constant

n = Freundlich model constant

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ enables the constants n and K_F to be determined. Figure 4.13 and 4.14 show Freundlich isotherm for both banana and orange peel sorbents.

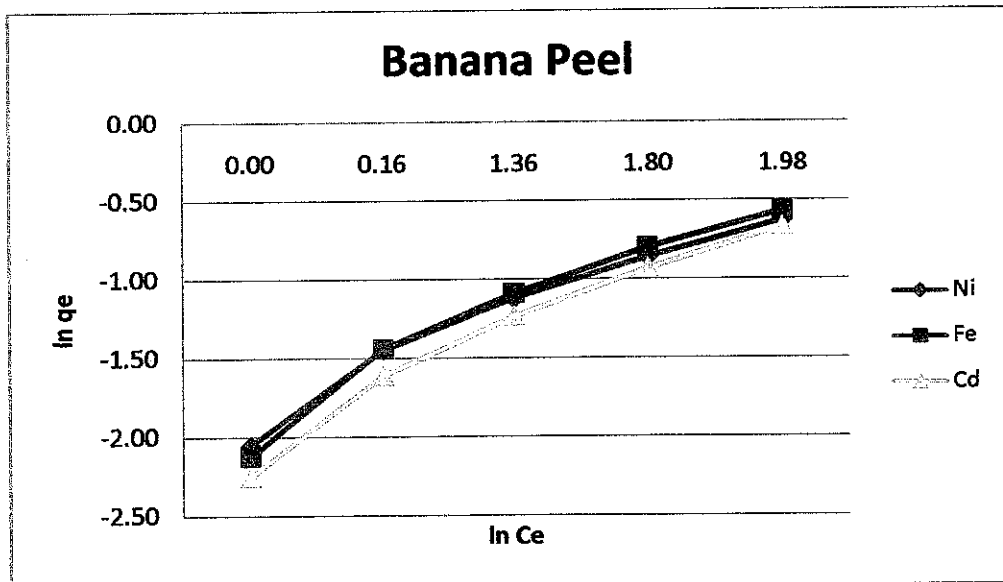


Figure 4.13: Freundlich Isotherm of Cd(II), Fe(III) and Ni(II) by banana peel sorbent.

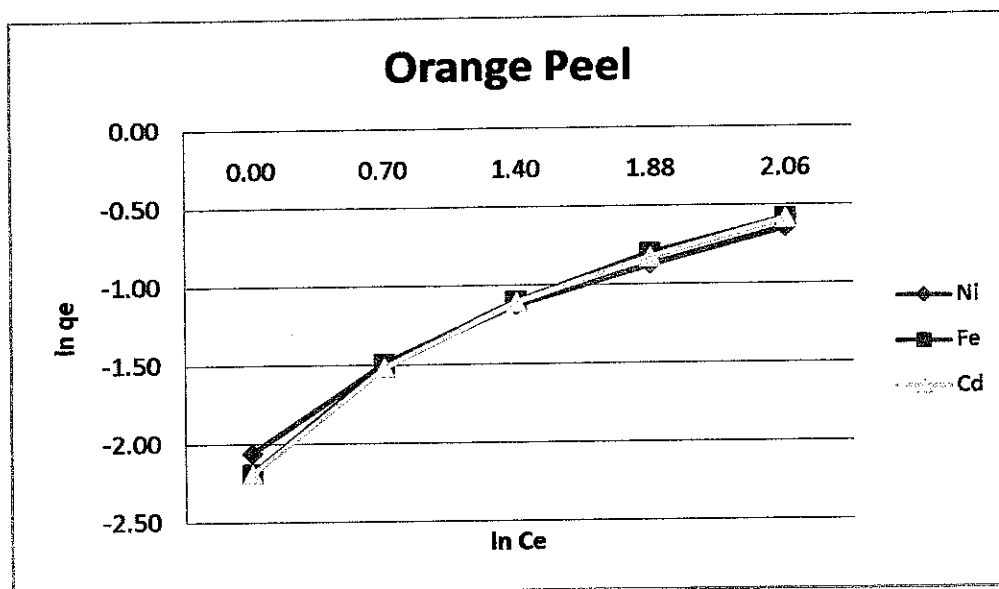


Figure 4.14: Freundlich Isotherm of Cd(II), Fe(III) and Ni(II) by orange peel sorbent.

