ADSORPTION OF CD(II), NI(II) AND CU(II) USING ACTIVATED ROCK MELON SHELL WASTE : KINETICS AND EQUILIBRIUM

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ADSORPTION OF CD(II), NI(II) AND CU(II) USING ACTIVATED ROCK MELON SHELL WASTE : KINETICS AND EQUILIBRIUM

AMALINA BINTI ROSLAN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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JANUARY 2014

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature	:
Name of main supervisor	: DR. IR. SAID NURDIN
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Date	: JANUARY 2014

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
Name : AMALINA BINTI ROSLAN
ID Number : KA11004
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Special dedication to both my father and mother that always gives the full support, love and stand beside me, my supervisor for all the knowledge and all my friends who involved in order completing this thesis.

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ABSTRACT

Heavy metals in wastewater exhibit a global concern of environment due to its toxicity characteristics to many organisms. Adsorption can be used for high separation efficiency of heavy metals in waste water. This method widely used in this industry using different type of adsorbent. The use of low-cost adsorbents has been investigated as a replacement for current costly methods of removing heavy metals from solution. The objective of this research is to investigate the potential of rock melon shell waste as alternative adsorbent to adsorb Cd (II), Ni (II) and Cu (II) ions on aqueous solution. In this research, rock melon shell is used to replace the highly cost adsorbent used in the waste water industry The rock melon shell will be dried, ground and separate by their size through sieve shaker. Then, the rock melon shell powder was activated in the furnace at temperature range 400 ˚C - 650 ˚C. The prepared adsorbent and adsorbate were used for testing the removal effect of the heavy metals by manipulating the parameters of solution pH, contact time and adsorbent dosage. The results were analyzed by using the Atomic Absorption Spectroscopy (AAS). The optimal process conditions were used for kinetic and adsorption equilibrium. The percentage removal of Cd (II), Ni (II) and Cu (II) had been measured and modeled. The percent adsorption of Cd (II), Ni (II) and Cu (II) increased with increased in pH, contact time and adsorbent dosage. However, it tends to achieve equilibrium state once the active sites of the adsorbent are fully occupied. The condition where it gave the highest percentage removal is at 120 minutes contact time, at pH=8 and adsorbent dosage of 0.3g which is exceed 99%. Adsorption of Cd (II), Ni (II) and Cu (II) ions from aqueous solution approved the second-order kinetic yielding good R^2 values of 1.00 and k values of 0.0781 to 0.1776.

ABSTRAK

Logam berat dalam air sisa mempamerkan satu kebimbangan global alam sekitar kerana ciri-ciri ketoksikan kepada kebanyakan organisma. Penjerapan boleh digunakan untuk kecekapan pemisahan logam berat yang tinggi dalam air sisa. Kaedah ini digunakan secara meluas dalam industri menggunakan jenis bahan penjerap yang berbeza. Penggunaan penjerap kos rendah telah disiasat sebagai penyelesaian untuk menggantikan kaedah mahal untuk penjerapan logam berat. Objektif kajian ini adalah untuk menyiasat potensi sisa kulit "rock melon" sebagai penjerap alternatif untuk menjerap Cd (II), Ni (II) dan Cu (II) ion pada larutan akueus. Dalam kajian ini, "rock melon" digunakan untuk menggantikan bahan penjerap yang berkos tinggi yang digunakan dalam industri untuk merawat air kumbahan. Kulit "rock melon" akan dikeringkan ditapis untuk mendapatkan saiz yang sama. Kemudian, serbuk kulit "rock melon" diaktifkan dalam relau pada suhu 400-650˚ C. Penjerapan logam berat dikaji dengan memanipulasi parameter pH larutan, masa sentuhan dan dos bahan penjerap. Keputusan telah dianalisis dengan menggunakan spektroskopi penyerapan atom (AAS). Keadaan proses yang optimum digunakan untuk keseimbangan dan kinetik penjerapan. Penyingkiran peratusan Cd (II), Ni (II) dan Cu (II) telah diukur dan dimodelkan. Peratus penjerapan Cd (II), Ni (II) dan Cu (II) meningkat dengan peningkatan pH, masa sentuhan dan dos bahan penjerap. Walau bagaimanapun, ia cenderung untuk mencapai keadaan keseimbangan apabila bahagian aktif bahan penjerap dihuni sepenuhnya. Keadaan di mana ia memberikan peratus penyingkiran tertinggi adalah pada 120 minit masa sentuhan, pada pH = 8 dan penjerap dos 0.3g yang melebihi 99%. Penjerapan Cd (II), Ni (II) dan Cu (II) ion dari larutan akueus membuktikan pseudo kedua berhasil dengan nilai R2 ialah 1.00 dan k nilai 0,0781-0,1776.

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LIST OF ABBREVIATIONS

AAS	Atomic Adsorption Spectrometer
Ag (II)	Silver (II)
Cd (II)	Cadmium (II)
Cu (II)	Copper (II)
g	grams
HCl	Hydrochloric Acid
L	liter
min	minutes
ml	milliliter
NaOH	Sodium Hydroxide
ppm	Part per million, mg/L
rpm	Rotation per minute
RMS	Rock melon shell
t	Time

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LIST OF SYMBOLS

^oC	Degree celcius
C_e	Equilibrium concentration
C_o	Initial concentration
K_f	Freundlich constant
K_L	Langmuir constant
K_{1ads}	Rate constant of pseudo-first order
K_{2ads}	Rate constant of pseudo-second order
M1	Molarity
n	Heterogeneity factor
q_e	Amount of metal reduction over specific amount of adsorbent
q_m	Maximum adsorption capacity
q_t	Amount of adsorption at time
R^2	Correlation coefficients
V1	Volume

1 INTRODUCTION

1.1 Introduction

In current situation, there are many people concern on heavy metals content that are contaminating our wastewater. It occurs, due to the discharge of large amount of metal contaminated wastewater that is normally from industries, commercial and domestic area. Generally, the wastewater that are generated from industrial were consist of several types of heavy metals such as Cadmium, Nickel, Copper Lead, Zinc and Chromium that are most hazardous among the chemical-intensive industries. It is due to their high solubility in aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorder.

Heavy metals removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange and electrochemical removal. These processes have significant disadvantages, which are for instance incomplete removal, high-energy requirements and production of toxic sludge (H.Eccleas, 1999).

Adsorption has become one of the alternative treatments, in recent years, the search for low cost adsorbents that have metal bindings capacities has intensified (W.C. Leung et al, 2000). The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products, agricultural wastes, biomass and polymeric materials (T.A. Kurniawan et al, 2005). There are many treatment processes that can be used for the removal of metal ions from wastewater, and certainly the cost plays an important role if not crucial the role for determining which one is to be applied. Consequently, in the last few decades alternative sorbents for the treatment of heavy metals contamination have been investigated. The most popular adsorbents among them are microbial biomass and lignocelluloses materials. These are natural materials available in large quantities and being waste products and have a low price.

1.2 Motivation

This work is conducted to remove heavy metal ions including Cd (II), Ni (II) and Cu (II) which has become a global concern in terms of environmental and wastewater aspects. Adsorption is a process one or more component of liquid stream adsorbed on the surface of solid adsorbent and separation is accomplished (Geankoplis, 2003). In this study, rock melon shell acts as adsorbents while the heavy metals are the adsorbate (adsorbed material). Conventional physico-chemical methods for removing heavy metals from waste streams have significant disadvantages and quite expensive and ineffective. Biosorption or biological method has proven to be an effective technology for the removal of heavy metals. Many low cost adsorbent have been used such as carrot residue (Al-Asheh et al. 2002), rice husk (Ghorbani et al. 2012) and tea industry waste (Cay et al. 2004) and for this work rock melon shell will be used as another waste material for the adsorbent.

Conventional treatment technologies for the removal of these toxic heavy metals are not economical and further generate huge quantity of toxic chemical sludge. Cellulosic agricultural waste materials are an abundant source for significant metal biosorption. The functional groups present in agricultural waste biomass viz. acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphydryl groups etc. have affinity for heavy metal ions to form metal complexes or chelates. The mechanism of biosorption process includes chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange etc (Sud et al, 2008). In the other hand, rock melon shell could be good adsorbents for the removal of heavy metals instead of being an agricultural waste that may increase environmental pollution in Malaysia. Besides that, this research also aims to convert waste to wealth

1.3 Problem Statement

Increasing in industrial activity is the main point behind most environmental pollution problems and ecosystem damage, coming from the accumulation of pollutants such as toxic metals such as copper, cadmium, nickel, etc (Pino et al., 2006). Heavy metal pollution has become a more serious environmental problem in the last several decades as a result of its toxicity and insusceptibility to the environment. Heavy metals can accumulate in the environment and cause serious damages to ecosystems and human health. Commercial activated carbon has been studied as an adsorbent for removal of heavy metals ions for several years due to the great specific surface area and pore structure, but it is expensive (Depci et al. 2009). Thus, an unconventional of low cost adsorption system is investigate using rock melon shell (RMS) that shows good precursor for activated carbon and was an attractive source in producing high capacity activated carbon.

Besides that, Malaysia Government is working to expand the rock melon farm because of the increasing in demand from the inside and outside of the country. Rock melon was chosen in this project because of its short maturity period of about 75 to 80 days and the huge demand for the fruit overseas. This shell of rock melon is said to be one of many agricultural waste and food industry waste which can cause environmental problem if not treated.

