

**REMOVAL OF METAL IONS FROM AQUEOUS SOLUTION
USING RICE HUSK-BASED ACTIVATED CARBON**

by

Nur Liyana Binti Ramlee

Dissertation submitted in partial fulfilment of
the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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Universiti Teknologi PETRONAS

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr. Anis Suhaila binti Shuib)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
May 2013

CERTIFICATION OF ORIGINALITY

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

(NUR LIYANA BINTI RAMLEE)

ABSTRACT

Industrial wastewaters frequently contain high levels of heavy metals and treatment is needed before disposal, in order to avoid water pollution. Research in recent years has focused on the use of rice husk as low-cost adsorbent for heavy metals removal. Since rice is the main food source in Malaysia with more than 2.4 million tonnes of paddy produced in Malaysia each year, it is possible to utilize rice husk as an alternative to existing activated carbon. This project focuses on the removal metal ions from aqueous solutions using rice husk-based activated carbon (RHAC). Rice husk-based activated carbon was prepared via chemical activation process using NaOH followed by carbonization process at 500°C. Morphological analysis was conducted using field emission scanning electron microscope (FESEM) on three samples, i.e. raw rice husk, treated rice husk and rice husk-based activated carbon. These three samples were also analyzed for their C, H, N content using CHN elemental analyzer. The textural properties of rice husk based activated carbon, i.e. surface area (354 m²/g), pore volume (0.29 cm³/g) and average pore diameter (6.84 nm) were determined. The adsorption studies using activated carbon for the removal of Pb(II), Zn(II) and Ni(II) ions from aqueous solution were carried out at fixed adsorbent dose (0.1 g) with varying initial metal ions concentration as a function of contact time at room temperature. The concentration of metal ions was determined using atomic adsorption spectrophotometer (AAS). Indicated by adsorption capacity, rice husk-based activated carbon adsorb Zn(II) ion better than Pb(II) and Ni(II) ions in single aqueous solution. Ni(II) has high adsorption selectivity compared to other metal ions when they are mixed together in a solution. The equilibrium data obtained from adsorption studies was found to fit Freundlich isotherm model.

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CHAPTER 1

PROJECT BACKGROUND

1.1 Background Study

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the presence of heavy metal ions is a major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries such as metal plating, mining operations, tanneries and smelting. According to Abdul et al., (2008), the treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange and adsorption. Figure 1 below depicts the contribution of heavy metals in water around Malaysia (Ashraf et al., 2011).

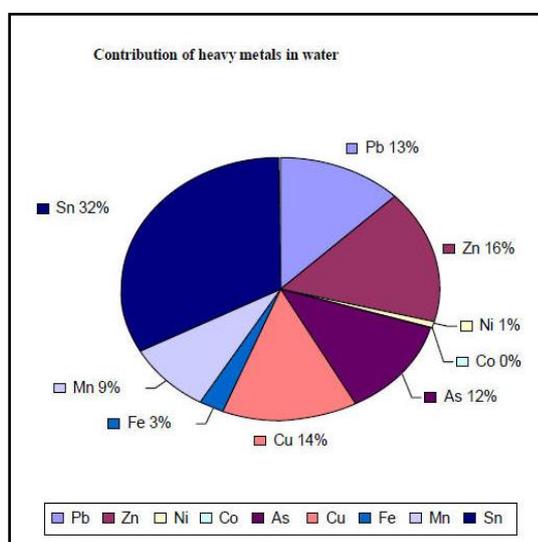


Figure 1.1: Contribution of heavy metals in water (Ashraf et al., 2011)

Studies on the treatment of effluent have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent (Chand et al., 2009). Despite its extensive use in the wastewater treatment industries, activated carbon remains as an expensive material compared to other adsorbent such as zeolite, resins and polymers. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low

cost alternatives to commercially available activated carbon. The low cost agricultural waste by-products such as rice husk, sugarcane bagasse, sawdust and coconut husk can be termed as a low cost adsorbent as it requires little processing and abundant in nature (Khan et al., 2004).