The model parameters determined by least squares fit of the experimental data were calculated and are listed in Table 4.1. In this study, Freundlich isotherm has a better fitting model than Langmuir as the former have high correlation regression coefficient than the latter which indicates the heterogenous coverage of metal ions on the surface of adsorbent.

The Freundlich model gives an adequate description of adsorption data over a restricted range of concentration, even though it is not based on the theoretical background (Igwe and Abia, 2007). Freundlich model is also suitable for a highly heterogenous surface and an adsorption isotherm lacking a plateau, indicating a multi layer adsorption.

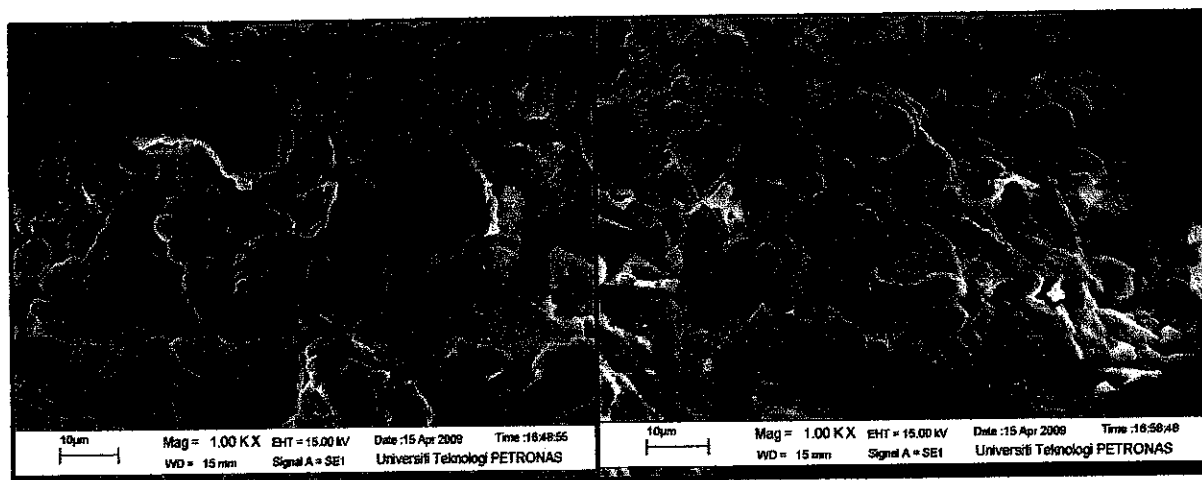
Table 4.1: Parameters of Langmuir and Freundlich sorption isotherms.

Langmuir Parameters				
Metal	q_m(mg/g)	K_L (L/mg)	R^2	slope ($1/q_m$)
Ni (BP)	0.484	-0.562	0.879	2.065
Ni (OP)	0.507	-1.027	0.834	1.974
Fe (BP)	0.792	0.437	0.814	1.262
Fe (OP)	8.282	0.013	0.152	0.121
Cd (BP)	1.941	0.029	0.233	0.515
Cd (OP)	7.085	0.014	0.069	0.141

Freundlich Parameters			
Metal	K_F	n	R^2
Ni (BP)	0.1051	0.564	0.880
Ni (OP)	0.1029	0.646	0.988
Fe (BP)	0.0972	0.599	0.962
Fe (OP)	0.0906	0.964	0.993
Cd (BP)	0.0827	0.840	0.954
Cd (OP)	0.0893	0.937	0.982