The purpose of this work is to evaluate the adsorption performance of locally derived rock melon shell for the removal of Cd (II), Ni (II) and Cu (II) ions from aqueous solutions by applying the deviation of certain parameters. This work focus on its adsorption kinetic data and the best fits equilibrium adsorption data using Isotherm Langmuir

1.5 Objectives

The following are the objectives of this research:

- To use activated rock melon shell as adsorbent, kinetic and adsorption isotherm of Cadmium (II), Nickel (II) and Copper (II) in aqueous solution.

1.6 Scope of This Research

The following are the scope of this research:

i) This study was done to observe the reduction of Cadmium (II), Copper (II) and Nickel (II) from aqueous solution using rock melon shell waste as adsorbent. The reduction of Cadmium (II), Copper (II) and Nickel (II) from aqueous solution was observed in term of its removal efficiency using the optimum operating condition determined.

ii) Observation and investigation of the effect of process condition for Cadmium (II), Nickel (II) and Copper (II) that can be removed by rock melon shell. During the experiment, the parameters were observed and the equilibrium point for each parameter is used for further investigation.

iii) Determination Cadmium (II), Nickel (II) and Copper (II) removal efficiency by analyzing the result of initial and final concentration for each manipulated variable using Atomic Absorption Spectrophotometer. The manipulated variables for this study are solution pH (pH 2, 4, 6, 8 and 10), contact time (40, 60, 80, 100, and 120 minutes), dosage of adsorbent (0.06, 0.12, 0.18, 0.24 and 0.30 grams) and initial concentration of adsorbate solution (20, 40, 60, 80 and 100 ppm).

iv) Determination of Langmuir adsorption isotherm and kinetic for Cadmium (II), Nickel (II) and Copper (II) that can be removed using rock melon shell as low cost adsorbents.

2 LITERATURE REVIEW

2.1 Heavy Metals in Wastewater

Nowadays, heavy metal contaminants in industrial wastewater commonly in petroleum refining, mining activities, paint industry, pesticides and many more have become an anxiety environment issues al all over the world (Ngah, 2008). Commonly there are several metals that have been classified as toxic metals if they are emitted to the environment in quantities that pose risks which including Cadmium (Cd), Nickel (Ni), Copper (Cu), Zinc (Zn), Lead (Pb) and many more (Barakat, 2011; Johnson; Wan Ngah, 2008). Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. So, this can bring serious health effect to human body. Besides that, the exposure of the heavy metals can also defect flora and fauna especially in Malaysia.

Although, heavy metals have many applications to domestic use but the release of these metal may effects human health together with ecosystems (Ozsoy, 2008; Fu, 2011). Nickel (Ni) is one of trace metal essentially need by human especially in stainless steel, catalyst and coins production. However, the excessive level of nickel may cause skin allergic, ingestion problem, asthma, carcinogenesis, causes of cancer and induced lipid peroxidation or cell death (Cempel and Nikel, 2006). Cadmium is not an essential to human life. A study by Bernard (2008) investigate that cadmium is well retained in human body as it was absorbed. Thus, it may cause damage to kidney especially proximal tubular cells as well as bone demineralization and increase the risk of lung cancer. Copper is a chemical element or soft metal with good conductivity. Instead of cadmium, copper also accumulate in human body. It may cause gastrointestinal disturbance, irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Besides, copper also will cause damage to kidney, lung and eyes.

The conventional processes for removing heavy metals from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition (Barakat, 2011). However these conventional techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludge and further the disposal is a costly affair (Ahluwalia and Goyal, 2005a).

Table 2-1: Current treatment technologies for heavy metals removal involving physical and/or chemical processes (Ahmaruzzaman, 2009)

Physical and/or chemical methods	Advantages	Disadvantages
Oxidation	Rapid process for toxic pollutants removal	High energy costs and formation of by-products
Ion exchange	Good removal of a wide range of heavy metals	Absorbent requires regeneration or disposal
Membrane filtration technologies	Good removal of heavy metals	Concentrated sludge production, expensive
Adsorption	flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Adsorbents requires regeneration
Coagulation/ flocculation	Economically feasible	High sludge production and formation of large particles
Electrochemical Treatment	Rapid process and effective for certain metal ions	High energy costs and formation of by-products
Biological treatment	Feasible in removing some metals	Technology yet to be established and commercialized

2.2 Activated Carbon As Adsorbent

Activated carbon is coal-based adsorbent that is widely used in industry to remove heavy metal from wastewater (Fu and Wang, 2011). Even though the use of activated carbon is efficient and well establish but it was expensive compared to other adsorbents, so, many researchers investigated a way to reduce the cost of activated carbon by add additives to the activated carbon such as alginate, tannic acid, magnesium and many more. Activated carbon has excellent adsorption properties which have been characterized by high specific area (Lo, et al, 2011). In spite of that, activated carbons have been use extremely because of its ability to removed variety types and amounts of heavy metals. Activated carbon is confirmed to be more efficient in term heavy metal removal but less efficient in term of cost consumption compare to agriculture waste adsorbents.

2.3 Agriculture Waste As Adsorbent

The use of activated carbon will cost a much compare to other adsorbents. Thus, researchers keep a research on searching appropriate adsorbents which using agriculture waste as adsorbents. Biosorption is emerging as a potential alternative to the existing conventional technologies for the removal and/or recovery of metal ions from aqueous solutions. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbents and possibility of metal recovery. Cellulosic agricultural waste materials are an abundant source for significant metal biosorption (Sud et al., 2007). New resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk can be used as an adsorbent for heavy metal uptake after chemical modification or conversion by heating into activated carbon (Barakat, 2011).

3 MATERIALS AND METHODS

3.1 Materials

i. Rock Melon Shell (RMS)

ii. Cadmium (II) Sulfate

iii. Nickel (II) Sulphate

iv. Copper (II) Sulphate

v. 0.1N NaOH

vi. 0.1N HCl

vii. Nitrogen gas

3.2 Apparatus

i. 250ml beaker

ii. 100ml conical flask

iii. 1L and 250ml Volumetric flask

iv. Stopper for conical flask

v. pH meter

vi. Atomic Absorption Spectrophotometer

vii. Glass rod

viii. Dropper

ix. Funnel

x. Whatman Filter paper 125mm

xi. Aluminium foil

xii. Cotton wool

xiii. Gauze cloth

3.3 *Overall Methodology Flowchart*

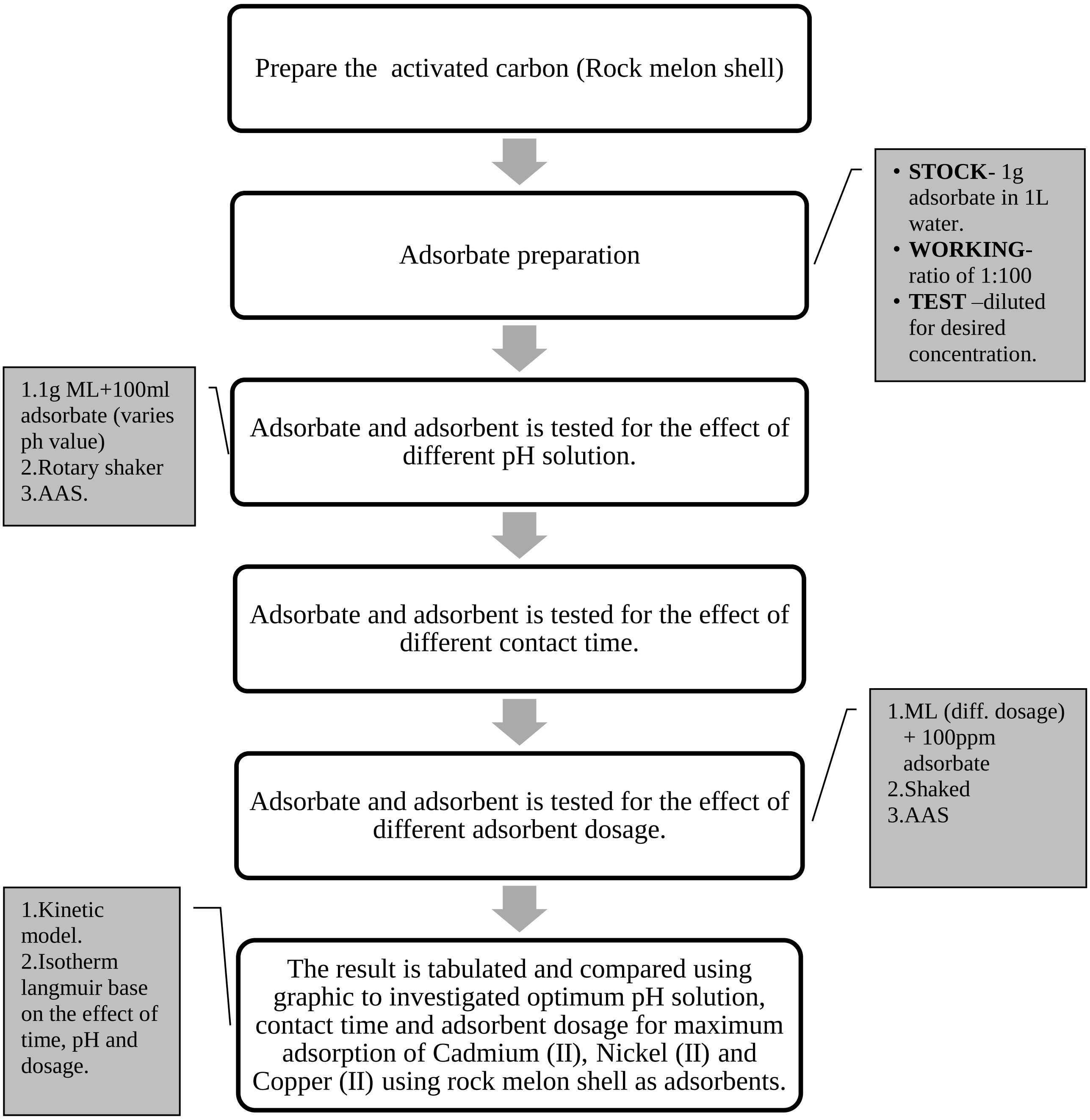

Figure 3-1: Overall flow chart for experimental methodology.