Rice husk, an agricultural waste, contains 70 – 85% of organic matter (lignin, cellulose, sugars) and the remainder consists of silica, which is present in the cellular membrane (Deiana et al., 2008). Besides, it has been reported as a good sorbent of many metals and basic dyes. According to the statistics compiled by the Malaysian Ministry of Agriculture (2011), there are 408,000 tonnes of rice husk produced in Malaysia annually. These rice husks can be made into activated carbons which are used as adsorbents in water purification or the treatment of industrial wastewater. It would add value to these agricultural commodities, help reduce the cost of waste disposal, and provide a potentially cheap alternative to the existing commercial carbons. The production of rice husk based-activated carbon (RHAC) as an adsorbent for the removal of lead ion, Pb(II), zinc ion, Zn(II) and nickel ion, Ni(II) from aqueous solution depend greatly on individual experimental conditions such as pH value, metal concentration, temperature, contact time, competing ions and particle size.

1.2 Problem Statement

Industrialization and urbanization have increased the degradation of environment through the discharge of wastewaters which resulted in significant amounts of heavy metals being deposited into ecosystems. In this context, a wastewater treatment process requires high operation and maintenance cost due to the expensive price of commercial activated carbon. Besides, rice husk dust and smoke could probably play a major role in the aggravation of airway diseases in agricultural areas.

1.3 Objective

The objectives of this project are:

- i. To synthesize rice husk-based activated carbon (RHAC).
- ii. To characterize the porosity, functional group, carbon, hydrogen, nitrogen, oxygen and silica content of rice husk.
- iii. To investigate the ability of the activated carbon for the removal of lead, Pb(II), zinc, Zn(II) and nickel, Ni(II) ions using adsorption method.

1.4 Scope of Study

In this study, the main subjects under investigation are:

- i. Producing activated carbon from rice husk that treated chemically with activation agent which is sodium hydroxide, NaOH before undergoes carbonization process in fixed bed adsorption column.
- ii. Characterization of raw rice husk (RRH), treated rice husk (TRH) and rice husk-based activated carbon (RHAC) by using various equipments.
- iii. Adsorption percentage and capacity of rice husk-based activated carbon towards the removal of lead, Pb(II), zinc, Zn(II) and nickel, Ni(II) ions using adsorption method.
- iv. Langmuir and Freundlich isotherms to interpret the equilibrium isotherm data.

1.5 Feasibility of Project within the scope and time frame

This project is feasible within the scope identified and the time allocated. The first half of this project will be focusing on the through literature review of the related researches to see the areas of improvement and to obtain the basic understanding and knowledge about the project. After that, planning will be done in order to determine the subjects to be studied, the methodology and the results to be collected from the experiment. Besides, the preparation of rice husk based activated carbon (RHAC) can be done in the first semester. The second half of the project mainly focuses on conducting experiments related with characterization of RRH, TRH and RHAC as well as adsorption studies. The result collected will then be analyzed and investigated critically.

In terms of scope of study, the project is feasible to be carried out in UTP as it has the required apparatus and equipment to run the sample. The main equipment such as the fixed bed activation unit and characterization equipment are available. Furthermore, raw rice husk from rice milling industry can be easily obtained. The scope of study chosen is also similar to other related researches done. So, it is relevant and can be used to compare directly with other literature readings. As such, this research project is feasible within the time frame and the scope of study. Strategic planning on the execution is needed for this research project to be completed on time and successfully.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metal

Heavy metal contamination exists due to the rapid growth of industrialization in the world that has caused changes in the chemical and biological properties of both surface and ground water (Ajmal et al., 2003). This has resulted in significant amounts of heavy metals being deposited into our ecosystems from many industrial sources such as metal plating, tanneries, mining and car radiator manufacturing. Metal like cadmium, zinc, chromium, nickel and lead are not biodegradable and are known to cause severe health and environment problem.

Lead is a soft metal that has known many applications over the years. It has been used widely since 5000 BC for application in metal products, cables and pipelines, but also in paints and pesticides. Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%). Besides, lead can accumulate in water and soils through corrosion of leaded pipelines in a water transporting system and through corrosion of leaded paints. It cannot be broken as it can only be converted to other form.

Zinc is a metal chemical element that usually used in galvanization, production of alloys, and final extraction using electricity. It is an essential mineral for humans and other biological creature. Zinc deficiency can cause growth retardation, infection susceptibility, diarrhea and other chronic illness. On the other hand, excessive consumption of zinc can cause ataxia, lethargy and copper deficiency to the human being. Soils contaminated with zinc happened due to the mining of zinc-containing ores and refining where the level of zinc in soil is in excess. Thus, it would interfere the ability of plants to absorb other essential metals, such as iron and manganese.

