REDUCTION OF Cd(II), Ag(II) AND Cu(II) USING RUBBER SEED SHELL : ADSORPTION ISOTHERM AND KINETICS

HAJAR ATHIRAH BINTI MOHD SUKRI

DEGREE OF BACHELOR OF CHEMICAL ENGINEERING

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by

HAJAR ATHIRAH BINTI MOHD SUKRI

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SUPERVISOR'S DECLARATION

"I hereby declare that I have checked this thesis and in my 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 supervisor	:	Dr. Ir. Said Nurdin
Position	:	URP Supervisor
Date	:	February 2013

STUDENT'S DECLARATION

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

Signature	:	
Name	:	Hajar Athirah Binti Mohd Sukri
Id number	:	KA10150
Date	:	February 2013

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REDUCTION OF Cd(II), Ag(II) AND Cu(II) USING RUBBER SEED SHELL: ADSORPTION ISOTHERM AND KINETICS

ABSTRACT

Increasing industry in Malaysia produce high amount of wastewater, thus increase the heavy metal contaminants that become global concern of environment. Adsorption of heavy metals by activated carbon will need higher cost compare to the other adsorbents. Thus, an alternative way of waste utilization is initializing by researcher to reduce wastewater management cost. The objective of this research is to investigate the potential of rubber seed shell as alternative adsorbent to reduce Cd(II), Ag(II) and Cu(II) ions from aqueous solution by find its kinetic and adsorption isotherm using batch techniques. The adsorbent and adsorbate prepared is used for testing the effect of removal of the ions by the variation parameters of solution pH (pH2, Ph4,pH6 pH8,pH10), contact time (40min, 60min, 80min, 100min, 120min), adsorbent dosage (0.1g, 0.2g, 0.3g, 0.4g, 0.5g) and initial concentration (20ppm, 40ppm, 60ppm, 80ppm, 100ppm). The optimum ph=6, effective time and dosage of 120min and 0.3g is use through all parameters variation. All the experiments are using batch adsorption process and finalize by shake using rotary shaker and analyze using Atomic Absorption Spectroscopy (AAS). This adsorption case fit Langmuir isotherm with correlation coefficient of 0.9991 and satisfactory Pseudo-second order kinetic with correlation coefficient of 1 for all metal and adsorption constant range 0.0662 to 0.1873 g/mg.min. This research approved that rubber seed shell can be used as an alternative adsorbent to reduce Cd (II), Ag (II) and Cu (II) ions from aqueous solution.

PENGURANGAN Cd(II), Ag(II) DAN Cu(II) MENGGUNAKAN LAPISAN LUAR BIJI GETAH: ISOTERMA PENJERAPAN DAN KINETIK.

ABSTRAK

Industri yang semakin meningkat di Malaysia menghasilkan jumlah air sisa yang tinggi, seterusnya meningkatkan kadar logam berat di dalam air sisa yang menjadi pencemaran alam sekitar. Penjerapan logam berat oleh karbon aktif memerlukan kos yang lebih tinggi berbanding dengan adsorben lain. Oleh itu, alternatif karbon aktif dimulakan oleh penyelidik untuk mengurangkan kos pengurusan air sisa. Objektif kajian ini adalah untuk menyiasat potensi lapisan luar benih getah sebagai adsorben alternatif untuk mengurangkan Cd (II), Ag (II) dan ion Cu (II) daripada larutan akueus dengan mencari kinetik dan isoterma penjerapan. Adsorben dan bahan terjerap disediakan dan digunakan untuk menguji kesan penyingkiran ion oleh parameter perubahan pH larutan (PH2, pH4, pH6 pH8, pH10), masa (40min, 60min, 80min, 100min, 120min), dos adsorben (0.1g, 0.2g, 0.3g, 0.4g, 0.5g) dan kepekatan awal (20ppm, 40ppm, 60ppm, 80ppm, 100ppm). pH optimum = 6, masa yang berkesan dan dos yang efektif adalah 120min dan 0.3g digunakan. Semua eksperimen menggunakan penggoncang dan analisis menggunakan Spektroskopi Serapan Atom (AAS). Kajian penjerapan ini memenuhi isoterma Langmuir dengan nilai R^2 adalah 0,9991 dan kinetik Pseudo kedua nilai R^2 adalah 1 untuk semua logam dan pemalar 0.0662-0.1873 g / mg.min. Kajian ini membuktikan bahawa lapisan luar benih getah boleh digunakan sebagai bahan penjerap alternatif untuk mengurangkan Cd (II), Ag (II) dan ion Cu (II) daripada larutan akueus.

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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
RSS	Rubber seed shell
t	Time

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LIST OF SYMBOLS

^{o}C	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

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Heavy metals in wastewater exhibit a global concern of environment due to its toxicity characteristics to many organisms (El-Ashtoukhy, Amin and Abdelwahab, 2008). 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 and Hanafiah, 2008). Malaysia has been an industrial develop country which also go through with same environment problem that other countries experienced.

Heavy metals can be considered if it exists with density of 5g per cubic centimeter (Barakat, 2011). Cadmium (II), Silver (II) Copper (II) is an example of heavy metal that commonly exists in industrial wastewater. Cd (II) and Cu (II) commonly come from coatings industry wastewater (Santos, 2007) while Ag (II) majorly from mines and quarries industries. Cadmium is an extremely toxic metal that leads to respiratory tract, kidney failure which may lead to fatal cause of renal failure by inhalation and may cause kidney, liver and bones fracture problem by ingestion. Copper metal and its alloy have been used over 1000 years. Although copper have been an essential needs in human health but it still can cause health problem to organism. One may experience irritation to nose, mouse and eyes which result dizziness, vomiting, diarrhea and stomachaches. In critical way, it may cause brain damage, renal damage and deposition in cornea. In the term of environmental, copper may interrupt activity in soils and activity of microorganism and earthworms. Silver very hazardous in case of eye contact (irritant) and severe over-exposure can result in death. Inflammation of the eye by silver is characterized by redness, watering, and itching.

In order to combat this problem, the traditionally used procedures for removal of metal is chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Johnson *et. al*, 2008). However, these techniques have certain disadvantages including incomplete metal removal, high reagent and energy consumption, production of toxic sludge or other waste products that require disposal. In other words, this traditional method is uneconomical and ineffective for concentration higher than allowable concentration. Thus, another method is discovering in this study to catch up with previous technology for metal removal. Adsorption process is selected in this study because it is effective and able to remove various levels of soluble heavy metals which is Cu(II), Cd(II) and Ag(II) in wastewater. Lately, interest has been focused on using low cost adsorbents or materials especially agricultural by products for the removal of heavy metal from industrial wastewater (Wong *et. al,* 2003). Several bio sorbents such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk have been used for the treatment of metals in aqueous solution (Barakat, 2010).

The benefits including environmental benefits from the reuse of solid waste which is rubber seed shell for this study have been investigate to evaluate its potential for the treatment of heavy metals in wastewater. In this current investigation, the potential of rubber seed shell has been assessed for the removal of metal ions such as silver, cadmium and copper. In the other hand, this study also investigates the effect of Ph solution, contact time, adsorbent dosage, and initial concentrations. The purpose of this research is to assess the probability of implementing rubber seed shell as adsorbents for the adsorption of heavy metals in wastewater by applying the deviation of certain parameters.

1.2 Problem Statement.

Heavy metals from Malaysia industrial wastewater discharge into the ecosystems including rivers and seas will cause water pollution if the effluents are not properly treating. In spite of that, the situation will increased the heavy metal contaminants in ecosystems and directly increased the wastewater management cost in plant. In addition, the use of commercial activated carbon is high cost and energy consumptions. Thus, an unconventional of low cost adsorption system is investigate using rubber seed shell (RSS) that shows good precursor for activated carbon and was an attractive source in producing high capacity activated carbon (Sun and Jiang, 2010). If the effluents are not suitable treated the company will need higher cost for the treatment.

In spite of that, Malaysia has become a rapid growth rubber country. According to the association of natural rubber producing countries, Malaysia is estimated own about 1,229,940 hectares of rubber plantation which resulted about 355,200,000 kg fat and 136,800,000 kg protein waste per year from rubber seed shell (Eka, Tajul and Wan Nadiah, 2010). This shell of *Hevea Brasiliensis* is said to be one of many agricultural waste which has become an environmental problem. Rubber seed shell can found at any rubber tree plantation areas such as Pahang which have the largest rubber plantation area followed by Johor, Perak, Kelantan and other state.

Thus, the purpose of this study is to investigate the probability of implementing rubber seed shell as adsorbents for the adsorption of heavy metals in wastewater by applying the deviation of certain parameters. This study focused on its adsorption kinetic data and the best fits equilibrium adsorption data using Isotherm Langmuir.

1.3 Objective.

- To reduce Cadmium (II), Silver (II) and Copper (II) by using rubber seed shell as adsorbent. In order to reduce these metals, a batch adsorption process is chose due to its easy and simplest method. Cadmium (II), Silver (II) and Copper (II) was added with rubber seed shell as adsorbent and some parameters was varied to get the results.

- To find the kinetic and isotherm Langmuir by implementing rubber seed shell as adsorbent for Cadmium (II), Silver (II) and Copper (II). Kinetic and isotherm Langmuir is important in adsorption because it described the mechanism of adsorption process and evaluated the value of maximum adsorption capacity using related equations.