4.3 Scanning Electron Microscope (SEM) Images

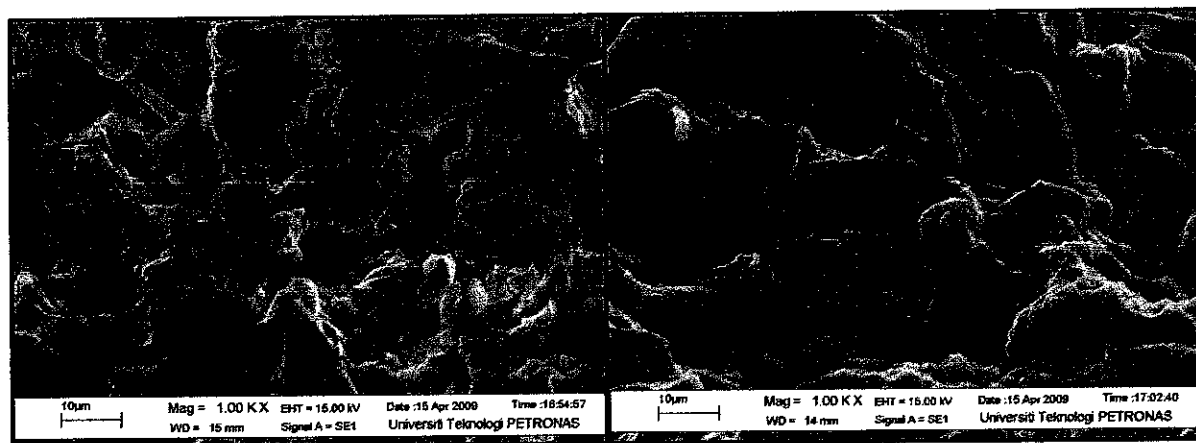
The surface morphology of banana and orange peels were studied with the use of SEM. A microporous structure (Figures 4.15 and 4.16) was observed at a resolution of 1000X for both sorbents. The original peels have a highly porous structure. After the adsorption process, it can be seen that the peels have a surface partially covered by heavy metals.



(a) Original Banana Peel

(b) Banana Peel after Adsorption

Figure 4.15: SEM images of Banana Peel (Initial Condition: 50ppm heavy metals solution)



(a) Original Banana Peel

(b) Banana Peel after Adsorption

Figure 4.16: SEM images of Orange Peel (Initial Condition: 50ppm heavy metals solution)

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This project shows the interest of a concept based on the waste to treat another waste or to resolve an environmental problem. The results obtained confirm that the low-cost materials tested can remove Cd(II), Fe(III) and Ni(II) ions from aqueous solution. The sorption performances are strongly affected by parameters such as: contact time, adsorbent mass, initial solution concentration and adsorbent material type. The amount of metal ions adsorbed by the peels increased with the increase of the adsorbent mass and initial solution concentration. The adsorption capacity was found to be 3 mg/g (Fe^{3+}), 2.52 mg/g (Ni^{2+}), and 2.35 mg/g (Cd^{2+}) using banana peel sorbent and was 3 mg/g (Fe^{3+}), 2.58 mg/g (Ni^{2+}) and 2.37 mg/g (Cd^{2+}) using orange peel sorbent. The results showed that a good fitting of heavy metals sorption equilibrium data was obtained with Freundlich model in all range of concentrations studied. From these results, highest removal of Cd(II), Fe(III) and Ni(II) were obtained with orange peel sorbent. The banana and orange peels appeared to be useful in the removal of trace metals from aqueous solution.

5.2 Recommendations

There are still some aspects and areas in the utilization of banana and orange peels as heavy metals adsorbent that must be studied to a greater extent. Here, some of the studies that could be conducted in the future would be recommended. These studies would greatly help to elevate the potential of utilizing banana and orange peels as the heavy metals adsorbent in the future.

1. Study of adsorption when other process parameters are varied.

In this study, the extent of adsorption for metals with a varying time, adsorbent mass and initial concentration was examined. Apart from these three parameters, other process parameters could also be used to determine their effect on the adsorption process such as

pH and temperature. It is also very important information to be obtained if banana and orange peels are to be used as commercial adsorbents.

2. The effect of different preparation methods on the adsorption process.

In the experiments conducted in this study, the banana and orange peels used were only cleaned and dried in the oven. No methods of preparation or activation were used to increase the adsorption capacity of the peels. This is to provide the basic information about the adsorption capacity of the peels. From here, different methods of preparation could be utilized to increase its capacity. A few of the methods that could be studied further are by activation via acid or base, heating at high temperature and others.

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Appendix A:**Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979.****Maximum Effluent Parameter Limits Standards A and B.**

Parameters		(Units)	Standard	
			A (1)	B (2)
1	Temperature	°C	40	40
2	pH	-	6.0 - 9.0	5.5 - 9.0
3	BOD5 @ 20°C	mg/l	20	50
4	COD	mg/l	50	100
5	Suspended Solids	mg/l	50	100
6	Mercury	mg/l	0.005	0.05
7	Cadmium	mg/l	0.01	0.02
8	Chromium, Hexalent	mg/l	0.05	0.05
9	Arsenic	mg/l	0.05	0.10
10	Cyanide	mg/l	0.05	0.10
11	Lead	mg/l	0.10	0.5
12	Chromium, Trivalent	mg/l	0.20	1.0
13	Copper	mg/l	0.20	1.0
14	Manganese	mg/l	0.20	1.0
15	Nickel	mg/l	0.20	1.0
16	Tin	mg/l	0.20	1.0
17	Zinc	mg/l	1.0	1.0
18	Boron	mg/l	1.0	4.0
19	Iron (Fe)	mg/l	1.0	5.0
20	Phenol	mg/l	0.001	1.0
21	Free Chlorine	mg/l	1.0	2.0
22	Sulphide	mg/l	0.50	0.50
23	Oil and Grease	mg/l	Not detectable	10.0