Nickel is a naturally occurring, lustrous, silvery-white metallic element. It is the fifth most common element on earth and occurs extensively in the earth's crust. However, most of the nickel is inaccessible in the core of the earth. Reflecting these characteristics, nickel is widely used in over 300,000 products for consumer,

industrial, military, transport, aerospace, marine and architectural applications. The biggest use is in alloying - particularly with chromium and other metals to produce stainless and heat-resisting steels. These are used for pots and pans, kitchen sinks as well in buildings, food processing equipment, medical equipment and chemical plants. Although nickel is a nutrient needed in human body, but high dose will cause serious health problem.

Malaysia is also concern about the discharge of heavy metals through the wastewater. Figure 2.1 shows the Environmental Quality Regulation 2009 from Ministry of Natural Resources and the Environment of Malaysia. These regulations apply to any premises which discharge industrial effluent to the environment. Besides, the regulations set procedures for the design and construction of industrial effluent treatment system and acceptable conditions of the discharge of industrial or mixed effluent.

Parameter (1)	Unit (2)	Standard	
		A (3)	B (4)
i. Temperature	°C	40	40
ii. pH Value	-	6.0-9.0	5.5-9.0
iii. BOD ₅ at 20°C	mg/L	20	50
iv. Suspended Solids	mg/L	50	100
v. Mercury	mg/L	0.005	0.05
vi. Cadmium	mg/L	0.01	0.02
vii. Chromium, Hexavalent	mg/L	0.05	0.05
viii. Chromium, Trivalent	mg/L	0.20	1.0
ix. Arsenic	mg/L	0.05	0.10
x. Cyanide	mg/L	0.05	0.10
xi. Lead	mg/L	0.10	0.5
xii. Copper	mg/L	0.20	1.0
xiii. Manganese	mg/L	0.20	1.0
xiv. Nickel	mg/L	0.20	1.0
xv. Tin	mg/L	0.20	1.0
xvi. Zinc	mg/L	2.0	2.0
xvii. Boron	mg/L	1.0	4.0
xviii. Iron (Fe)	mg/L	1.0	5.0
xix. Silver	mg/L	0.1	1.0
xx. Aluminium	mg/L	10	15
xxi. Selenium	mg/L	0.02	0.5
xxii. Barium	mg/L	1.0	2.0
xxiii. Fluoride	mg/L	2.0	5.0
xxiv. Formaldehyde	mg/L	1.0	2.0
xxv. Phenol	mg/L	0.001	1.0
xxvi. Free Chlorine	mg/L	1.0	2.0
xxvii. Sulphide	mg/L	0.50	0.50
xxviii. Oil and Grease	mg/L	1.0	10
xxix. Ammoniacal Nitrogen	mg/L	10	20
xxx. Colour ADMI*		100	200

Figure 2.1: Environmental Quality Act 1974, Environmental Quality (Industrial Effluent) Regulations 2009.

2.2 Rice Husk

Adsorption is one of the physico-chemical treatment process found to be effective in removing heavy metals from aqueous solution using low cost adsorption (Bailey et al., 1999). The utilization of rice husk as the precursor to produce activated carbons that can be used as adsorbents for heavy metals removal from industrial wastewater could alleviate the problems of its disposal and management. It would also add value to this agricultural waste and provide a potentially cheap alternative to existing commercial activated carbons (Chuah et al., 2005).

Rice husk is the by-product of the rice milling industry. There are approximately 140 million tonnes of rice husk available for the utilization based on 571 million tonnes of rice produced annually, mainly from developing countries. It is mainly used as a low-value energy resource, burned in-situ or discarded causing some disposal and environmental problems. According to the Malaysia Ministry of Agriculture and Agro-Based Industries in 2011, the annual production of rice in Malaysia has increased significantly from 2008 to 2009. Rice husk contains about 20 % silica and the remaining 80% includes cellulose, hemicelluloses, lignin, and mineral components. It is insoluble in water, chemically stable and has high mechanical strength. Due its high cellulose and lignin content, rice husk can be utilized as the raw material to prepare activated carbon having highly porous structure in micropores range with high specific surface area (Deiana et al., 2008). In addition, the ability of rice husk-based activated carbon for removal of metal ions and organic molecules from aqueous phase solution has been proven from the previous studies (Vimal et al., 2009).