1.4 Scope of the Study.

- This study was done to observe the reduction of Cadmium (II), Copper (II) and Silver (II) from aqueous solution using rubber seed shell as adsorbent. The reduction of Cadmium (II), Copper (II) and Silver (II) from aqueous solution was observed in term of its removal efficiency using the optimum operating condition determined.

- Observation and investigation of the effect of process condition for Cadmium (II), Silver (II) and Copper (II) that can be removed by using rubber seed shell. During the experiment, the parameters were observed and the equilibrium point for each parameters is used for further investigation.
- Determination Cadmium (II), Silver (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)
- Determination of Langmuir adsorption isotherm and kinetic for Cadmium (II), Silver (II) and Copper (II) that can be removed using rubber seed shell as low cost adsorbents which is rubber seed shell.

1.5 Rationale and Significance.

This study is conducted to remove heavy metal ions including Cd (II), Ag (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, rubber seed shell acts as adsorbents while the heavy metals are the adsorbate (adsorbed material). Physical and chemical methods are available for heavy metal removal but it was quite expensive and ineffective. Hence, many research and study is conducted previously to find other natural resources which is using biological methods that could be an alternative methods. Other agricultural waste materials such as tea waste, rice husk, coconut husk, oil palm fibre, orange peel ,sawdust, jackfruit peel, peanut husk and many more are an example of low cost agricultural waste instead of rubber seed shell which available in Malaysia.

The usage of agricultural waste materials as an adsorbent is the only way to reduce agricultural waste instead of reducing pollution. Rationally, the rubber plant product including rubber latex and leaves is used in industry, so the rubber seed are the waste of the rubber plant. This study will reduce environment pollution by the usage of rubber seed shell in wastewater treatment and make rubber plant waste become a useful material that will give benefits to industrial and other sectors in Malaysia. Rubber seed shell is choosing in this research because of its moisture, volatile matters and fixed carbon characteristics that can replaced a conventional activated carbon adsorbents according to Sun and Jiang, (2010). Besides that, rubber seed shell also effective for variation concentration, economically practicable and easily to found as waste product at rubber production and plantation areas. In the other hand, rubber seed shell could be good adsorbents for the removal of heavy metals instead of being an agricultural waste that may increase environmental pollution in Malaysia and other rubber growth country. Besides that, this research also aims to convert waste to wealth.

CHAPTER 2

LITERATURE REVIEW

Excessive level of heavy metals that are discharged to the ecosystem become global issues and concern nowadays (Oszoy *et. al*, 2008; Johnson *et. al*, 2008 and Fu *et. al*, 2011). 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 *et. al ,2008* ; Ngah and Hanafiah, 2008). This global issue considered risky because of rapid industrialization and it may cause several health problem to human instead of defect flora and fauna especially to Malaysia. These heavy metals commonly come from industrial wastewater that is not properly treating.

Although, heavy metals have many applications to domestic use but the release of these metal may effects human health together with ecosystems (Ozsoy *et. al*, 2008; Fu and Wang, 2011). 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, stomach aches, dizziness, vomiting and diarrhea. Besides, copper also will cause damage to kidney, lung and eyes. Over exposure to silver may lead to the decreased of blood pressure, diarrhea, stomach irritation and decreased respiration. In addition, long-term inhalation or ingestion of soluble silver compounds may cause agrarian.

2.1 Activate Carbon as Adsorbents.

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.

2.2 Agriculture Waste as Adsorbents.

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. A study by Wong (2003) investigates the potential of modified rice husk as adsorbents. The study agreed that the modified rice husk by column closely with the levels of batch equilibrium studies. Besides that, *bagasse* (an agricultural waste from sugar processing) were also have been studied the usage as adsorbents by Mohan and Singh (2002) which shows that the heavy metal removal capacity is increase as the temperature is increase and the data fits both Freundlich and isotherm Langmuir. The isotherm data and mechanism is achieved by using the same manipulated variables as this study. A similar agricultural waste as rubber seed shell also has been investigated. They are including cocoa shell, hazelnut shell and pecan shell (Johnson *et. al*, 2008). Each of these adsorbents shows different results, isotherm data and heavy metal removal potential. In spite of that, rubber seed shell is target to have similar results like other low cost adsorbent before since rubber seed shell is estimated 300kg/ha which is easy to found (Eka, Tajul and Wan Nadiah, 2010).

CHAPTER 3

MATERIALS & METHODS

3.1 Materials.

This study main material is rubber seed which come from Pahang state rubber plantation area. The chemicals involved in this study are Cadmium (II) sulphate, Silver (II) sulphate, Copper (II) sulphate, sodium hydroxide and hydrochloric acid. Cadmium (II) sulphate, Silver (II) sulphate and Copper (II) sulphate purchased from sigma Aldrich and used as an adsorbate for this adsorption study. Sodium hydroxide and hydrochloric acid was used to control pH during all experiment was get from University Malaysia Pahang chemical engineering laboratory.

3.2 Overall Methodology Flow Chart.

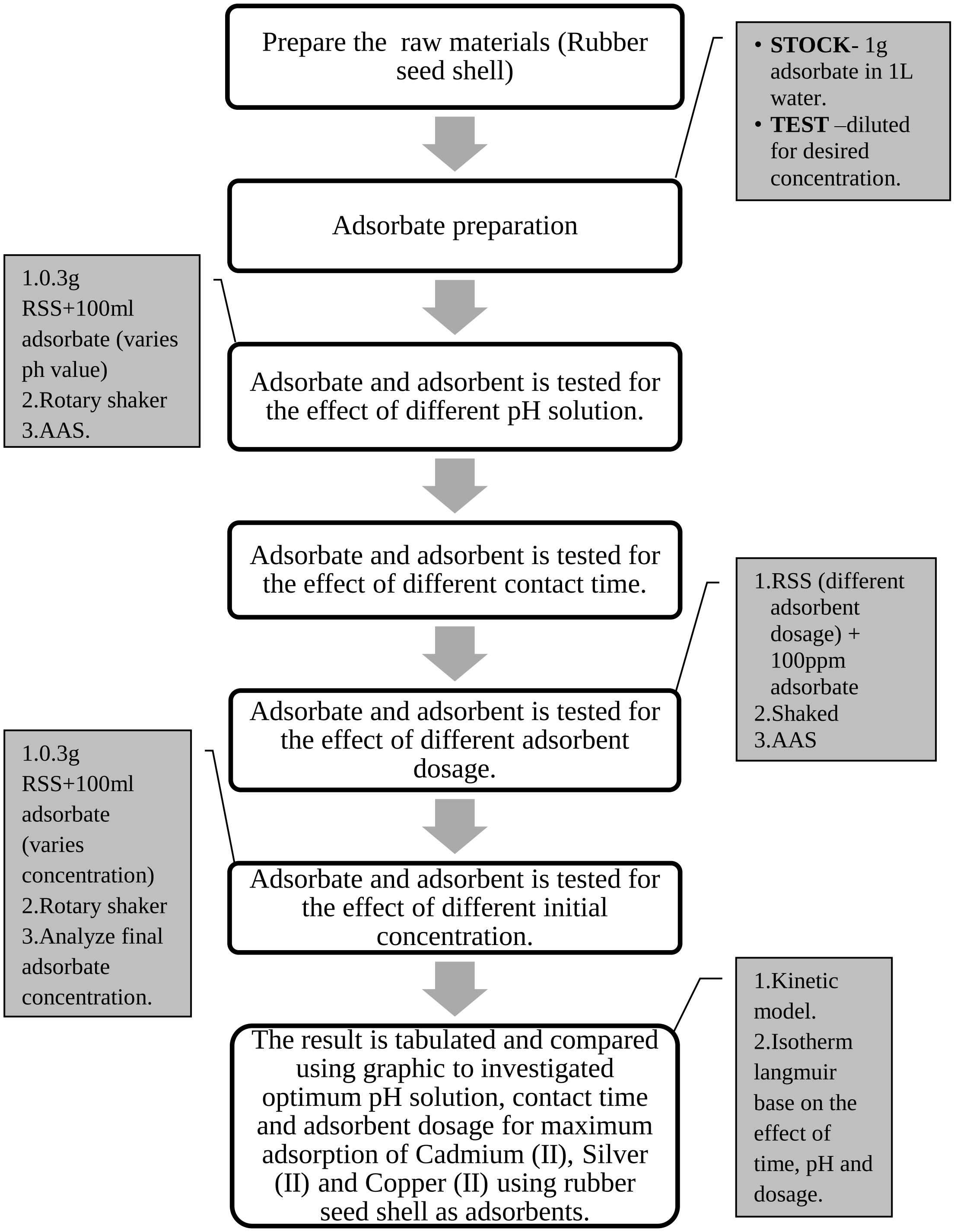

Figure 3.1: Overall flow chart for experimental methodology.

3.3 Experimental Methodology.

3.3.1 Rubber Seed Shell.

The study of heavy metal removal from wastewater used rubber seed shell as the main materials. Rubber seed shell was obtained from rubber plantation areas in Pahang state. Wash the rubber seed shell with deionized water, to remove dirt and impurities. The rubber seed shells were dried in the open air and grinded. The grinding product in form of powder was sieved using a laboratory sieve and the 160 μm portion was separated. This portion was washed with deionized water several times until the wash DI water was free of colour and turbidity. The clean powders proceed to oven at 80 ˚C to be dried and kept it in a sealed polythene bag. This step is important to make sure the powder kept in fresh for the next procedures.