Standard A: for discharge upstream of drinking water take-off

Standard B: for inland waters

Appendix B:

Heavy Metals adsorption capacity for agricultural waste adsorbents.

Material	Adsorption capacity (mg/g)						References
	Cd ⁺²	Cr ⁺³	Cr ⁺⁶	Hg ⁺²	Pb ⁺²	Zn ⁺²	
Douglas fir bark	-	-	-	100	-	-	Maari et al., 1974
Exhausted coffee	1.49	-	1.42	-	-	-	Orhan and Buyukgungor, 1993
Waste tea	1.69	-	1.55	-	-	-	Orhan and Buyukgungor, 1993
Walnut shell	1.5	-	1.33	-	-	-	Orhan and Buyukgungor, 1993
Untreated pinus sylvestris bark	-	8.69	-	-	-	-	Aves et al., 1993
Treated pinus sylvestris bark	-	9.77	-	-	-	-	Aves et al., 1993
Turkish coffee	1.17	-	1.63	-	-	-	Orhan and Buyukgungor, 1993
Black oak bark	25.9	-	-	403	-	-	Teles and Baca, 1994
Sawdust	-	-	10.1, 16.05 4.44	-	-	-	Bryant et al., 1992 Dikshit, 1999 Zarraz, 1995
Redwood bark	27.4, 32	-	-	250	8.3-192	-	Maari et al., 1974 Randall et al., 1974
Pinus pinsater bark	9	19.45	-	-	9.33, 1.59	-	Teles and Baca, 1993-94 Vazquez et al., 1994
Nut shell	1.3	-	1.47	-	-	-	Orhan and Buyukgungor, 1993
Hardwickia, binata, bark	34	-	-	-	-	-	Deshkar et al., 1990
Formaldehyde-polymerized peanut skins	74	-	-	-	205	-	Randall et al., 1978
Exhausted coffee	1.49	-	1.42	-	-	-	Orhan and Buyukgungor, 1993
Lignin	-	-	-	-	1945	95	Srivastava et al., 1994
Sulfuric acid lignin	-	-	-	153	-	-	Maari et al., 1974
Xanthate sawdust	21.4	-	-	30.1- 42.1	31.1- 41.4	-	Flynn et al., 1990
Irish sphagnum moss peat	-	-	119, 43.9	-	-	-	Sharma and Foster, 1992, 1995
Sphagnum moss peat	5.8	29	-	-	40	-	McLeland and Rock, 1993
Restiunso peat	5.058	4.63	-	16.2	20.839	-	Tummaruori and Aho, 1990a,b
Modified peat	-	76	-	-	230	-	Kertman et al., 1993
Dry redwood leaves	-	-	-	175	-	-	Maari et al., 1974
Dyed bamboo pulp	-	-	-	15.6	15.0	-	Shukla and Sakhardane, 1992
Undyed bamboo pulp	-	-	-	9.2	9.4	-	Shukla and Sakhardane, 1992
Dyed jute	-	-	-	13.7	14.1	-	Shukla and Sakhardane, 1992
Dyed sawdust	-	-	-	19.0	24.0	-	Shukla and Sakhardane, 1992
Modified wood	37	-	17	532	135	-	Maari and Friedman, 1974
Moss	48.5	-	-	-	-	-	Low and Lee, 1991
Orange peel (white inner skin)	-	-	125	-	-	-	Maari et al., 1974
Orange peel (outer skin)	-	-	275	-	-	-	Maari et al., 1974
Senna leaves	-	-	250	-	-	-	Maari et al., 1974
Undyed sawdust	-	-	-	9.5	7.3	-	Shukla and Sakhardane, 1992
Copper-treated moss	-	18.9	7.1	-	-	-	Low and Lee, 1995
Petiole felt-cake of palm	10.9	-	5.32	-	11.4	9.0	Iqbal et al., 2002
Black gram husk	49.74	-	-	-	-	-	Saeed and Iqbal, 2003
Rice husk ash	20.24	-	-	93.93	-	-	Kumar and Bandyopadhyay, 2005
Modified hardwickia, binata, bark	-	-	-	21	-	-	Deshkar et al., 1990