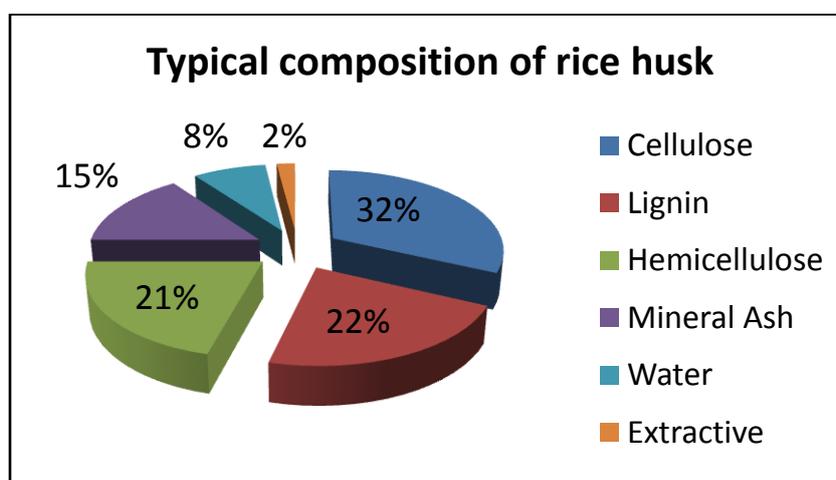


Figure 2.2: Typical composition of rice husk (Rahman et al., 2004)

2.3 Adsorption

Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption and coprecipitation. Studies on the treatment of effluent bearing heavy metal have revealed adsorption to be a highly effective technique for the removal of heavy metal from waste stream and activated carbon has been widely used as an adsorbent (Chand et al., 1994). Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (adsorbate).

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorptions. Adsorption is usually described through isotherms which connect the amount of adsorbate on the adsorbent, with its pressure or concentration. In wastewater treatment, the most widely used method is adsorption onto the surface of activated carbon for the removal of heavy metal in wastewater stream. There are several factors affecting the rate of adsorption such as surface area of adsorbent, temperature, pressure and contact time.

Adsorbent	Heavy metal removal efficiency (%)						
	Cr(VI)	Ni (II)	Cu(II)	Zn(II)	Cd(II)	Hg(II)	Pb(II)
Rice husk carbon	>99	-	≈100	≈100	≈100	-	≈100
Rice husk (water and HCl washed)	79	-	80	85	85	-	-
Phosphate-treated rice husk	-	-	-	-	>90	-	-
Dyestuff-treated rice hulls (red)	39.7	61.6	78.8	75.1	99.2	92.7	99.8
Dyestuff-treated rice hulls (yellow)	39.1	60.8	70.0	61.3	83.3	93.3	100.0
Tartaric acid modified rice husk	-	-	>80	-	-	-	>95
Rice hull biomass	98.93	-	-	-	97.96	-	99.43
Rice husk carbon	-	-	≈100	≈100	≈100	-	≈100
Raw rice husk	66	-	-	-	-	-	-

Figure 2.3: Types of rice husk as adsorbent for heavy metal (Khan et al., 2004)

Metal ion/dyes	Temperature (°C)	Maximum sorption capacity at equilibrium, (mg/g)	Constant (l/mg)
Au	20	39.84	0.059
	30	50.50	0.050
	40	64.10	0.031
Co	20	0.32	1.62
Cr(III)	20	1.90	0.48
Cu	20	1.21	0.90
	27	29	0.10
	50	22	0.05
	70	18	0.03
Hg(II)	29–31	66.66 ($d_p = 37-50 \mu\text{m}$)	0.0037
		55.55 ($d_p = 63-130 \mu\text{m}$)	0.003
		40.00 ($d_p = 130-600 \mu\text{m}$)	0.0025
	15	9.3200	0.0115
	30	6.7200	0.0158
Ni(II)	20	0.23	1.62
Pb	27	108	0.09
	50	105	0.02
	70	96	0.01
	15	12.3460	0.3250
	30	12.6100	0.1630
Zn(II)	20	0.75	1.94
Acid yellow 36 dye	30	86.9	0.002
Acid blue dye	25	50.0	0.1

Figure 2.4: Langmuir isotherms using rice husk as adsorbent (Chuah et al., 2005)