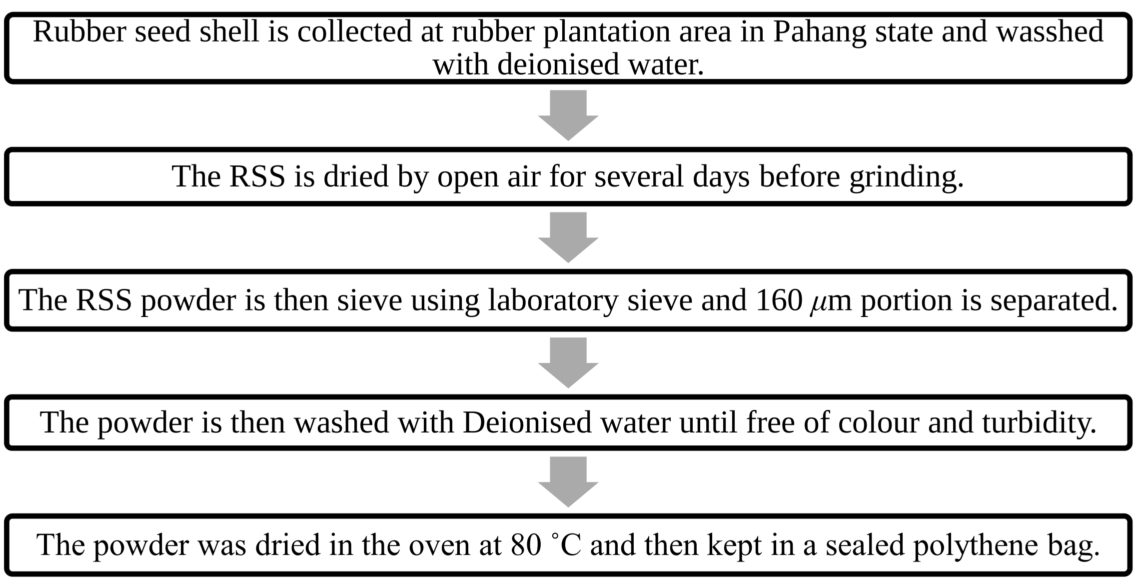

Figure 3.2: Flow diagram of preparation of rubber seed shell (RSS)

3.3.2 Preparation of Adsorbate.

Stock solution will be prepared by dissolved 100mg of Cadmium (II) sulphate, Silver (II) sulphate and Copper (II) sulphate in 1L of distilled water in different volumetric flask.

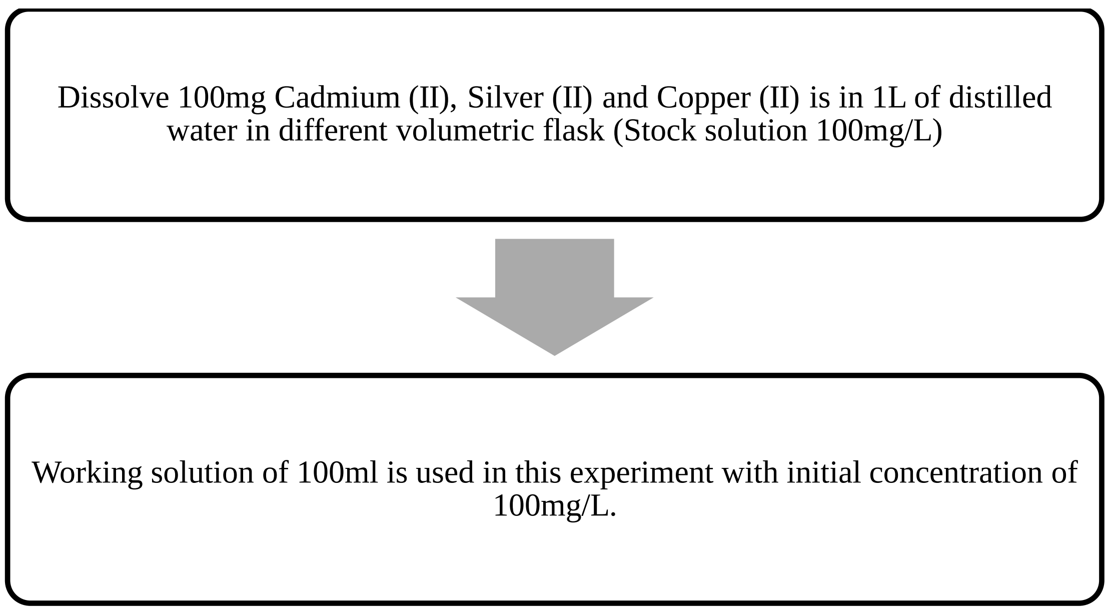

Figure 3.3: Flow diagram of preparation of adsorbate.

3.3.3 Effect of pH Solution.

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

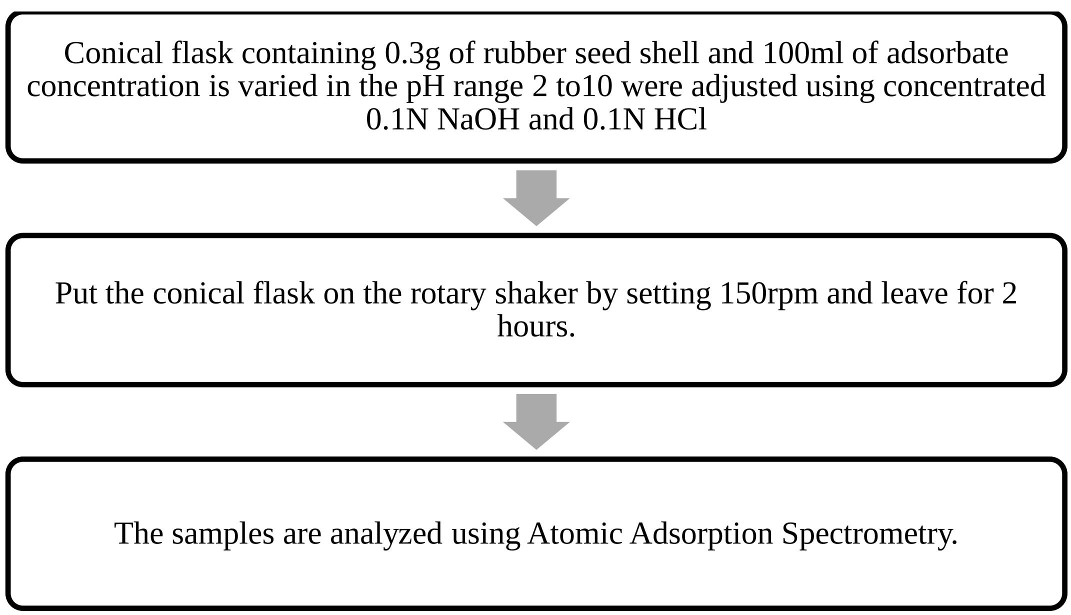

Figure 3.4: Flow diagram of pH solution.

3.3.4 Effect of Contact Time.

In order to evaluate the effect of contact time over heavy metals removal, the adsorbate solution was mixed with 0.3g of RSS powder. The mixture was shaked 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.

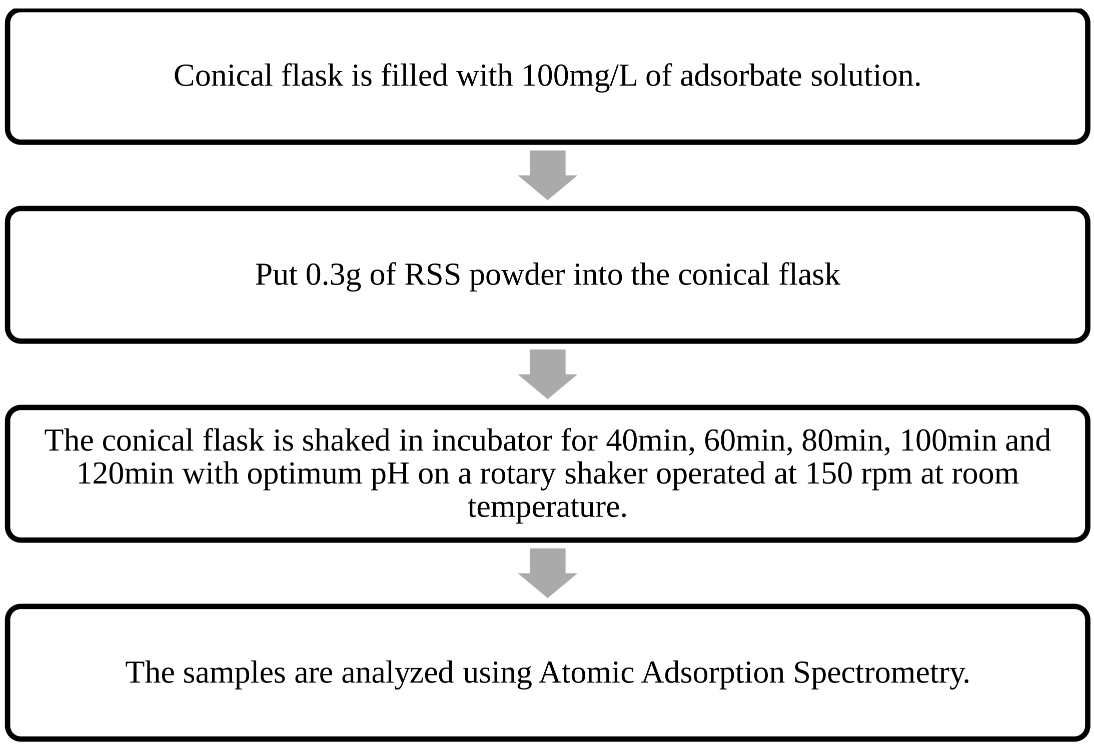

Figure 3.5: Flow diagram of the effect of contact time.