3.4 Experimental Methodology

3.4.1 Activated Carbon Preparation (Rock melon shell)

Rock melon shell (RMS) waste will be used as the main raw material in this work. The RMS will be dried crushed in a mill to get a grain size of 2mm. Phosphoric acid 40 % w/w will be added to the crushed shells at a ratio of 1:2 (g GAC/g H3PO4) to prepare the impregnate samples. These samples will be carbonized in a furnace at 500–700˚C for 1.12 h under nitrogen (N2) flow of 120 mL min-1 at a heating rate of 10 ˚C min-1. The carbonized sample (activated carbon) will be washed several times with distilled water to remove the phosphoric acid, and then check the pH of the washing water until the value is constant. Then the activated carbons will be dried in an oven at 80 ˚C per 24h.

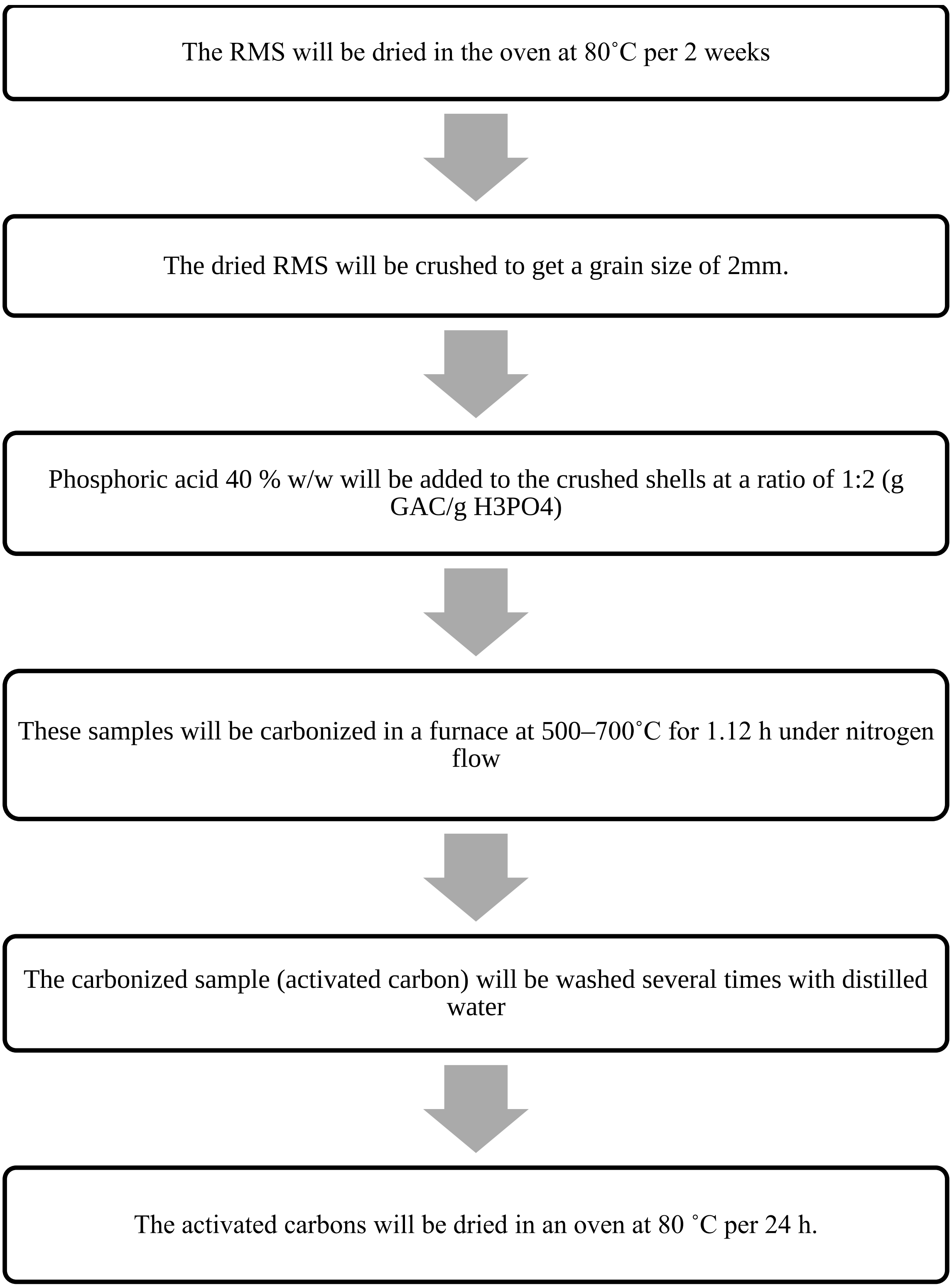

Figure 3-2: Flow diagram of preparation of rock melon shell (RMS)

3.4.2 *Adsorbate preparation*

This work will be conducted based on three heavy metal which are cadmium (II), nickel (II) and copper (II). Stock solution will be prepared by dissolving 100mg of cadmium (II) sulphate, nickel (II) sulphate and copper (II) sulphate in 1L of distilled water in different volumetric flask.

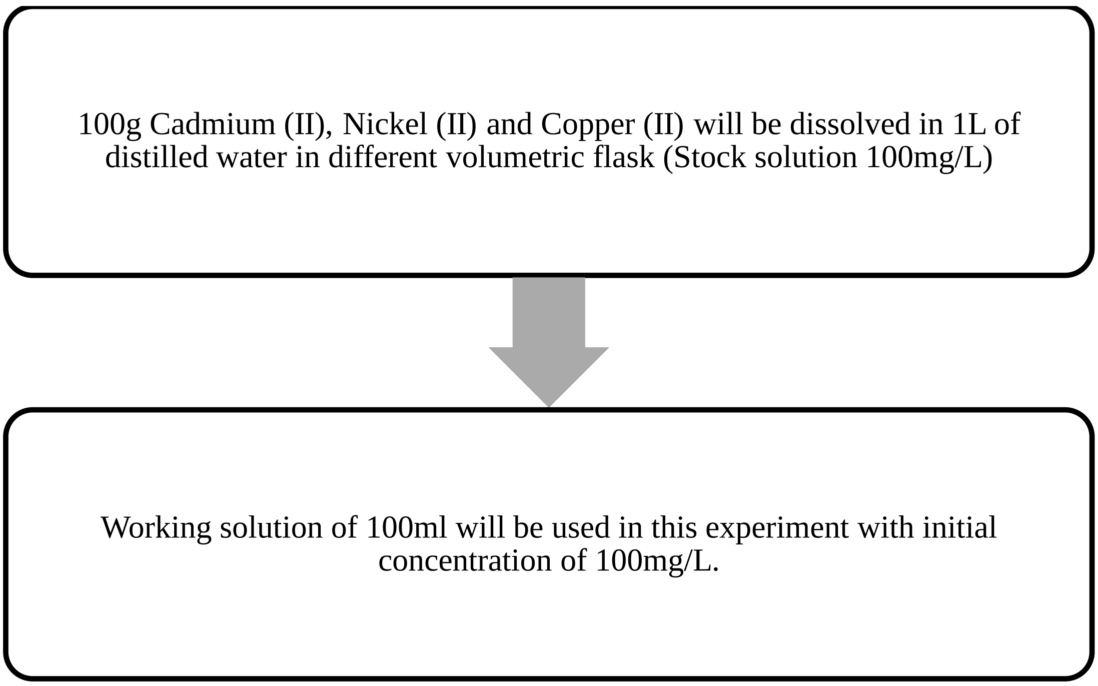

Figure 3-3: Flow diagram of preparation of adsorbate

3.4.3 Effect of pH

This experiment involve adsorption process which the RMS powder is use as adsorbents. 0.3 g of the adsorbent kept constant with 100 ml adsorbate for this experiment. 0.1N NaOH and 0.1N HCl is used to change pH from 2 to 10 so that the change in volume of the solution can be negligible. Adsorbate solution will be performed at 25˚C at the variable pH value which are 2, 4, 6, 8 and 10 on a rotary shaker operated at 150 rpm for 2 hours. The sample is filtered using Whatman filter paper 125mm before analyzed with Atomic Adsorption Spectrometry.