Metal ion/dyes	Temperature (°C)	Adsorption intensity, $1/n$	Adsorption capacity, K (mol/g)
Cr (VI)		0.6387	56.6
Hg (II)	15	0.4932	0.4179
	30	0.4691	0.5363
Pb	15	0.2475	4.7097
	30	0.3094	3.4986
Zn (II)	20	0.909	2.238
Acid yellow 36	30	0.435	2.1

Figure 2.5: Freundlich isotherms using rice husk as adsorbent (Chuah et al., 2005)

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

The methodology for conducting this research project is exploration and discovery. The result obtained through the research of the removal of metal ions using rice husk-based activated carbon can be used as a basis of comparison with other researches that have been done. The results can hence further enhance the research and development of removal of Pb(II), Zn(II) and Ni(II) using rice husk-based activated carbon. The experimental work of this project is divided into three stages. The first stage involves the preparation of rice-husk based-activated carbon. The second stage is to characterize the raw rice husk, treated rice husk and rice husk-based activated carbon using various equipments. The last stage is performing adsorption studies on the percentage removal and adsorption capacity of metal ions as well as their isotherm activity.

3.2 Experimental Procedures

The experimental procedures for the preparation of rice husk activated carbon are based on method proposed by Yupeng et al., (2002), Abdul et al., (2008), Grigis (1999) and Taha et al., (2011). These procedures are divided into 3 parts; preparation of raw rice husk, treatment of raw rice husk using sodium hydroxide and preparation of rice husk-based activated carbon by carbonization process.

3.2.1 Stage 1: Preparation of rice husk-based activated carbon (RHAC)



Figure 3.1: The schematic diagram of the preparation of RHAC

3.2.1.1 Preparation of raw rice husk (RRH)

Raw rice husk can be obtained from the rice mills in Malaysia.

- i. Rice husk is washed several times with distilled water to remove any adhering materials.
- ii. The rice husk is dried in the oven at 80°C for 24 hours to remove all the volatile components and moisture content exist in the rice husk.
- iii. The dried rice husk is grinded and sieved to obtain 1mm size of raw rice husk (labelled as RRH).

3.2.1.2 Treatment of raw rice husk (TRH)

This procedure is carried out according to the method used by Abdul et al., (2008) and Taha et al., (2011) with some modification. Sodium hydroxide, NaOH is used as an activation agent for the treatment of raw rice husk. 1.0M of NaOH is prepared by the dilution of NaOH using ratio of 1:10 (rice husk: NaOH, w/v).

- i. 1.0 M sodium hydroxide, NaOH is prepared.
- ii. 80 grams of raw rice husk (RRH) is mixed with 800ml of 1.0 M sodium hydroxide, NaOH in 1000ml beaker.
- iii. Beaker containing sample is sealed with aluminium foil.
- iv. The sample is stir continuously by using magnetic stirrer for 24 hours.
- v. After 24 hours, the sample is filtered to obtain chemically treated rice husk (labelled as TRH)
- vi. In this process, TRH is repeatedly washed with distilled water until the pH of the filtrate in the range of 6-7.
- vii. The TRH is dried in the oven at 80°C for 24 hours.
- viii. The TRH is weighed by using weighing scale.

3.2.1.3 Preparation of rice husk-based activated carbon (RHAC)

The method for the carbonization of rice husk is described by Yupeng et al., (2002) and Grigis (1999) and Taha et al., (2011). In order to convert TRH into activated carbon, the TRH will be carbonized in the fixed bed activation unit with the presence of nitrogen flow.

- i. 6.0 g of TRH is weighed by using weighing scale.
- ii. The crucible and crucible lid are wrapped internally using aluminium foil. This is to prevent the oxidation of TRH with contaminant that exists in the crucible.
- iii. After weighed, the TRH is placed into the wrapped crucible and closed with the crucible lid.
- iv. The crucible containing rice husk is wrapped externally and put into the fixed bed activation unit with the presence of nitrogen flow at 500°C for 2 hours.
- v. The sample is taken out once the temperature of the fixed bed activation unit has reached 25°C.
- vi. The rice husk-based activated carbon (labelled as RHAC) is weighed by using weighing scale.
- vii. The total yield (Y_T) of RHAC is calculated as:

$$Y_T = \left(\frac{\text{Weight of RHAC}}{\text{Weight of TRH}} \right) \times 100\% \quad (1)$$