3.3.5 Effect of Adsorbent Dosage.

Initial adsorbate solution concentration of 100 mg/L was used with adsorbent sample varying in weight of 0.1 grams, 0.2 grams, 0.3 grams, 0.4 grams and 0.5 grams. The contact time and pH kept constant at 120min and pH=6 that was obtained from previous experiment before conduct the effect of rubber seed shell dosage experiment at 25˚C. Samples are filtered using Whatman filter paper and analyzed using AAS.

Fill the conical flask with 100mg/L of adsorbate solution.

↓

The flask is shaked in incubator after add rubber seed shell powder of (0.1g-0.5g).

↓

The samples are analyzed using Atomic Adsorption Spectrometry.

Figure 3.6: Flow diagram of the effect of adsorbent dosage.

3.3.6 Effect of Initial Concentration.

In this experiment, the initial adsorbate solution concentration was varied from 20mg/L, 40mg/L, 60mg/L, 80mg/L and 100mg/L. The effect of initial concentration is analyzed using constant solution optimum pH, 0.3g of adsorbent dosage and sample contact time of 120 minutes and the sample was shaked on a rotary shaker operated at 150rpm and 25^0C.

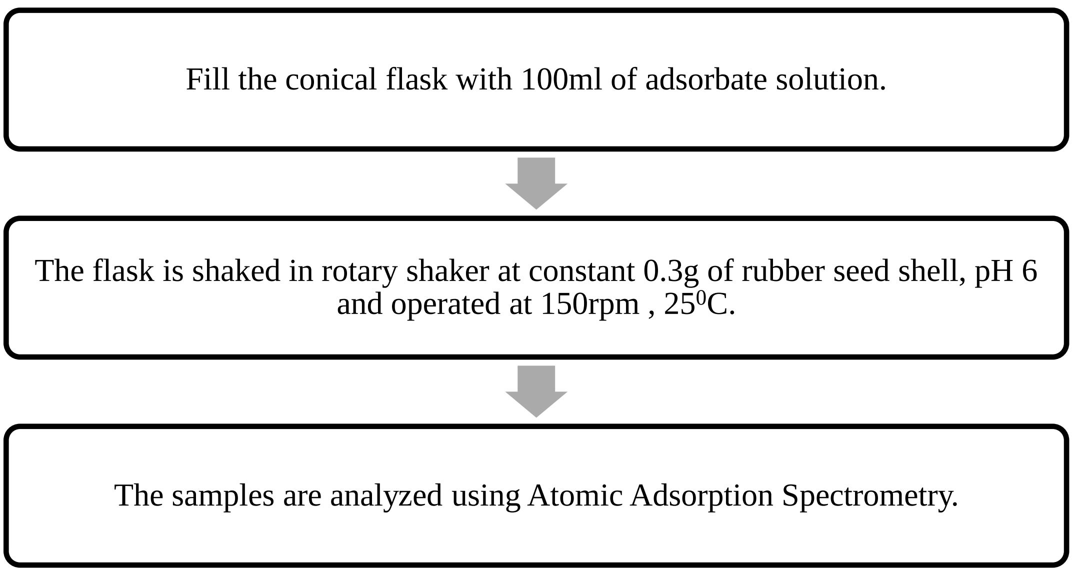

Figure 3.7: Flow diagram of the effect of initial concentration.

Experiment on the four variables, effect of pH solution, contact time, adsorbent dosage and initial concentration was done for adsorbate, Cadmium (II) sulfate, Silver (II) sulfate and Copper (II) sulfate solution.

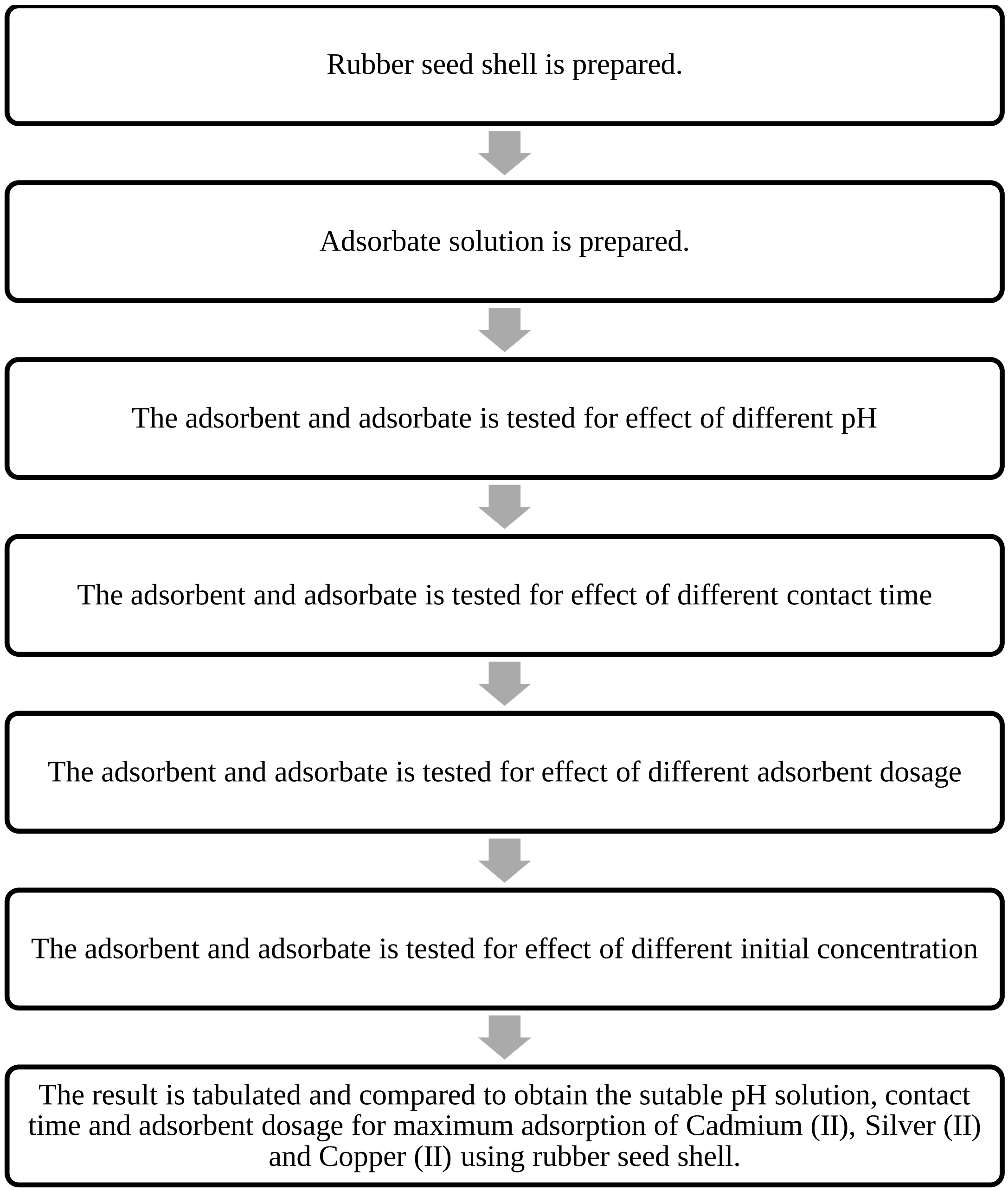

Figure 3.8: Flow diagram of reduction of Cd(II), Ag(II) and Cu(II) using rubber seed shell process.

3.3.7 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 3.1.

$$M_1V_1 = M_2V_2 \tag{3.1}$$

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.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Effect of Solution pH

The pH of the solution has a major impact on the uptake of heavy metal, since it determines the surface charge of the adsorbent which means the degree of ionization and speciation of the adsorbate (El-Ashtoukhy, 2008). In order to establish the effect of pH was studied at different pH values which were conducted by varying the optimum pH range from pH=2 to pH=10 for heavy metals. The graph heavy metal removal efficiency, % versus solution pH is plotted by using Equation 4.1 and shown in Figure 4.1.