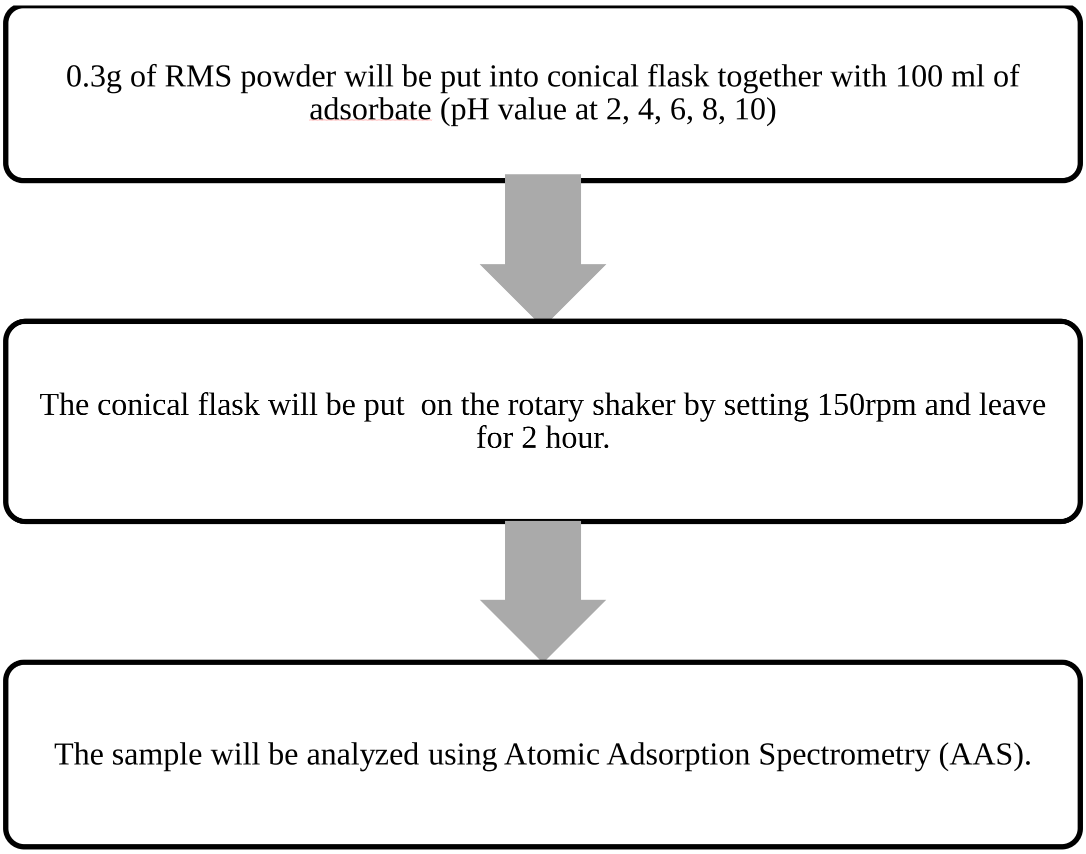

Figure 3-4: Flow diagram of the effect of initial adsorbate solution concentration (pH solution)

3.4.4 Effect of Contact Time

In order to evaluate the effect of contact time over heavy metals removal, the adsorbate solution is mix with 0.3g of rock melon shell powder. The mixture then shake on a rotary shaker operated at 150 rpm and 25˚C. The effect of contact time is investigated with varies of time which was 20 minutes to 2 hours with the gap of 20 minutes at optimum pH from previous experiment. The sample is filtered using Whatman filter paper 125mm and analyzed with Atomic Adsorption Spectrometry.

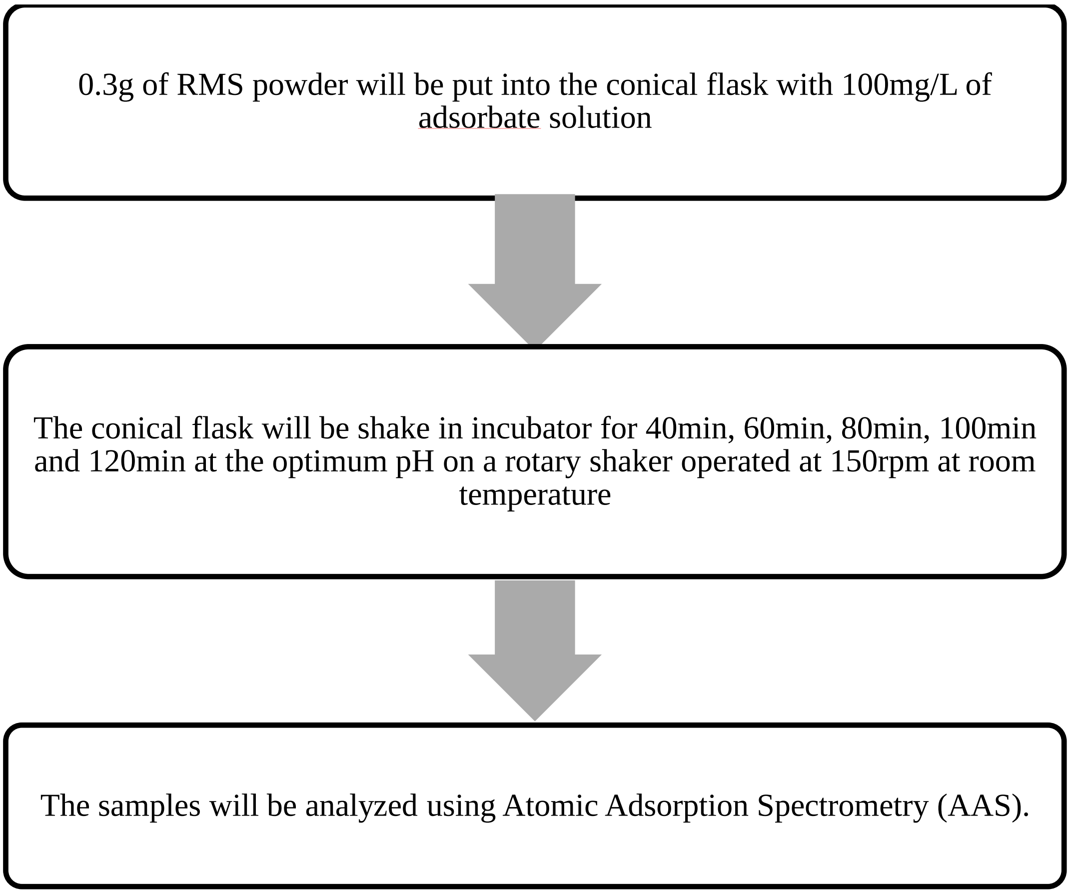

Figure 3-5: Flow diagram of the effect of contact time

3.4.5 *Effect of adsorbent dosage*

100mg/L of initial adsorbate concentration will be used with different adsorbent weight, 0.1 grams, 0.2 grams, 0.3 grams, 0.4 grams and 0.5 grams. The contact time and pH are at optimum level that can be obtained from previous experiment. This experiment will be conducted at room temperature. Samples are filtered using Whatman filter paper and analyzed using AAS.

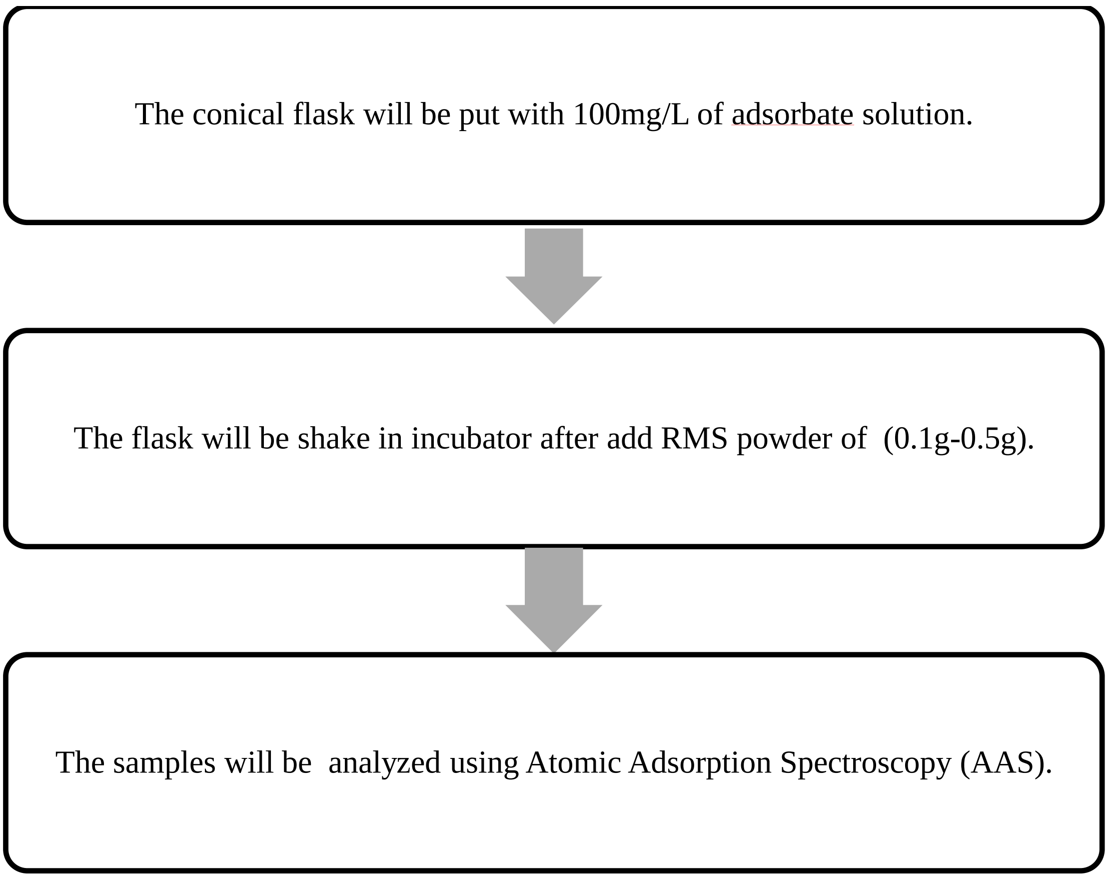

Figure 3-6: Flow diagram of the effect of adsorbent dosage

3.4.6 *Analyzing Sample*

Standard solutions are prepared before running the Atomic Adsorption Spectrometer. Solutions are prepared by diluting 1000mg/L of standard into a 100ml volumetric flask for concentration 50mg/l with standard solution ranging from 0 to 10 by using the Equation

$$M1V1 = M2V2$$

Samples that are filtered will be diluted to 10mg/L in 100ml volumetric flask, having the dilution factor of 10 using the same equation. The standards are then titrated with 1 drop nitric acid and then the samples are analysed based on the AAS procedures, where final concentration of heavy metal solution are obtained.