3.2.2 Stage 2: Characterization of RRH, TRH and RHAC

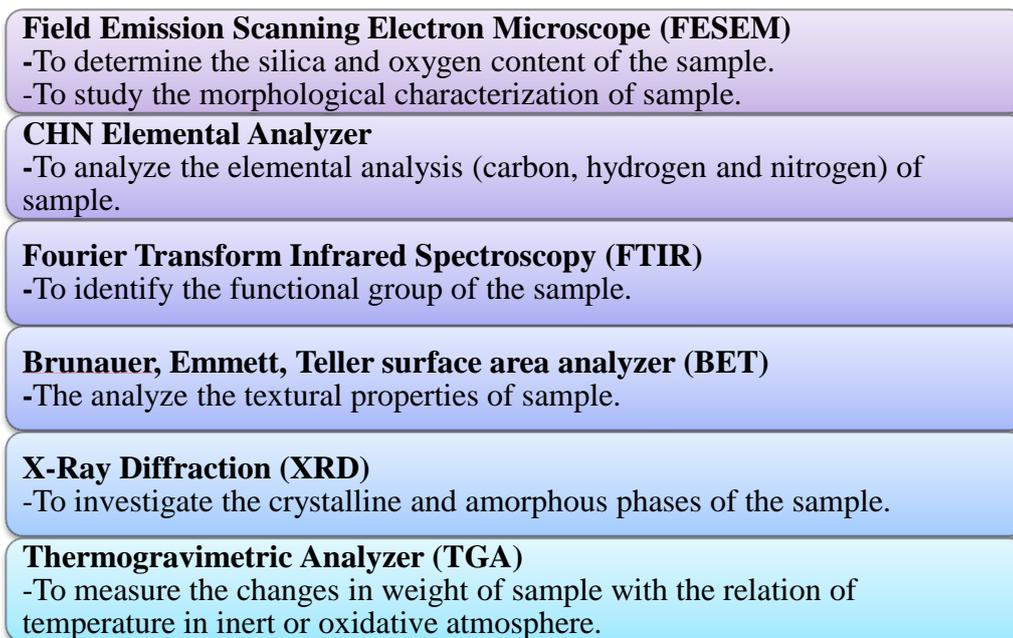


Figure 3.2: Characterization of RRH, TRH and RHAC using several equipments.

3.2.3 Stage 3: Adsorption studies

Adsorption studies are determined according to the method proposed by Taha et al., (2011).

- i. Solution of 25 ppm Pb(II) ions is prepared by mixing the appropriate amount of $\text{Pb}(\text{NO}_3)_2$ with distilled water.
- ii. The same procedures are applied for the preparation of 25 ppm Zn(II) and 25 ppm Ni(II) ions solutions using ZnCl_2 and NiCl_2 , respectively (MERCK).
- iii. 0.1 g of RHAC with 25 ml of 25 ppm Pb(II) ion solution in Erlenmeyer flasks.
- iv. The flask is shaken in the rotary shaker at 150 rpm at room temperature.
- v. After shaking for a preset interval time, the mixture is filtered.
- vi. The concentration of Pb(II) ion in the filtrate is analyzed using Atomic Adsorption Spectrophotometer (AAS).
- vii. The adsorption studies are also conducted using various concentration of Pb(II) ion solution (50, 100, 150, 200 ppm) for different time interval.
- viii. Step (iii) until (vii) are repeated by using Zn(II) and Ni(II) ions solution.
- ix. The procedures are repeated by mixing the three solutions in an Erlenmeyer flask.
- x. The adsorption percentage and capacity are calculated by:

$$\text{Percentage adsorption} = \frac{(C_i - C_t)}{C_i} \times 100 \quad (2)$$

$$\text{Adsorption capacity, } q_t = \left[\frac{(C_i - C_t)}{W} \right] \times V \quad (3)$$

where:

C_i = Initial metal ion concentration

C_t = Metal ion concentration at time t

W = Dry weight of adsorbent used

V = Volume of metal ion solution

3.3 Equipments and Chemicals

Table 3.1: List of lab instruments required

No.	Lab Instrument
1.	Field Emission Scanning Electron Microscope (FESEM)
2.	CHN Elemental Analyzer
3.	Fourier Transform Infrared Spectroscopy (FTIR)
4.	Brunauer, Emmett, Teller surface area analyzer (BET)
5.	X-Ray Diffraction (XRD)
6.	Thermogravimetric Analyzer (TGA)
7.	Atomic Adsorption Spectrophotometer (AAS)
8.	Fixed Bed Activation Unit
9.	Rotary Shaker
10.	Oven
11.	Grinder
12.	Siever
13.	Calibrated pH water