$$\%\, Removal\ Efficiency = \frac{C_O - C_e}{C_e} \, X \, 100 \qquad (4.1)$$

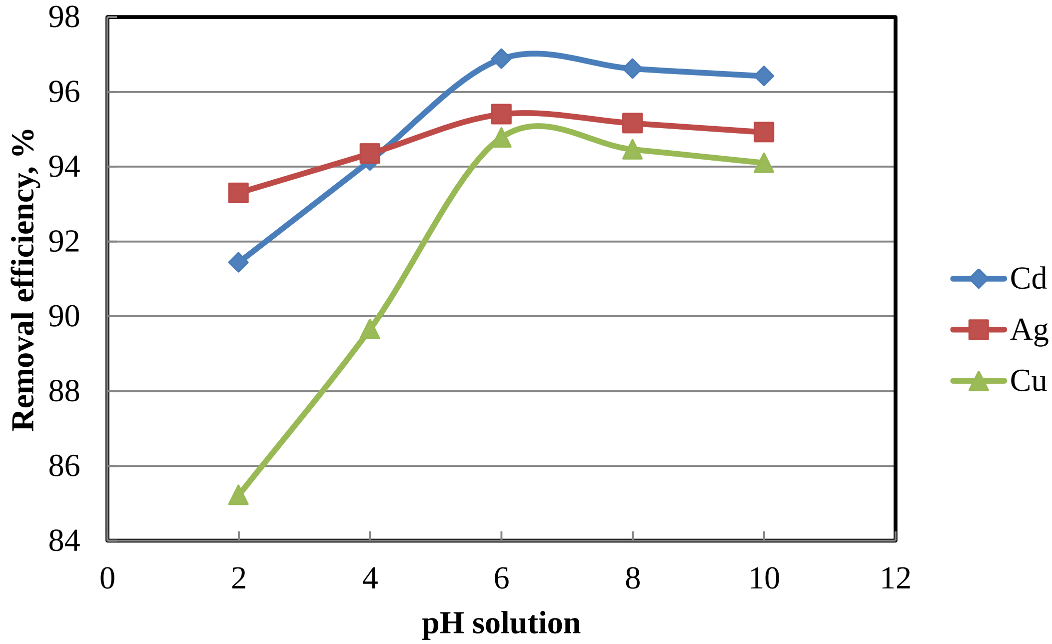

Figure 4.1: Effect of pH on Cd(II), Ag(II) and Cu(II) (Initial concentration = 100 mg/L, Adsorbent dosage = 0.3 g and contact time = 2 hours).

Figure 4.1 shows the effect of solution pH on the adsorption of heavy metal. The maximum removal of heavy metal were observed at pH= 6 and significantly decreased by reducing the pH values and slightly decreased at higher pH values. The decrease in adsorption at low pH values may be due to the competitiveness of hydrogen and heavy metal ions on the sorption sites. Referring to El-Ashtoukhy *et. al*, (2008) as solution pH further increased, heavy metal became insoluble and produces precipitation which makes it impossible for adsorption process to happen resulting in the decrease the rate of adsorption. Barakat, (2011) agrees that an acidic pH ranging from 2 to 6 is effective for metal removal by low cost adsorbents. The sorption of cadmium decrease at higher pH value because cadmium starts to precipitating at higher pH values resulting impossible sorption occur (Benguella and Benaisse,2002). Besides, Kaewsarn *et. al*,

(2001) supported that when the pH value increased, the competing effect of $H3O+$ ions decreased and positively charged metal (II) ions took up the free binding sites.

4.2 Effect of Adsorbent Dosage

One of the parameters that strongly affect the sorption capacity is the concentration of the adsorbents. Adsorbent dosage is an important parameter since it determines the capacity of an adsorbent for a given initial concentration of the adsorbate (Aydin, Bulut and Yerlikaya, 2008). With the fixed metal initial concentration of 100 ppm, it can easily be inferred that the percent removal of metal ions increases with increasing weight of adsorbents as shown from figure below. Amount of adsorbent was varied from 0.1g to 0.5 g with fixed initial concentration, pH=6 and contact time of 120 minutes. The results indicated the percent removal of metal increased with the increase in the amount of adsorbent and removal efficiency. The graph heavy metal removal efficiency, % versus adsorbent dosage is plotted by using Equation 4.1 and shown in Figure 4.2.

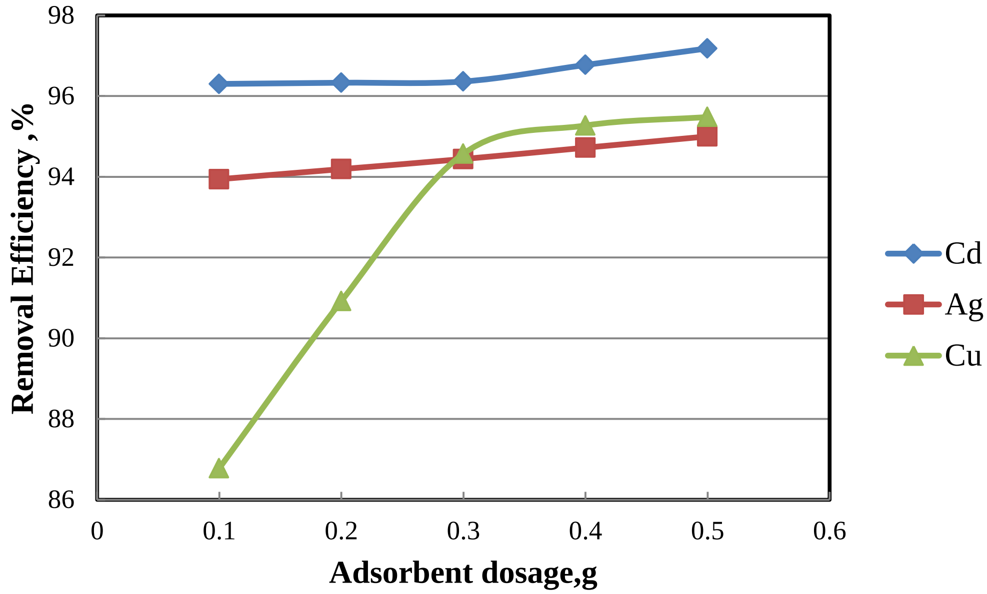

Figure 4.2: Effect of Adsorbent Dosage on Cd(II), Ag(II) and Cu(II) (Initial concentration = 100 mg/L, pH Solution = 6 and contact time = 2 hours).

From figure 4.2 above, it shows the influence of adsorbent dosage (g) on the heavy metals removal. It shows that the increasing of adsorbent dosage generally increased the metal removal until the equilibrium was reached at 0.3g for every each metal. This happened due to availability of surface area of adsorption. The increase quantity of adsorbent result the increase of adsorption surface area which then improves the metal removal. This can be explained by the fact that a fixed mass of adsorbent can only adsorb a certain amount of metal. Senthilkumar *et. al*, (2011) agrees that the adsorption sites remain unsaturated during the adsorption whereas the number of sites available for adsorption sites increases by increasing the adsorbent dose.

4.3 Effect of Contact Time

The effect of contact time on the copper (II), Silver (II) and Cadmium (II) reduction was studied and the result is shown in Figure 4.3. The equilibrium time required for the adsorption of heavy metals Cu (II), Ag (II) and Cd (II) is studied by fixing 0.3g/L of the rubber seed shell adsorbent into initial concentration of 100mg/L and data is taken at different time intervals. The graph of heavy metal removal efficiency, % versus contact time, minute were plotted by using Equation 4.1 and shown in Figure 4.3.

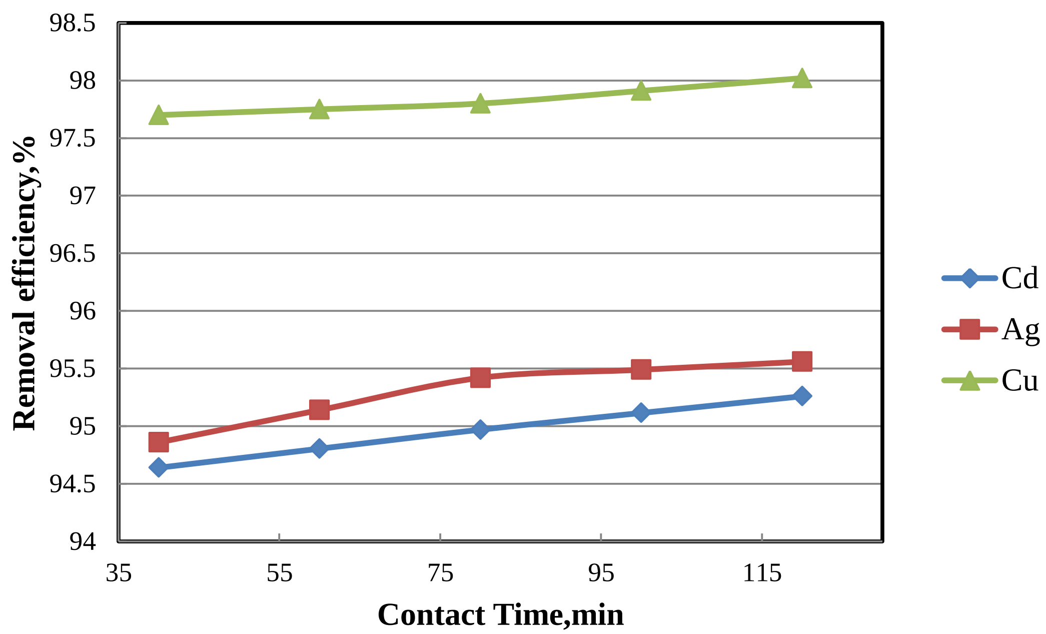

Figure 4.3: Effect of contact time on Cd (II), Ag (II) and Cu (II) (Initial concentration = 100 mg/L, pH Solution = 6 and adsorbent dosage = 0.3g).

The data obtained from the reduction of copper (II), Silver (II) and Cadmium (II) ions into the rubber seed shell showed that the adsorption increases with increase of contact time as shown in figure 4.3. The reduction of copper (II), Silver (II) and Cadmium (II) was rapid for the first 80 minutes and equilibrium was nearly reached after 120 minutes. Hence, in the presence work the 120 minutes is chosen as the equilibrium time. The rate in percent of copper (II), Silver (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 (Senthilkumar *et. al*, 2011). 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.