4 RESULT AND DISCUSSION

4.1 Effect Of pH Solution On Cd(II), Ni(II) And Cu(II) Reduction.

The pH of the solution gives the most impact on the heavy metals removal, since it determines the surface charge of the adsorbent which means the degree of ionization and speciation of the adsorbate. In order to study the effect of pH on the heavy metals removal, the pH were set at different value range from pH=2 to pH=10. Removal efficiency for the effect of pH solution is calculated using

$$\% \text{ Removal efficiency} = \frac{C_o - C_e}{C_e}$$

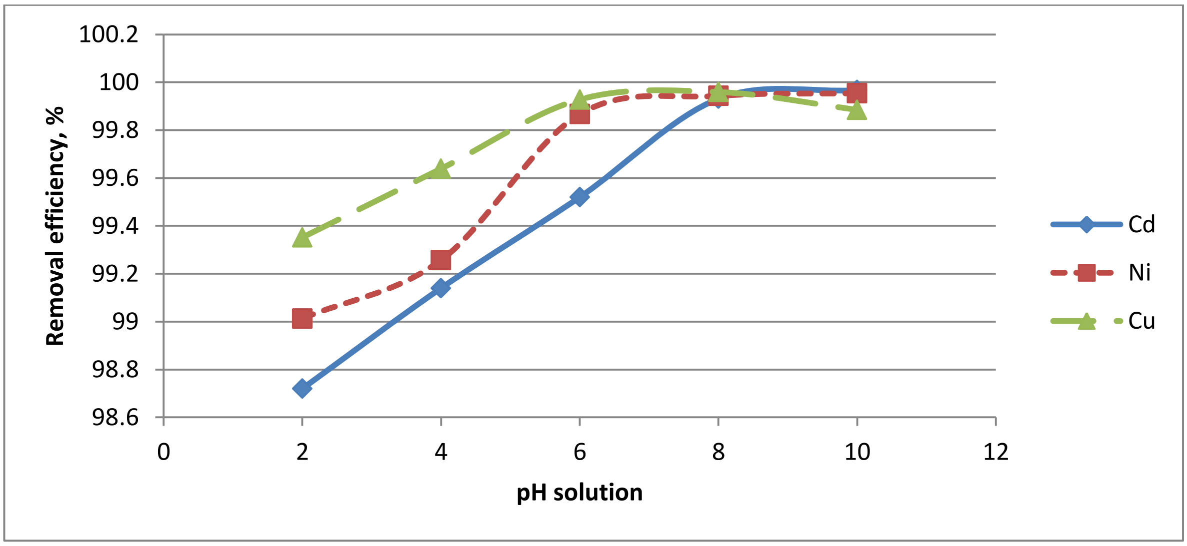

Figure 4-1: Effect of pH on Cd(II), Ni(II) and Cu(II)

Initial concentration = 100mg/L, adsorbent dosage = 0.3g and contact time = 120 min
Figure 2 shows the effect of pH on the adsorption of cadmium (II), nickel (II) and copper (II). The optimum condition for pH to remove maximum amount of the heavy metals is at pH= 8. Decreasing the pH value will decrease he adsorption efficiency of the heavy metals. The decrease in adsorption at low pH values may be due to the competitiveness of hydrogen and heavy metal ions on the sorption sites. The equilibrium adsorption (qe) was found to increase with increasing pH (Hameed at el.,2008).

4.2 Effect Of Contact Time On Cd(II), Ni(II) And Cu(II) Reduction.

The effect of contact time on the removal of cadmium (II), nickel (II) and copper (II) were studied and the result is shown in the Figure 3 below. As shown in the graph, it illustrates the effect of adsorption efficiency. The equilibrium time required for the removal of heavy metals was studied by fixing 0.3g//100ml of the activated rock melon shell into initial concentration of 100mg/L and data is taken at different time intervals. The graph of heavy metals removal efficiency versus contact time were plotted by using the formula below

$$\% \text{ Removal efficiency} = \frac{C_o - C_e}{C_e}$$

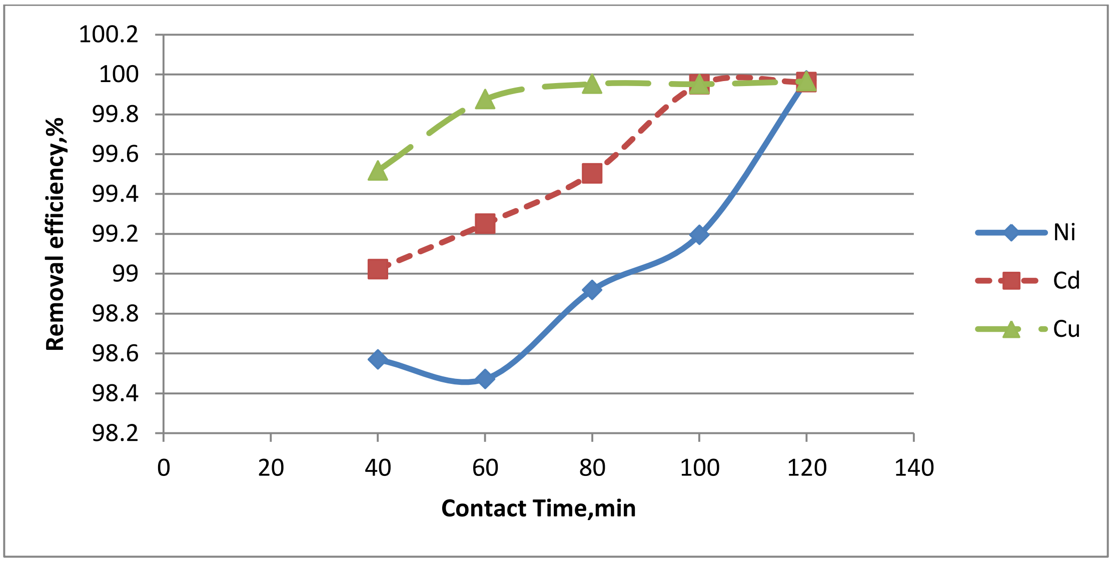

Figure 4-2: Effect of contact time on Cd(II), Ni(II) and Cu(II)

Initial concentration = 100mg/L, pH solution = 8 and adsorbent dosage = 0.3g

Based on the graph plotted, it demonstrates that as the contact time increases, the percent of metal adsorption were also increase. In this result, it indicates that more heavy metals can be adsorbed by the activated rock melon shell as the contact time increase. The reduction of copper (II), Nickel (II) and Cadmium (II) was rapid for the first 80 minutes and equilibrium was nearly reached after 120 minutes. The rate in percent of copper (II), nickel (II) and Cadmium (II) ions reduction is higher in the beginning due to the larger surface area of the adsorbent being available for the adsorption of the metals. As the surface adsorption sites being exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior sites of the adsorbent particles. It would be for that a large number of vacant surface sites were available for adsorption during the initial stage of the treatment time and after a lapse of time, less remaining vacant surface sites were available (Laila et. al., (2012).

4.3 *Effect Of Adsorbent Dosage On Cd(II), Ni(II) And Cu(II) Reduction.*

The effect of adsorbent dosage on the removal of cadmium (II), nickel (II) and copper (II) were studied and the result is shown in the Figure 4 below. With the fixed metal initial concentration of 100ppm, it can easily be inferred that the percent removal of metal ions increase with the increasing of adsorbent dosage. Amount of adsorbent were varied from 0.1g to 0.5g with fixed initial concentration= 100mg/L, pH=8 and contact time =120 minutes. The graph of heavy metals removal efficiency versus adsorbent dosage were plotted by using the formula below

$$\% \text{ Removal efficiency} = \frac{C_o - C_e}{C_e}$$

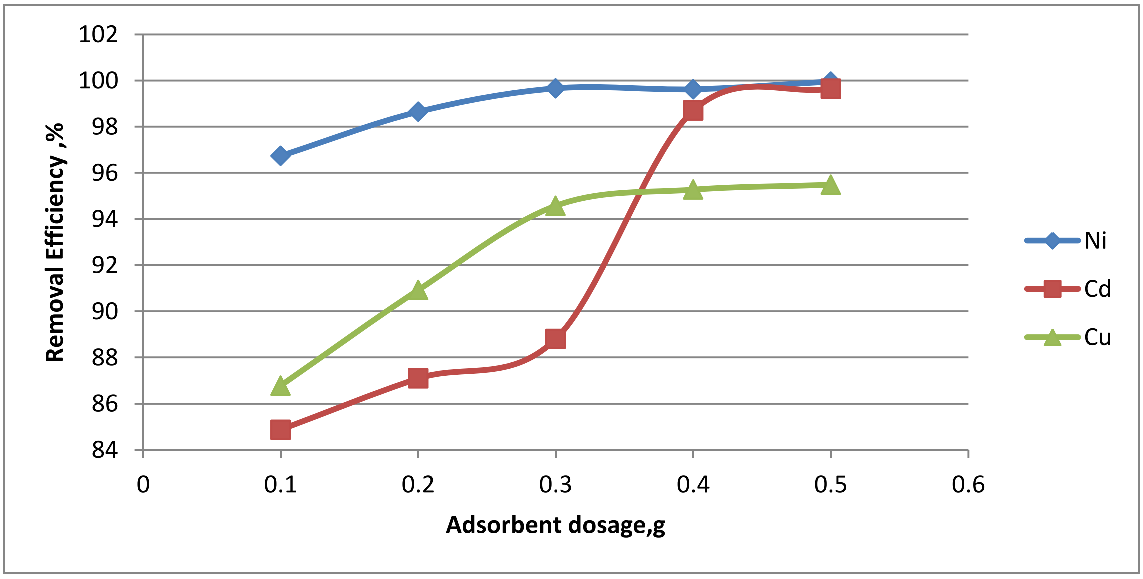

Figure 4-3: Effect of adsorbent dosage on Cd(II), Ni(II) and Cu(II)