Table 3.2: List of chemicals required

No.	Chemical
1.	Sodium Hydroxide, NaOH
2.	Lead (II) Nitrate, $Pb(NO_3)_2$
3.	Zinc (II) Chloride, $ZnCl_2$
4.	Nickel (II) Chloride, $NiCl_2$
5.	Distilled water

3.4 Flow Chart

The waterfall model derives its name from the cascading effect from one phase to the other as illustrated below. In this model each phase has a well defined start and end point with identifiable deliverables from one phase being passed to the next phase before it can be begin.

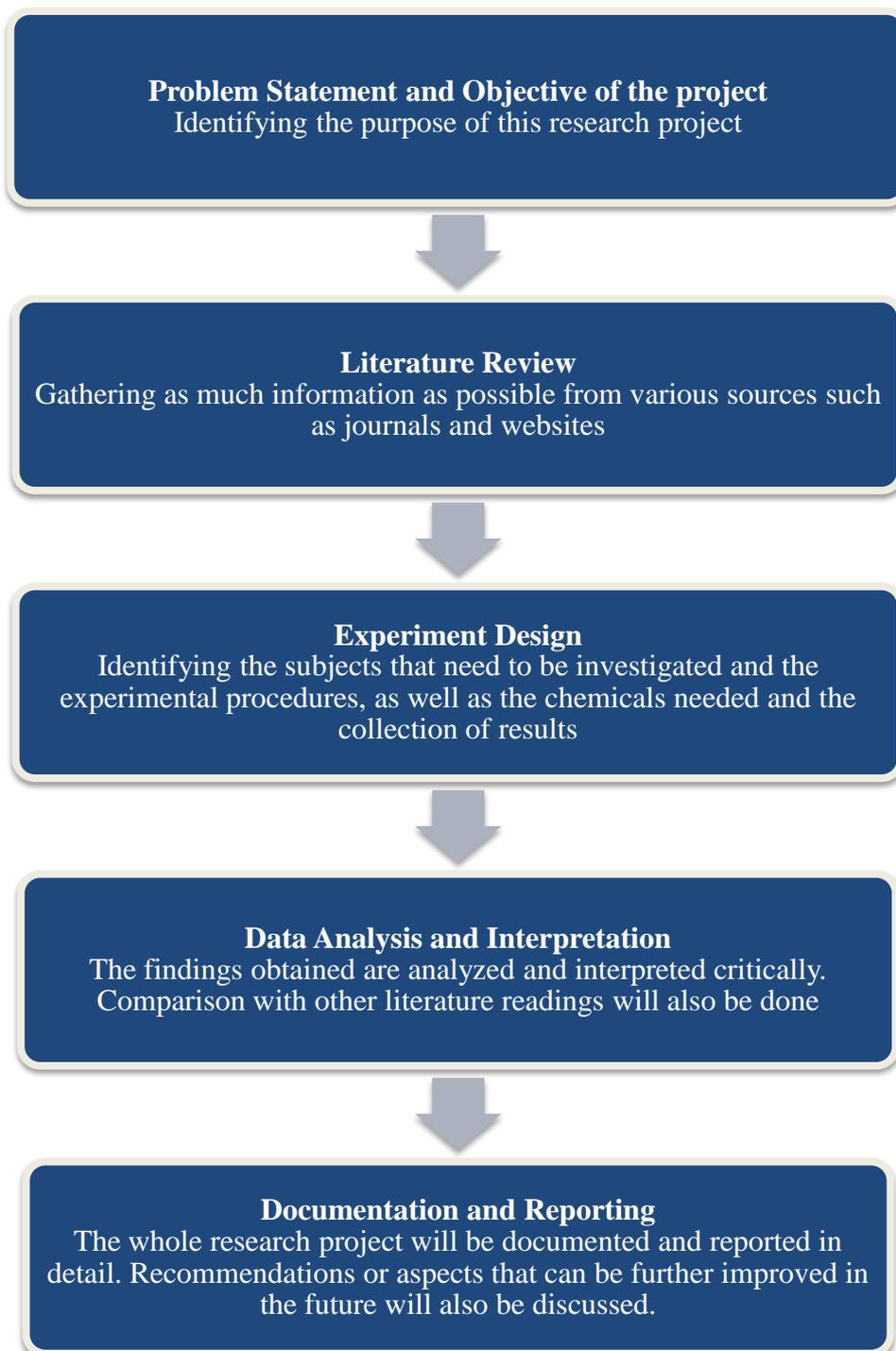


Figure 3.3: The flowchart of project activities

3.5 Key Milestones

Several key milestones must be achieved in order to meet the objective of this project.