4.4 Effect of Initial Concentration.

The adsorption of copper (II), Silver (II) and Cadmium (II) by the rubber seed shell was studied at different initial concentration varied from 20 to 100 mg/L and observed with constant solution pH=6, contact time of 120minutes and 0.3g of adsorbent. The graph of heavy metal removal efficiency, % initial concentration, mg/L were plotted by using Equation 4.1 and shown in Figure 4.4.

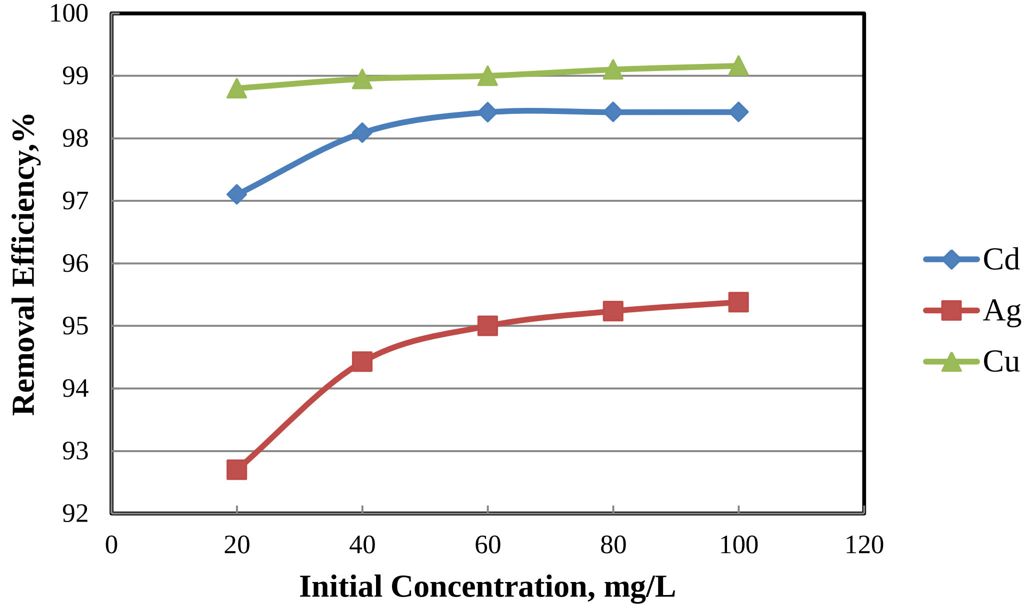

Figure 4.4: Effect of initial concentration on Cd (II), Ag (II) and Cu (II) (pH Solution = 6, contact time = 120 min and adsorbent dosage = 0.3g).

Figure above shows the effect of initial metal concentration to the reduction of Cd (II), Ag (II) and Cu (II). Generally, all metal shows rapid increase of removal at first 60 mg/L while the metal removals slowly achieve equilibrium at 60 mg/L forward. Besides, it also clear that with the increasing initial concentrations, the percent metal removal will become equilibrium. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the liquid and solid phases, hence a higher initial concentration of metal ions may increase the adsorption capacity (Oszoy *et. al*, 2008). El-Ashtoukhy *et. al*, (2008) believe that at low concentrations, the metals are adsorbed by specific sites while with the increasing concentrations, the specific sites are saturated and the exchange sites are filled.

4.5 Adsorption Equilibrium.

Adsorption isotherm is a mathematical model that is important to establish the most appropriate correlation for the equilibrium curves and to optimize the design of an adsorption system (Hameed *et. al*, 2008). The most commonly used isotherms are Langmuir and Freundlich isotherms which are used to find out the relation between the equilibrium concentrations of the adsorbate in liquid phase and in the solid phase (Senthilkumar *et. al*, 2011). Experimental isotherm data were conducted at an equilibrium time of 120 minute, constant adsorbent dosage of 0.3g, and adsorbate solution with pH=6. Interact with adsorbents and is critical in optimizing the use of adsorbents.

4.5.1 The Langmuir Isotherm.

Langmuir is the most important model of monolayer adsorption, based on the assumption that there are a fixed number of adsorption sites, each sites can hold only one adsorbate molecule at which all sites are equivalent and no interaction between adsorbed molecules (Zheng *et. al*, 2007). The linear Langmuir equation (Senthilkumar *et. al*, 2011) is as Equation 4.2.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4.2}$$

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 q_m is the maximum amount of metal ions required (mg/g). The Langmuir equation can be rearranged to linear form as Equation 4.3 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/qe versus 1/Ce in the Figure 4.5.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e} \tag{4.3}$$

Where q_m is the maximum adsorption capacity for Cadmium, Silver 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 3.57 mg/g to 24.57 mg/g. Langmuir isotherm fitted well this adsorption case with the correlation coefficient of 0.9991.

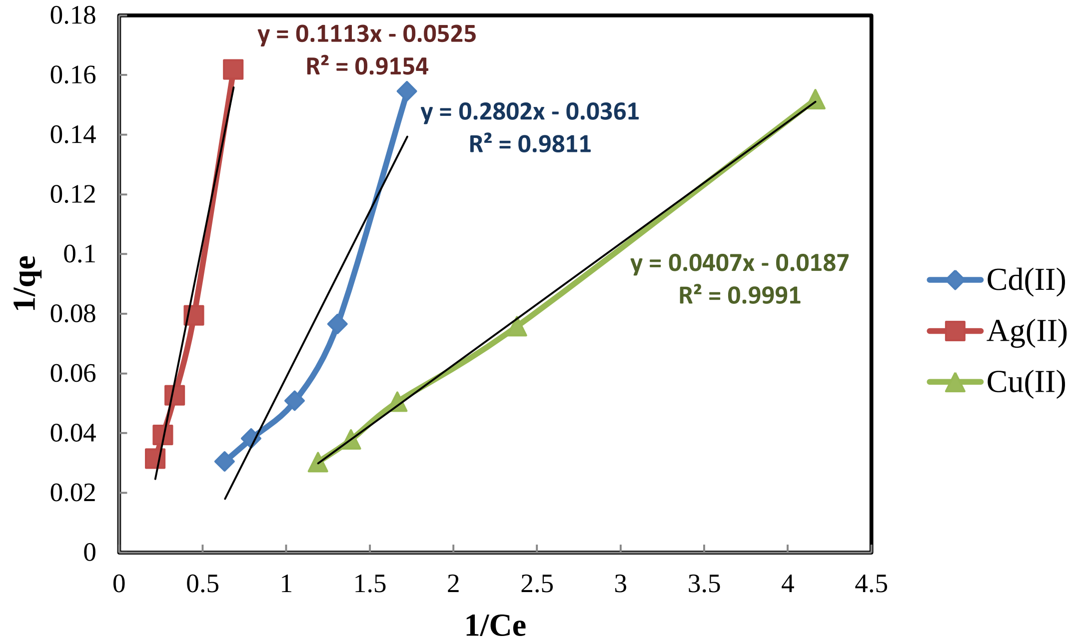

Figure 4.5: Langmuir Isotherm of Cd(II), Ag(II) and Cu(II) Adsorption Using Rubber Seed Shell.

4.5.2 The Freundlich Isotherm.

The freundlich isotherm model is an empirical relationship describing the adsorption of solute from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amounts of Cd(II), Ag(II) and Cu(II) heavy metals adsorbed per unit mass of adsorbent, q_e and the concentration of the metals at equilibrium, C_e.

Senthilkumar *et. al,* (2011) agrees that the Freundlich isotherm is purely empirical based on sorption on heterogeneous surface which can be expressed by the Equation 4.4:

$$q_e = K_f C_e^{1/n} \tag{4.4}$$

Where K_f and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. 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 Equation 4.5 by Zheng *et. al,* (2007).

$$\log q_e = \log K + \frac{1}{n} \log C_e \tag{4.5}$$

Where K_f and n are the Freundlich adsorption isotherm constants. Where, K_f is known as the indicators of the adsorption capacity and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. The ability of Freundlich model to fit the experimental data was examined from the graph plotted below. Graph was plotted by log C_e vs. log q_e to construct the intercept value of K_f and the slope of n as shown in Figure 4.6. From Figure 4.6 the Freundlich constants K_f values ranging from -0.24 to 0.20 and n were found to be 0.63 to 0.79. The magnitudes of K_f and n show easy separation of Cd(II), Ag(II) and Cu(II) ions from the aqueous solution. The value of K_f interception is an indicating of the adsorption capacity progress of the adsorbent. And value for the slope of 1/n indicates the effect of concentration on the adsorption capacity and represents as adsorption intensity. Freundlich isotherm fit this adsorption case with the correlation coefficient of 0.9976 which is come after the Langmuir isotherm with the correlation coefficient of 0.9991 which give Langmuir isotherm fit well for this adsorption case. Freundlich isotherm gives the parameters, n; indicative of bond energies between metal ions and the adsorbent while K related to the bond strength (El-Ashtoukhy *et. al*, 2008).