Appendix C:

C.1 Data for Experiment A - Effects of Adsorbent Mass

0.1g	Banana Peel			Orange Peel		
	Concentration (ppm)			Concentration (ppm)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	50.00	50.00	50.00	50.00	50.00	50.00
1H	40.88	0.00	48.77	38.44	0.00	48.43
3H	40.65	0.00	48.52	38.10	0.00	48.22
5H	40.33	0.00	48.43	37.95	0.00	48.19
7H	39.06	0.00	48.42	37.85	0.00	48.25
0.5g	Banana Peel			Orange Peel		
	Concentration (ppm)			Concentration (ppm)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	50.00	50.00	50.00	50.00	50.00	50.00
1H	35.76	0.00	40.65	33.87	0.00	39.95
3H	35.60	0.00	40.24	33.76	0.00	39.84
5H	35.59	0.00	40.13	33.24	0.00	39.73
7H	35.38	0.00	40.11	33.22	0.00	39.70
1g	Banana Peel			Orange Peel		
	Concentration (ppm)			Concentration (ppm)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	50.00	50.00	50.00	50.00	50.00	50.00
1H	20.85	0.00	30.12	19.05	0.00	29.76
3H	20.75	0.00	30.06	18.94	0.00	29.45
5H	20.62	0.00	30.04	18.65	0.00	29.33
7H	20.58	0.00	30.04	18.65	0.00	29.28
2g	Banana Peel			Orange Peel		
	Concentration (ppm)			Concentration (ppm)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	50.00	50.00	50.00	50.00	50.00	50.00
1H	10.18	0.00	25.88	9.66	0.00	24.79
3H	10.12	0.00	25.71	9.34	0.00	24.55
5H	10.04	0.00	25.43	9.29	0.00	24.32
7H	9.91	0.00	25.39	9.27	0.00	24.28

C.2 Metal Uptake (mg/g) for Experiment A

0.1g	Banana Peel			Orange Peel		
	Metal Uptake (mg/g)			Metal Uptake (mg/g)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	0.00	0.00	0.00	0.00	0.00	0.00
1H	13.68	75.00	1.85	17.34	75.00	2.36
3H	14.03	75.00	2.22	17.85	75.00	2.67
5H	14.51	75.00	2.36	18.08	75.00	2.72
7H	16.41	75.00	2.37	18.23	75.00	2.63
0.5g	Banana Peel			Orange Peel		
	Metal Uptake (mg/g)			Metal Uptake (mg/g)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	0.00	0.00	0.00	0.00	0.00	0.00
1H	4.27	15.00	2.81	4.84	15.00	3.02
3H	4.32	15.00	2.93	4.87	15.00	3.05
5H	4.32	15.00	2.96	5.03	15.00	3.08
7H	4.39	15.00	2.97	5.03	15.00	3.09
1g	Banana Peel			Orange Peel		
	Metal Uptake (mg/g)			Metal Uptake (mg/g)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	0.00	0.00	0.00	0.00	0.00	0.00
1H	4.37	7.50	2.98	4.64	7.50	3.04
3H	4.39	7.50	2.99	4.66	7.50	3.08
5H	4.41	7.50	2.99	4.70	7.50	3.10
7H	4.41	7.50	2.99	4.70	7.50	3.11
2g	Banana Peel			Orange Peel		
	Metal Uptake (mg/g)			Metal Uptake (mg/g)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	0.00	0.00	0.00	0.00	0.00	0.00
1H	2.99	3.75	1.81	3.03	3.75	1.89
3H	2.99	3.75	1.82	3.05	3.75	1.91
5H	3.00	3.75	1.84	3.05	3.75	1.93
7H	3.01	3.75	1.85	3.05	3.75	1.93

C.3 Percentage Adsorption (%) for Experiment A

Mass	Banana Peel			Orange Peel		
	% Adsorption			% Adsorption		
	Ni	Fe	Cd	Ni	Fe	Cd
0.1g	21.88	100.00	3.16	24.30	100.00	3.50
0.5g	29.24	100.00	19.78	33.56	100.00	20.60
1g	58.84	100.00	39.92	62.70	100.00	41.44
2g	80.18	100.00	49.22	81.46	100.00	51.44