Initial concentration = 100mg/L, pH solution = 8 and contact time = 120min

Dosage of adsorbent can be defined as the mass of activated carbon (g) in the fixed volume of the aqueous solution (mL). As illustrated in Figure 4 below, it shows the influence of adsorbent dosage (g) on the heavy metals removal. It can be clearly defined that, the heavy metals removal in the aqueous solution increases with increasing of sorbent amount. The equilibrium was reach at 0.3g of adsorbent dosage. The adsorptive capacity of activated carbon available was not fully utilized at higher adsorbent dosage. This may possibly occur due to the equilibrium concentration different. This can be explained by the fact that a fixed mass of adsorbent can only adsorb a certain amount of metal.There is low driving force for adsorption at higher adsorbent dosage was occurred (Ozturk and Kavak., 2005).

4.4 Adsorption Equilibrium

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species. If the adsorbent and adsorbate are contacted long enough, equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. The equilibrium relationship is described by adsorption isotherms. Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms. These isotherms relate metal uptake per unit mass of adsorbent, qe, to the equilibrium adsorbate concentration in the bulk fluid phase Ce.

4.4.1 The Langmuir Isotherm

In this study, the Langmuir and Freundlich isotherm were used to describe the relationship between the amount of heavy metals adsorbed and its concentration of equilibrium in solutions. Langmuir isotherm assumes that the adsorption process were take place at a specific homogenous sites between the adsorbent (Ozturk and Kavak., 2005):

$$\mathrm{qe} = \frac{q_m \mathrm{K}_L \mathrm{Ce}}{1 + \mathrm{K}_L \mathrm{Ce}}$$

Where q_e is the amount of metal reduction over specific amount of adsorbent (mg/g), C_e is equilibrium concentration of the solution (mg/L), and qm is the maximum amount of metal ions required (mg/g). The Langmuir equation can be rearranged to linear form as below for the accessibility of plotting and defining the Langmuir constants (K_L) and maximum adsorption capacity of rubber seed shell (q_m). The values of q_m and K_L can be determined from the linear plot of $1/q_e$ versus $1/C_e$:

$$\frac{1}{qe} = \frac{1}{\mathrm{qm}} + \frac{1}{\mathrm{qmK}_L}\frac{1}{Ce}$$

Where q_m is the maximum adsorption capacity for Cadmium, Nickel and Copper ions uptake, mg/g and K_L the Langmuir adsorption constant in L/mg. The graph $1/q_e$ of plotted against $1/C_e$ yielding the value of ranging from 3.38mg/g to 142.85mg/g. Langmuir isotherm fitted well this adsorption case with the correlation coefficient of 0.9896.

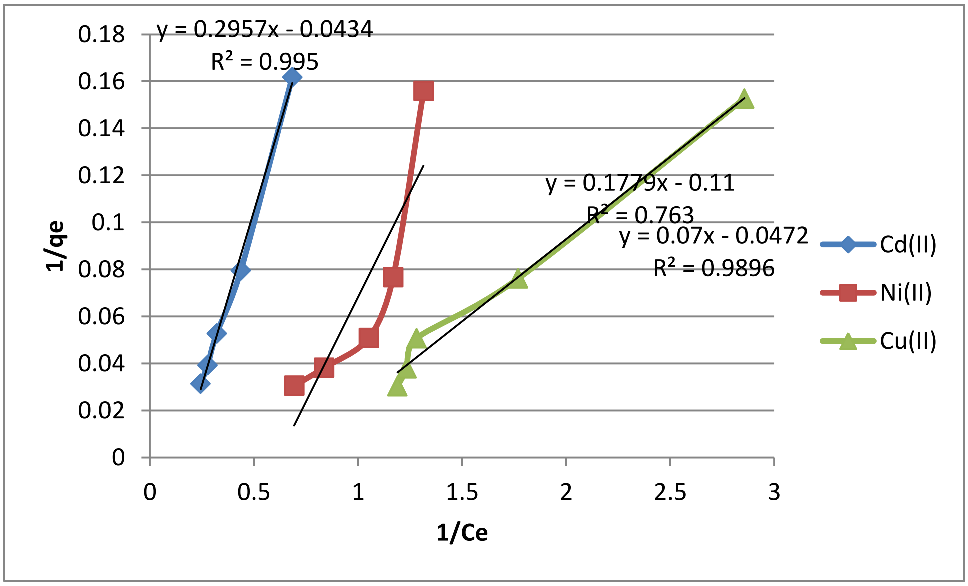

Figure 4-4: Langmuir adsorption isotherm of Cd(II), Ni(II) and Cu(II)

4.4.2 The Freundlich Isotherm.

Freundlich Isotherm is a multilayer adsorption model which considers the interaction between adsorbate molecules are given by the following equation (Ozturk and Kavak., 2005):

$$q_e = k_f C_e^{1/n}$$

Where K_f and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity. Similar to the Langmuir isotherm, the Freundlich equilibrium constant also evaluated from the intercept and the slope. The Freundlich equation can be linearized in logarithmic form for the constant determination as below by Zheng (2007):

$$\log q_e = \log k_f + 1/n \log C_e$$

where K_f and n are the Freundlich constants, the characteristics of the system. K_f and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log Ce vs. log qe was employed to generate the intercept value of K_f and the slope of n. From Fig. 5 the Freundlich constants K_f constants values ranging from 0.085 to 0.64 and n were found to be 0.60 to 0.82. The magnitudes of K_f and n show easy separation of nickel ions from the aqueous solution and indicate favourable adsorption. The intercept K_f value is an indication of the adsorption capacity of the adsorbent; the slope 1/n indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. As seen from Table 1, n value was found high enough for separation. The Freundlich isotherm is more widely used but provides no information on the monolayer adsorption capacity in contrast to the Langmuir model. Freundlich isotherm fitted well with the correlation coefficient of 0.9971.

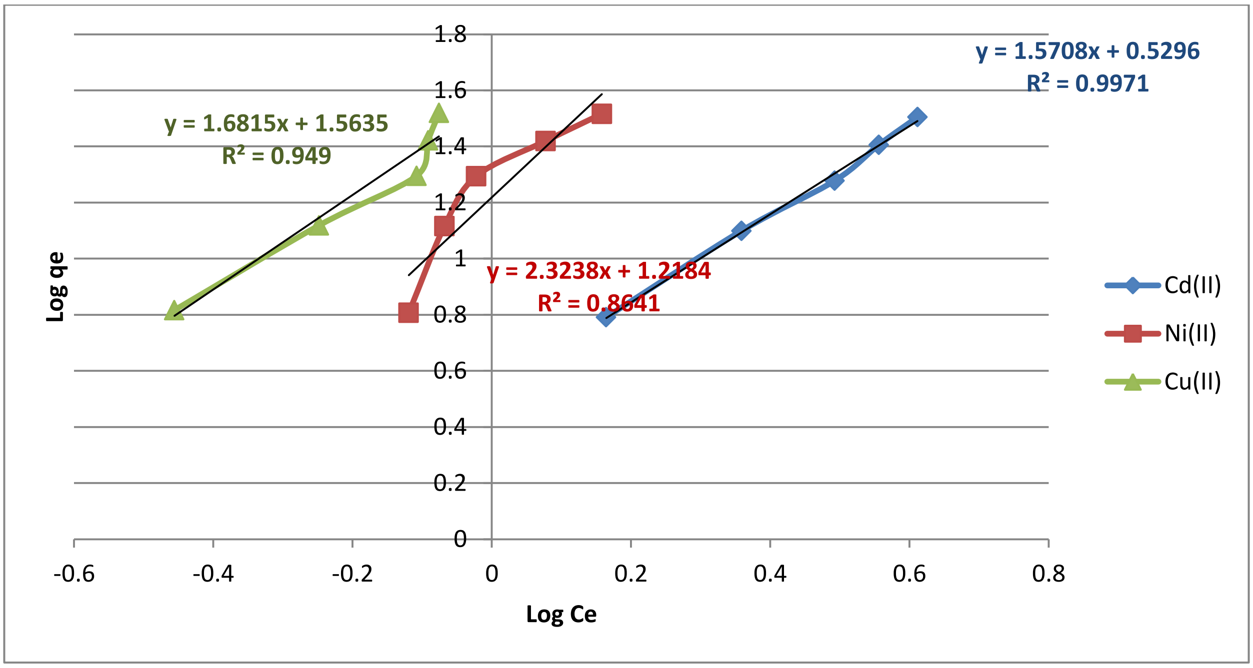

Figure 4-5: Freundlich adsorption isotherm of Cd(II), Ni(II) and Cu(II)

From the graph, corresponding isotherm the Langmuir and Freundlich adsorption constats with the correlation coefficients were calculated and presented in Table 1

Table 4.1: Langmuir and Freundlich adsorption isotherm model constants.