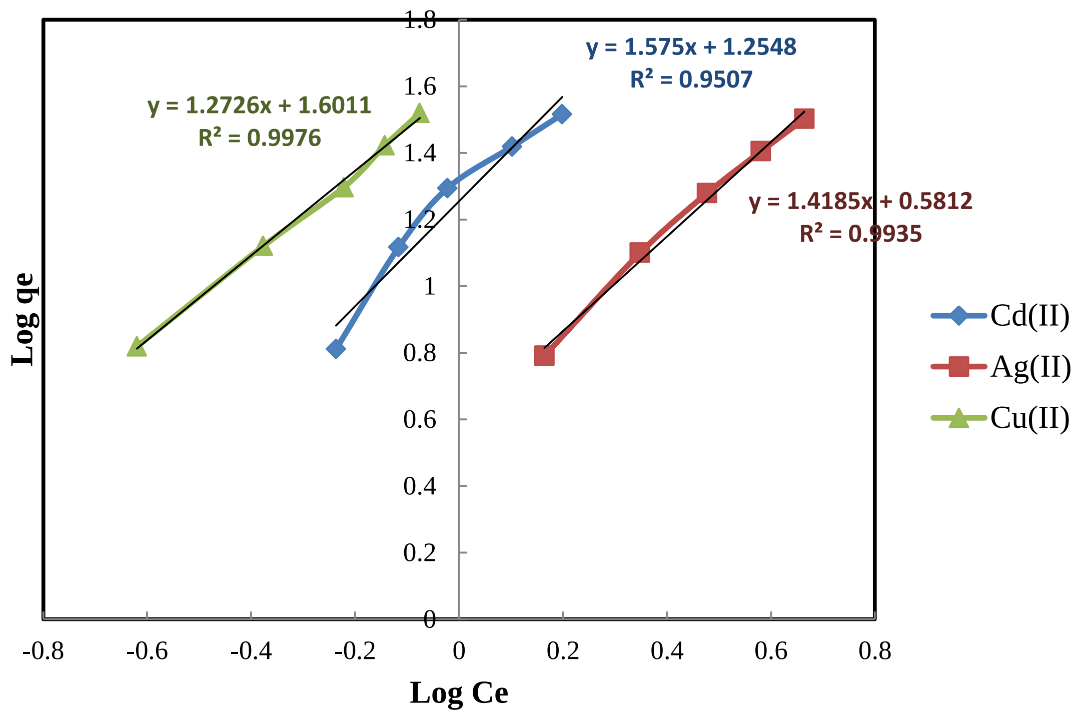

Figure 4.6: Freundlich Isotherm of Cd(II), Ag(II) and Cu(II) Adsorption Using Rubber Seed Shell.

From the graph, corresponding isotherm the Langmuir and Freundlich adsorption constats with the correlation coefficients were calculated and presented in Table 4.1.

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	8.9847	0.4716	0.9154	0.0985	0.6349	0.9507
Ag	3.5688	0.1288	0.9811	-0.2356	0.7049	0.9935
Cu	24.5700	0.4594	0.9991	0.2044	0.7857	0.9976

4.6 Adsorption Kinetics.

Various kinetics models such as pseudo-first order, pseudo-second order, elovich models and intraparticle diffusion, have been use for their rationality with the adsorption experimental data (Senthilkumar *et. al*, 2011). As this adsorption case, the validity of pseudo-first order and pseudo-second order is investigated. The study of adsorption kinetics explained the solute uptake rate and this rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process. The pseudo-first-order rate equation is given as (Oszoy *et. al*, 2008) Equation 4.6.

$$\log(q_e - q_t) = \log q_e - \frac{k_{1ad}}{2.303}t \tag{4.6}$$

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), Ag (II) and Cu (II) heavy metals ions are observed in the graph below

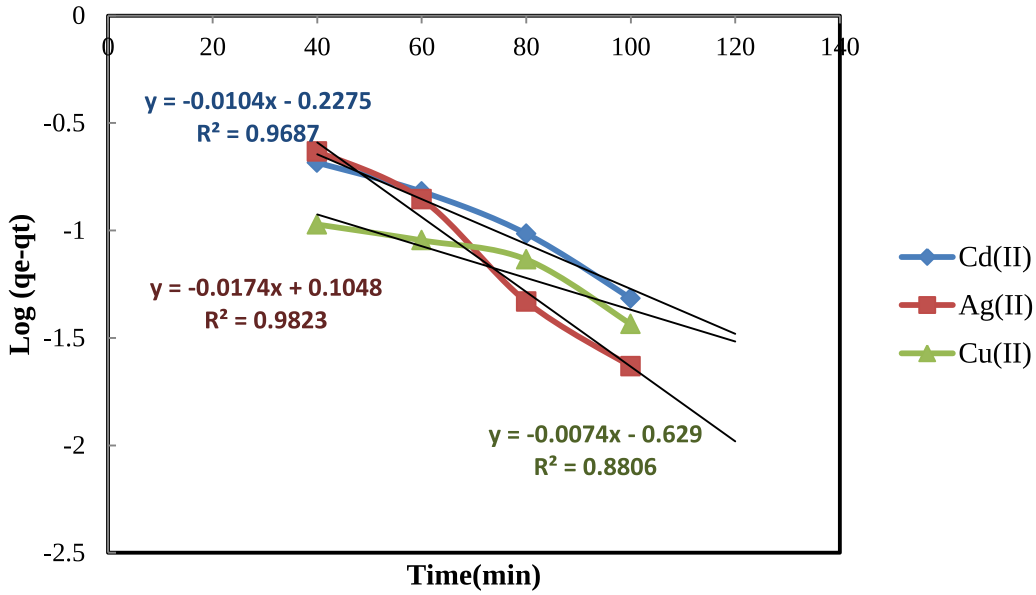

Figure 4.7: Pseudo-first order kinetic for Cd(II), Ag(II) and Cu(II) adsorption using rubber seed shell.

The kinetic data were further analyzed using Pseudo-second order kinetic model. Senthilkumar *et.al,* (2011) supported that this model is based on the assumption that the sorption follows second order sorption and can be expressed as Equation 4.7.

$$\frac{dq_t}{dt} = k\,(q_e - q_t)^2 \qquad (4.7)$$

Integrating the equation above by applying the boundary condition, gives the linear form equation as Equation 4.8.:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \qquad (4.8)$$

Where h=kqe2 (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/qt versus t in Figure 4.8 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. Calero *et. al*, (2011) agree that the pseudo-second order model is based on the assumption that the rate limiting step might be chemical biosorption involving valency forces through sharing or exchange of electrons between cations and biosorbent which resulted good correlation of the data.

The plots of the linearized form of the pseudo-second order adsorption kinetic at different Cd (II), Ag (II) and Cu (II) concentrations using rubber seed shell are shown in Fig. 4.8. The pseudo-first-order pseudo-second-order rate constants and corresponding correlation coefficients determined from Figures 4.7 and 4.8 are presented in Table 4.2. From the calculated values below, the adsorption process of Cd (II), Ag (II) and Cu (II) heavy metal ions are more satisfactory towards pseudo-second order kinetics due to higher value of R2 which is 1. Pseudo-first order and Pseudo-second order adsorption constant including correlation coefficient is shown in Table 4.2.

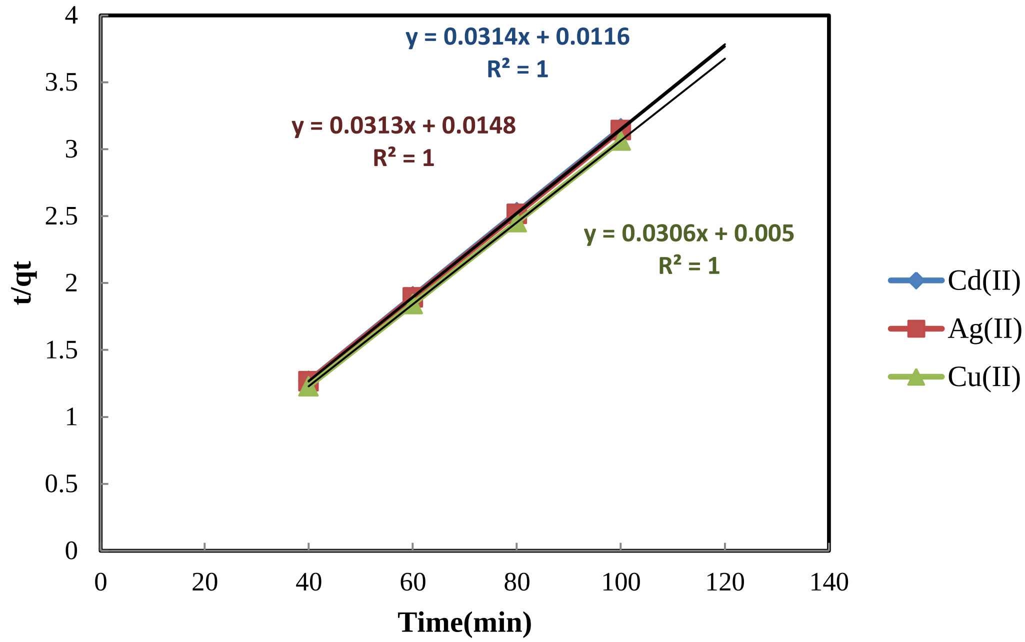

Figure 4.8: Pseudo-second order kinetic for Cd(II), Ag(II) and Cu(II) adsorption using rubber seed shell.

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)	0.0239512	0.9687	0.084996552	1
Ag(II)	0.0400722	0.9823	0.06619527	1
Cu(II)	0.0170422	0.8806	0.187272	1

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusion.