Appendix D:

D.1 Data for Experiment B - Effects of Initial Solution Concentration

10ppm	Banana Peel			Orange Peel		
	Concentration (ppm)			Concentration (ppm)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	10.00	10.00	10.00	10.00	10.00	10.00
1H	8.73	0.00	9.46	8.36	0.00	9.46
3H	8.65	0.00	9.37	8.27	0.00	9.37
5H	8.62	0.00	9.35	8.23	0.00	9.35
7H	8.62	0.00	9.35	8.19	0.00	9.35
20ppm	Banana Peel			Orange Peel		
	Concentration (ppm)			Concentration (ppm)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	20.00	20.00	20.00	20.00	20.00	20.00
1H	8.04	0.00	9.37	7.91	0.00	9.28
3H	7.99	0.00	9.28	7.85	0.00	9.24
5H	7.84	0.00	9.25	7.82	0.00	9.20
7H	7.82	0.00	9.24	7.79	0.00	9.19
30ppm	Banana Peel			Orange Peel		
	Concentration (ppm)			Concentration (ppm)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	30.00	30.00	30.00	30.00	30.00	30.00
1H	7.78	0.00	9.02	7.65	0.00	8.79
3H	7.72	0.00	8.94	7.43	0.00	8.70
5H	7.71	0.00	8.91	7.41	0.00	8.70
7H	7.68	0.00	8.88	7.39	0.00	8.67
40ppm	Banana Peel			Orange Peel		
	Concentration (ppm)			Concentration (ppm)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	40.00	40.00	40.00	40.00	40.00	40.00
1H	6.48	0.00	8.89	6.03	0.00	8.47
3H	6.43	0.00	8.83	5.95	0.00	8.42
5H	6.41	0.00	8.71	5.73	0.00	8.39
7H	6.40	0.00	8.71	5.57	0.00	8.36

D.2 Metal Uptake (mg/g) for Experiment B

10ppm	Banana Peel			Orange Peel		
	Metal Uptake (mg/g)			Metal Uptake (mg/g)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	0.00	0.00	0.00	0.00	0.00	0.00
1H	0.10	0.75	0.04	0.12	0.75	0.04
3H	0.10	0.75	0.05	0.13	0.75	0.05
5H	0.10	0.75	0.05	0.13	0.75	0.05
7H	0.10	0.75	0.05	0.14	0.75	0.05
20ppm	Banana Peel			Orange Peel		
	Metal Uptake (mg/g)			Metal Uptake (mg/g)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	0.00	0.00	0.00	0.00	0.00	0.00
1H	0.90	1.50	0.80	0.91	1.50	0.80
3H	0.90	1.50	0.80	0.91	1.50	0.81
5H	0.91	1.50	0.81	0.91	1.50	0.81
7H	0.91	1.50	0.81	0.92	1.50	0.81
30ppm	Banana Peel			Orange Peel		
	Metal Uptake (mg/g)			Metal Uptake (mg/g)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	0.00	0.00	0.00	0.00	0.00	0.00
1H	1.67	2.25	1.57	1.68	2.25	1.59
3H	1.67	2.25	1.58	1.69	2.25	1.60
5H	1.67	2.25	1.58	1.69	2.25	1.60
7H	1.67	2.25	1.58	1.70	2.25	1.60
40ppm	Banana Peel			Orange Peel		
	Metal Uptake (mg/g)			Metal Uptake (mg/g)		
	Ni	Fe	Cd	Ni	Fe	Cd
0H	0.00	0.00	0.00	0.00	0.00	0.00
1H	2.51	3.00	2.33	2.55	3.00	2.36
3H	2.52	3.00	2.34	2.55	3.00	2.37
5H	2.52	3.00	2.35	2.57	3.00	2.37
7H	2.52	3.00	2.35	2.58	3.00	2.37

D.3 Percentage Adsorption (%) for Experiment B

Concentration	Banana Peel			Orange Peel		
	% Adsorption			% Adsorption		
	Ni	Fe	Cd	Ni	Fe	Cd
10ppm	13.80	100.00	6.50	18.10	100.00	6.50
20ppm	60.90	100.00	53.80	61.05	100.00	54.05
30ppm	74.40	100.00	70.40	75.37	100.00	71.10
40ppm	84.00	100.00	78.23	86.08	100.00	79.10