Heavy metal	Langmuir			Freundlich		
	q_{max}, mg/g	K_c, 1/mg	R^2	K_f, (mg/g)(1/mg)^(1/n)	n	R^2
Cd	3.381805884	0.177544809	0.995	0.184577875	0.636618284	0.9971
Ni	5.621135469	0.20292299	0.763	0.08578989	0.820748523	0.8641
Cu	142.8571429	2.671428571	0.9896	0.194097886	0.594707107	0.949

4.5 *Adsorption Kinetics.*

In order to study the controlling mechanism of adsorption processes, pseudo first and second order equations are applied to model the kinetics of cadmium (II), nickel (II) and copper (II) adsorption onto activated rock melon shell powder. A linear form of pseudo-first-order model was described in the form:

$$\log (q_e - q_t) = \log q_e - \frac{K_{1ad}}{2.303} t$$

Where q_e and q_t are the amount of adsorption at equilibrium at time t, respectively, and k_{1ad} is the rate constant of the pseudo-first order adsorption process. The adsorption data will provide a straight line pseudo-first order graph and the value of adsorption rate constant, k_{1ad} can be compute. All three Cd (II), Ni (II) and Cu (II) heavy metals ions are observed in the figure 7 below. If the plot was found to be linear with good correlation coefficient, indicating that pseudo first order equation is appropriate to Cd (II), Ni (II) and Cu (II) ions sorption on the prepared activate carbon. So, the adsorption process is a pseudo-first-order process (Lagergren, 1898 and Ho, 1999). From the graph, it was observed that the pseudo-first-order model did not fit well and not to be in linear form.

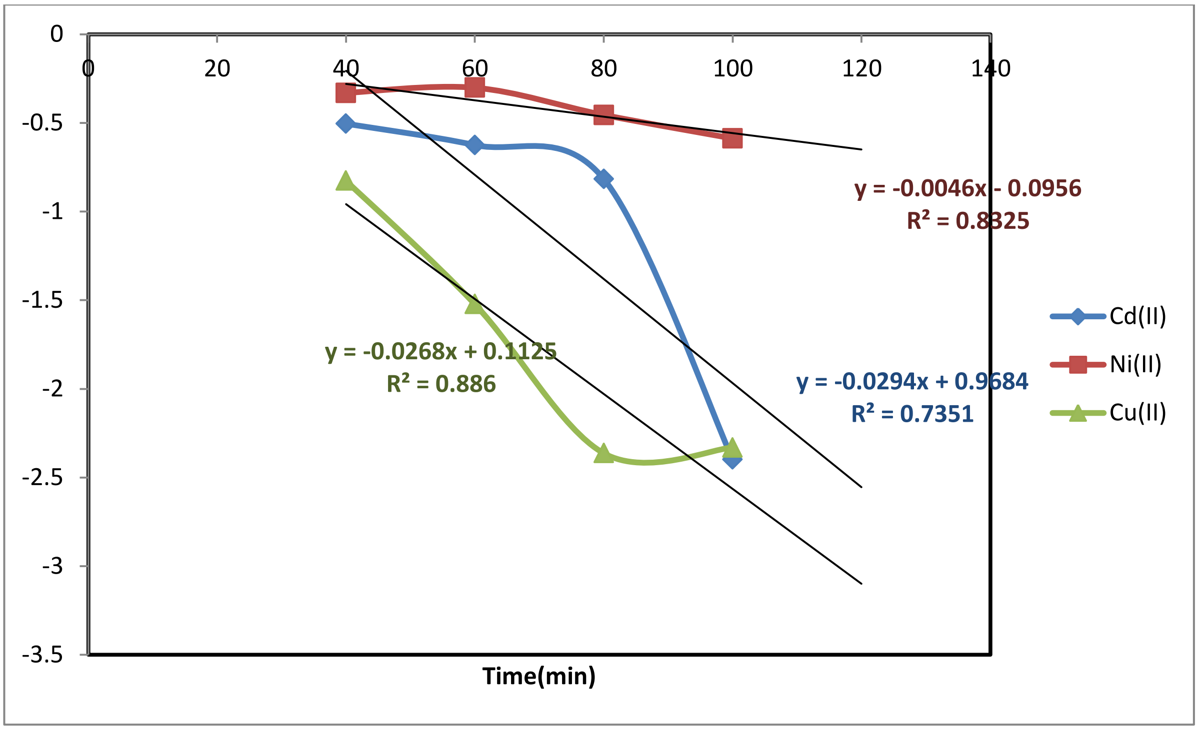

Figure 4-6: Pseudo –first order kinetic for Cd(II), Ni(II) and Cu(II) adsorption using activated rock melon shell.

The pseudo second order kinetic can be expressed in a linear form as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t$$

Where $h=kq_e^2$ (mg g-1 min-1) which can be known as the initial adsorption rate and k is the rate constant of pseudo-second order adsorption (g mg-1 min-1). The graph of t/q_t versus t should give a straight line graph if this kinetic model suits this adsorption case. In addition, k and h can be determined from the slope and the intercept of the graph.

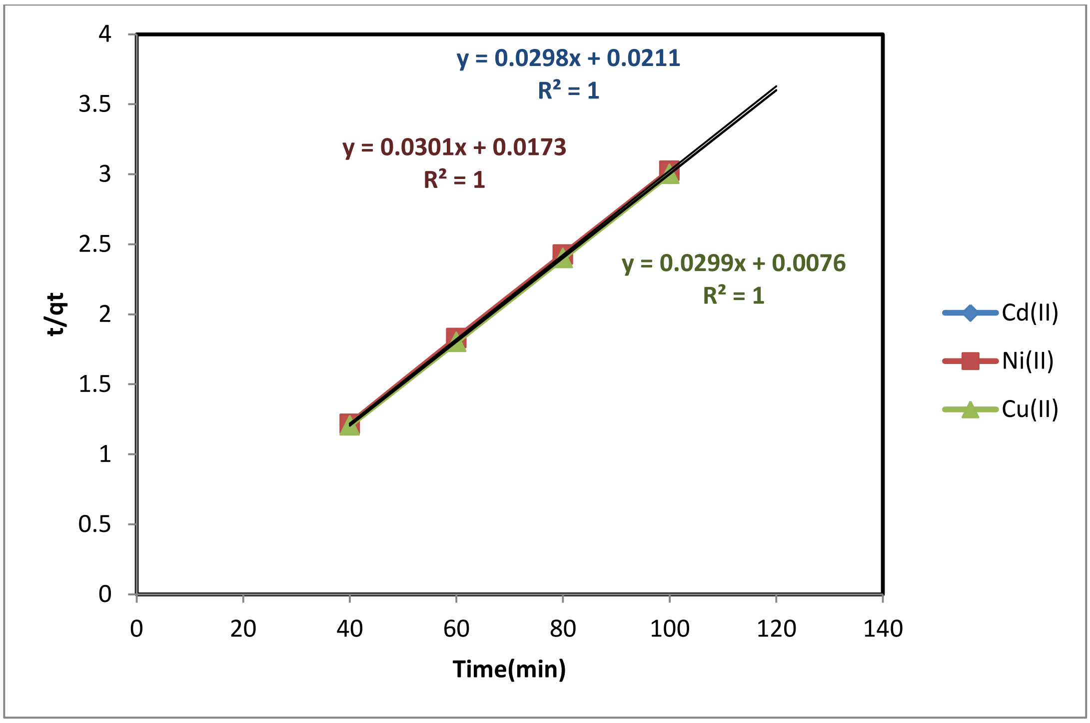

Figure 4-7: Pseudo –second order kinetic for Cd(II), Ni(II) and Cu(II) adsorption using activated rock melon shell.

Pseudo-first order and Pseudo-second order adsorption constant including correlation coefficient is shown in table 2.

Table 4-2: Pseudo-first order and pseudo-second order kinetic model constants.

Heavy Metal	Pseudo 1st Order		Pseudo 2nd Order	
	k1ads, L/min	R^2	k2ads, g/mg. min	R^2
Cd(II)	0.0677082	0.7351	0.076555172	1
Ni(II)	0.0105938	0.8325	0.061216892	1
Cu(II)	0.0617204	0.886	0.178802	1

The plot of t/qt versus t for pseudo-second-order model (Fig. 8) yields very good straight lines (correlation coefficient, R2 =1) as compared to the plot of pseudo-first order. The pseudo-second-order rate constants were in the range of 0.0610 to 0.1788 g mg-1 min-1. The theoretical values of qe also agree very well with the experimental ones. Both facts suggest that the adsorption of Cd(II), Ni(II) and Cu(II) ions by activated rock melon shell powder follows the pseudo-second-order kinetic model, which relies on the assumption that chemisorption may be the rate-limiting step. In chemisorption (chemical adsorption), the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface .

5 CONCLUSION

5.1 Conclusion

The proposed method of activated carbon from rock melon shell waste by adsorption mechanism has found to be successful. The results indicate that the activated carbon from rock melon shell waste affect the adsorption process of Cd (II), Ni (II) and Cu (II) ions from aqueous solution by the variation of solution pH, contact time and adsorbent dosage. The highest adsorption was found by the time of 120 minutes, pH of 8 and adsorbent dosage of 0.3g. Adsorption of Cd (II), Ni (II) and Cu (II) ions from aqueous solution approved the second-order kinetic yielding good R^2 values of 1.00 and k values of 0.0781 to 0.1776.

5.2 Recommendations

Based on the results obtain in this work, a few recommendations that need to be considered for future establishment of data in order to get better data and higher efficiency of metal removal. The perspective that need to be considered are :

i) It will be effective if there are more experiment on various adsorbents could be done continuously.

ii) Try to add another economically adsorbents.

REFERENCES

Ahmaruzzaman M. Energy Fuels 2009;23 (3):1494.

Babel S., Kurniawan, T.A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water*: A review. J. Hazard.Mater*, B97, 219–243.

Bailey S.E., Olin T.J., Brika R.M., Adrian D.A. (2008). A review of potentially low-cost sorbent for heavy metals. *Water Resources*, 33: 2469–2479.

Barakat M.A. (2011) .New trends in removing heavy metals from industrial wastewater, *Arabian journal of chemistry*, 4, 361-377.

Bernard A. (2008). Cadmium & its adverse effects on human health, *Review article: Indian J Med Res, 128,* 557-664.

Cempel M., Nikel G., (2006) .Nickel : a review of its sources and environmental toxicology, *Polish J. Of Environ. Stud.*,15, 375-382.

Demibras A. (2008). Economic and environmental impacts of the liquid bio fuels. *Energy Edu Sci Technol* 22:37-58.

El-Ashtoukhy E.S.Z., Amin N.K., Abdelwahab O. (2008). Removal of Lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent, *Journal of desalination,* 223, 62-173.

Fu F., Wang Q. (2011). Removal of heavy metal ions from wastewaters : A review, *Journal of environmental management*, 92, 407-418.

Geankoplis, C.J, (2003). Transport Processes and separation process principles(includes unit operations). New Jersey: *Person Education, Inc*. p 761.

Hameed B.H., Mahmoud D.K., Ahmad A.L., (2008). Equilibrium modeling and kinetic studies on the adsorption of basicdye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste. *Journal of Hazardous Materials* ,158 (2008) 65–72

Ho Y.S., McKay G., The sorption of lead(II) ions on peat, Water Res. 33 (1999) 578–584

Inam E., Etim U., Eduok U., Essien J. (2012). Heavy Metals Sorption Potential of Calcareous shells of Animal Origin. *Interntional Journal of Chemical, Environmental and Pharmaceutical Research* 3,184-194.

Johnson T.A., Jain N., Joshi H.C., Prasad S. (2008). Agricultural and agro-processing wastes as low cost adsorbents for metal removal from wastewater: A review, *Journal of scientific & Industrial research*, 67, 647-658.

Lagergren S., Zur theorie der sogenannten adsorption geloester stoffe,Kungliga Svenska Vetenskapsakad, Handl. 24 (1898) 1–39.

Laila A.K., Feras F., Mohamad A.H.,Omar A.K., (2012).Adsorption from Aqueous Solution onto Natural and Acid Activated Bentonite. *American Journal of Environmental Science*, 2012, 8 (5), 510-522.

Lo S.F., Wang S.Y., Tsai M.J., Lin L.D. (2011). Adsorption capacity and removal efficiency of heavy metal ions by Moso and Ma bamboo activated carbons, *Chemical engineering research and design*, CHERD-926, 10 pages.

Ngah W.S.W., Hanafiah M.A.K.M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review, *Biosource Technology*, 99, 3935-3948.

Ozsoy H.D., Kumbur H., Saha B., Leeuwen J.H.V. (2008). Use of Rhizopus Oligosporus produced from food processing wastewater as a biorsorbent for Cu(II) ions remocal from the aqueous solutions . *Bioresource Technology*, 99, 4943-4948.

Ozturk, N., Kavak, D., (2005). Adsorption of boron from aqueous solution using fly ash:and column studies. *Journal of hazardous Materials*. B127, 81-88.

Pino G.H., Mesquita de L.M.S., Torem M.L. Biosorption of heavy metals by powder ofgreen coconut shell. *Sep. Sci. Technol*. 41 (2006) 3141–3153.

Santos A.C.V.D., Masini J.C. (2007). Evaluating the removal of Cd (II), Pb (II) and Cu(II) from a wastewater sample of a coating industry by adsorption onto vermiculite, *Applied clay science*, 37, 167-174.

Sud D., Mahajan G.Kaur M.P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions. *Bioresource Technology*, 99 , 6017–6027

Sun K., Jiang J.C. (2010). Preparation and characterization of activated carbon from rubber seed shell by physical activation with steam, *Biomass and bio energy* , 34, 539 - 544.

Tsai W.T., Chen H.R, Kuo K.C, Lai C.Y, Su T.C, Chang Y.M, Yang J.M (2009). The adsorption of methylene blue from aqueous solution using waste aquacultural shell powders. *J. Environ. Eng. Manage*, 19(3), 165-172 ,165-166

Wong K.K., Lee C.K., Low K.S., Haron M.J. (2003). Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk, *Process Biochemistry*, 39, 437-445.

APPENDICES

APPENDIX A

Figure A1: Rock melon shell before drying

Figure A2: Rock melon shell after drying and grinding

Figure A3: Sample after shaking on rotary shaker

Figure A4: Sample filtered using Whatman Filter Paper

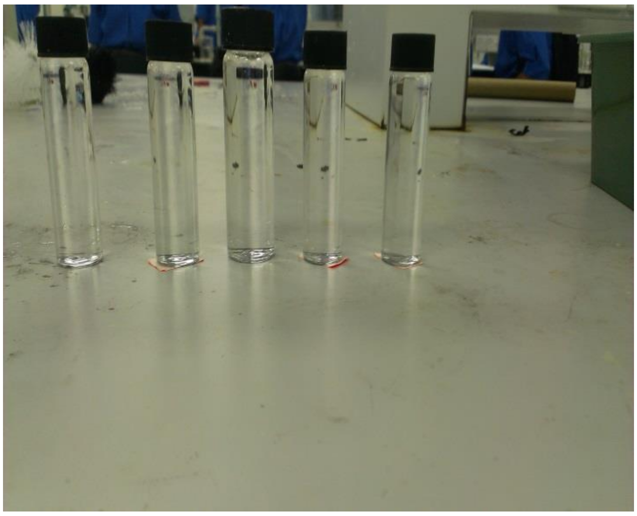

Figure A5: Sample ready for AAS analyzing

APPENDIX B

Table B1: Effect of solution pH on Cd (II)

Cd (II)			
Solution pH	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
2	100	1.28	98.72
4	100	0.86	99.14
6	100	0.48	99.52
8	100	0.069	99.931
10	100	0.033	99.967

Table B2: Effect of solution pH on Ni (II)

Ni (II)			
Solution pH	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
2	100	0.987	99.013
4	100	0.743	99.257
6	100	0.133	99.867
8	100	0.057	99.943
10	100	0.046	99.954

Table B3: Effect of solution pH on Cu (II)

Cu (II)			
Solution pH	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
2	100	0.648	99.352
4	100	0.361	99.639
6	100	0.072	99.928
8	100	0.041	99.959
10	100	0.115	99.885

Table B4: Effect of contact time on Cd (II)

Cd (II)			
Contact Time, min	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
40	100	0.977	99.023
60	100	0.75	99.25
80	100	0.497	99.503
100	100	0.051	99.949
120	100	0.039	99.961

Table B5: Effect of contact time on pH on Ni (II)

Ni(II)			
Contact Time, min	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
40	100	1.431	98.569
60	100	1.528	98.472
80	100	1.082	98.918
100	100	0.806	99.194
120	100	0.031	99.969

Table B6: Effect of contact time on Cu (II)

Cu (II)			
Contact Time, min	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
40	100	0.482	99.518
60	100	0.125	99.875
80	100	0.048	99.952
100	100	0.049	99.951
120	100	0.035	99.965

Table B7: Effect of adsorbent dosage on Cd (II)

Cd(II)			
Adsorbent dosage, g	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
0.1	100	15.13	84.87
0.2	100	12.91	87.09
0.3	100	11.2	88.8
0.4	100	1.306	98.694
0.5	100	0.356	99.644

Table B8: Effect of adsorbent dosage on Ni (II)

Ni(II)			
Adsorbent dosage, g	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
0.1	100	3.267	96.733
0.2	100	1.357	98.643
0.3	100	0.34	99.66
0.4	100	0.381	99.619
0.5	100	0.046	99.954

Table B9: Effect of adsorbent dosage on Cu (II)

Cu(II)			
Adsorbent dosage, g	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
0.1	100	13.22	86.78
0.2	100	9.08	90.92
0.3	100	4.94	95.06
0.4	100	4.73	95.27
0.5	100	4.52	95.48

Table B10: Effect of initial concentration on Cd(II), Ni(II) and Cu (II)

Initial conc., mg/L	**Removal Efficiency, %**		
	Cd	**Ni**	**Cu**
20	92.7	96.2	98.3
40	94.3	97.9	98.6
60	94.8	98.4	98.7
80	95.5	98.5	99.0
100	95.9	98.6	99.2