From the result we can conclude rubber seed shell has been successfully approved to act as an adsorbent for adsorption of Cd (II), Ag (II) and Cu (II) ions from aqueous solution. The adsorption process has been affected by the variation of solution pH, contact time, and adsorbent dosage. The highest adsorption was found by the time of 120 minutes, pH of 6 and adsorbent dosage of 0.3g. The reduction of Cd (II), Ag (II) and Cu (II) ions from aqueous solution using rubber seed shell fitted Freundlich and Langmuir Isotherm with correlation coefficient of 0.9976 and 0.9991. Besides, reduction of Cd (II), Ag (II) and Cu (II) ions from aqueous solution also approved Pseudo second-order kinetic yielding good R^2 values of 1.00 and k values of 0.0662 to 0.1873.

5.2 Recommendations.

Some recommendations have been made to improve the result for future work which are various adsorbent could be used to make comparison in term of kinetics and adsorption isotherm. Many other agriculture waste have been investigated such are orange peel, pomegranate peel, almond shell, rice husk, mango leaves and many more. Each adsorbent showed different equilibrium data, kinetics and adsorption isotherm.

Add other conventional adsorbents such as activated carbon and compare the results in term of all important aspects in adsorption. In addition, the use of real wastewater also could be done in order to investigate the absolute removal efficiency of rubber seed shell to industrial wastewater instead of using aqueous solution.

CHAPTER 6

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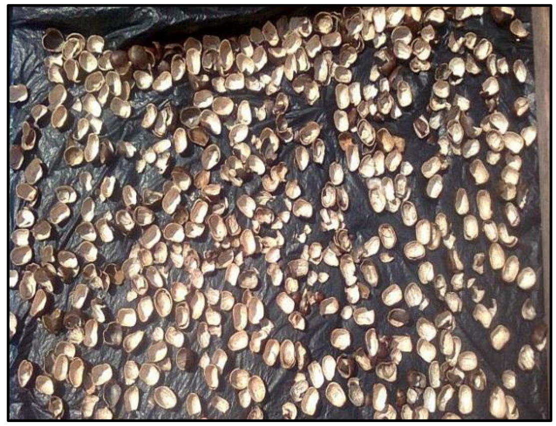
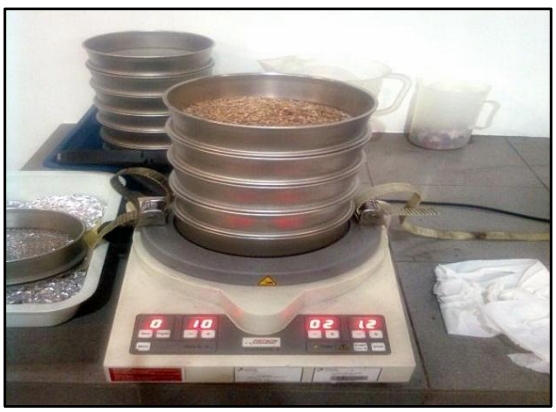
APPENDICES

APPENDIX A

Appendix A1: Rubber seed shell before removing the seed.

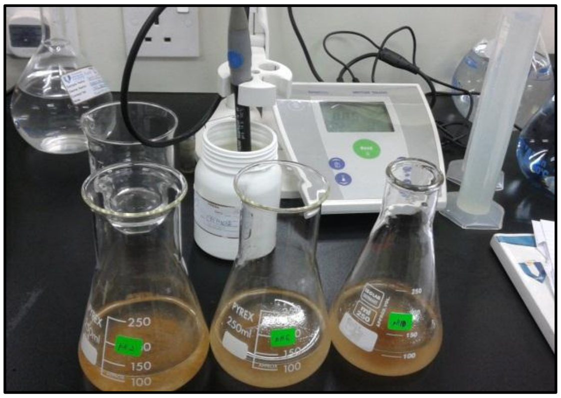


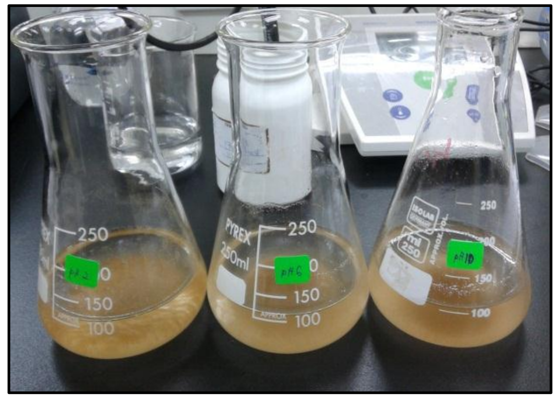
Appendix A2: Rubber seed shell after removing the seed.



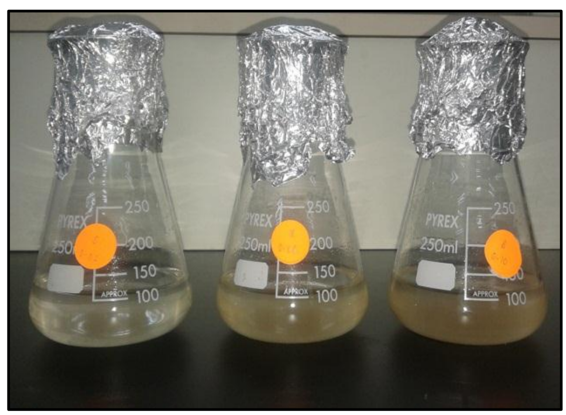
Appendix A3: Sieving the rubber seed shell powder.

Appendix: Rubber seed shell after grinding.

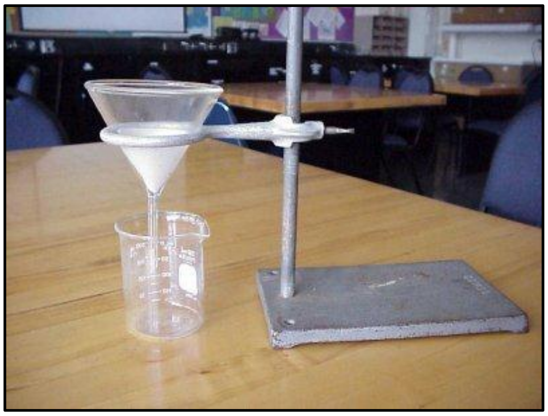




Appendix A5: Adjusting the pH of sample. **Appendix A6:** Sample before shaking on rotary shaker.



Appendix A7: Sample shaked on rotary shaker. **Appendix A8:** Sample after shaked.



Appendix A9: Sample filtered using Whatman Filter Paper.

Appendix A10: Sample ready for AAS Analyzing.

Appendix A11: Filter the sample before analyse using AAS.

Appendix A12: RSS Powder.

APPENDIX B: RESULT DATA

Appendix B1: Effect of solution pH on Cd (II).

Cd (II)			
Solution pH	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
2	100	8.56	91.44
4	100	5.84	94.16
6	100	3.12	96.88
8	100	3.38	96.62
10	100	3.58	96.42

Appendix B2: Effect of solution pH on Ag (II).

Ag (II)			
Solution pH	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
2	100	6.70	93.30
4	100	5.65	94.35
6	100	4.60	95.40
8	100	4.84	95.16
10	100	5.08	94.92

Appendix B3: Effect of solution pH on Cu (II).

Cu (II)			
Solution pH	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
2	100	14.78	85.22
4	100	10.00	90.00
6	100	5.22	94.78
8	100	5.54	94.46
10	100	5.90	94.10

Appendix B4: Effect of adsorbent dosage on Cd (II).

Cd(II)			
Adsorbent dosage, g	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
0.06	100	3.70	96.30
0.12	100	3.67	96.33
0.18	100	3.64	96.36
0.24	100	3.23	96.77
0.3	100	2.82	97.18

Appendix B5: Effect of adsorbent dosage on Ag (II).

Ag(II)			
Adsorbent dosage, g	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
0.06	100	6.06	93.94
0.12	100	5.81	94.19
0.18	100	5.56	94.44
0.24	100	5.28	94.72
0.3	100	5.00	95.00

Appendix B6: Effect of adsorbent dosage on Cu (II).

Cu(II)			
Adsorbent dosage, g	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
0.06	100	13.22	86.78
0.12	100	9.08	90.92
0.18	100	4.94	95.06
0.24	100	4.73	95.27
0.3	100	4.52	95.48

Appendix B7: Effect of contact time on Cd (II).

Cd(II)			
Contact Time, min	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
40	100	5.36	94.64
60	100	5.19	94.81
80	100	5.03	94.97
100	100	4.88	95.16
120	100	4.74	95.26

Appendix B8: Effect of contact time on Ag (II).

Ag (II)			
Contact Time, min	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
40	100	5.14	94.86
60	100	4.86	95.14
80	100	4.58	95.42
100	100	4.51	95.49
120	100	4.44	95.56

Appendix B9: Effect of contact time on Cu (II).

Cu (II)			
Contact Time, min	**Initial concentration, mg/L**	**Final concentration, mg/L**	**Removal efficiency, %**
40	100	2.30	97.70
60	100	2.25	97.75
80	100	2.20	97.80
100	100	2.09	97.91
120	100	1.98	98.02

Appendix B10: Effect of initial concentration on Cd (II), Ag (II) and Cu (II).

Initial conc., mg/L	Removal Efficiency, %		
	Cd	**Ag**	**Cu**
20	97.10	92.70	98.80
40	98.09	94.43	98.95
60	98.42	95.00	99.00
80	98.42	95.24	99.10
100	98.42	95.38	99.16