Table 3.3: Key Milestones for Final Year Project (FYP I & 2)

No.	Milestones	Suggested Week
FYP 1		
1	Completion of literature review on adsorption studies	Week 4
2	Completion of extended proposal	Week 6
3	Rice husk-based activated carbon (prepared)	Week 14
4	Completion of interim draft report	Week 13
5	Completion of interim report	Week 14
FYP 2		
1	Rice husk-based activated carbon (characterized)	Week 3
2	Completion of progress report	Week 7
3	Completion of adsorption studies	Week 11
4	Completion of draft report	Week 11
5	Completion of dissertation (soft bound)	Week 12
6	Completion of technical paper	Week 12
7	Submission of project dissertation (hard bound)	Week 14

3.6 Gantt Chart for Final Year Project 1

Table 3.4: Gantt Chart for Final Year Project 1 (FYPI)

No.	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Title	■	■													
2	Preliminary Research Work and Literature Review		■	■	■	■										
3	Submission of Extended Proposal Defence						●									
4	Preparation for Oral Proposal Defence							■								
5	Oral Proposal Defence Presentation									■						
6	Detailed Literature Review									■	■	■	■	■		
7	Preparation of rice husk-based activated carbon									■	■	■	■	■	■	●
8	Preparation of Interim Report			■	■	■	■	■		■	■	■	■	■		
9	Submission of Interim Draft Report														●	
10	Submission of Interim Final Report															●

● Suggested milestone
 ■ Process

3.7 Gantt Chart for Final Year Project 2

Table 3.5: Gantt Chart for Final Year Project 2 (FYP2)

No.	Detail / Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Characterization of Rice Husk-Based Activated Carbon	■	■	●												
2	Submission of Progress Report							●								
3	Adsorption Studies				■	■	■	■		■	■	■	●			
4	Pre-SEDEX											●				
5	Submission of Draft Report												●			
6	Submission of Draft Report (soft bound)													●		
7	Submission of Technical Paper													●		
8	Oral Presentation														●	
9	Submission of Project Dissertation (Hard Bound)															●

● Suggested milestone
 ■ Process

CHAPTER 4

RESULT AND DISCUSSION

4.1 Preparation of Raw Rice Husk (RRH)

Preparation of raw rice husk includes the process of cleaning, drying, grinding and sieving the rice husk. Based on observation, there is a lot of paddy and other impurities were floating on the water. After being washed, the rice husk was dried in the oven at 80°C for 24 hours as shown in Figure 4.1. The main purpose of this process is to remove impurities and moisture from rice husk.



Figure 4.1: Cleaning and drying process of raw rice husk.

The next procedure is the grinding of dried rice husk by using grinder as shown in Figure 4.2. This step was carried out by adjusting the grinding time at 20 seconds for each sample. On the other hand, Figure 4.3 shows the sieving process in order to obtain 1mm size of rice husk.



Figure 4.2: Grinding of dried rice husk using grinder.



Figure 4.3: Sieving process.

4.2 Treatment of Raw Rice Husk with Sodium Hydroxide

Treatment of raw rice husk is one of the crucial processes in synthesizing rice husk-based activated carbon. The major purpose is to reduce the amount of silica content in the rice husk by mixing the RRH with 1M of sodium hydroxide, NaOH in the ratio of 1:10 (RRH:NaOH, w/v). Figure 4.4 shows the reaction between silicon oxide and sodium hydroxide to produce sodium silicate (Na_2SiO_3). This treatment was carried out for 24

hours at room temperature with continuous stirring; to increase the contact time between the RRH and activation agent. The process is described in Figure 4.5.

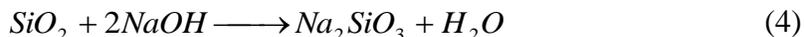


Figure 4.4: Reaction of silicon oxide with sodium hydroxide.

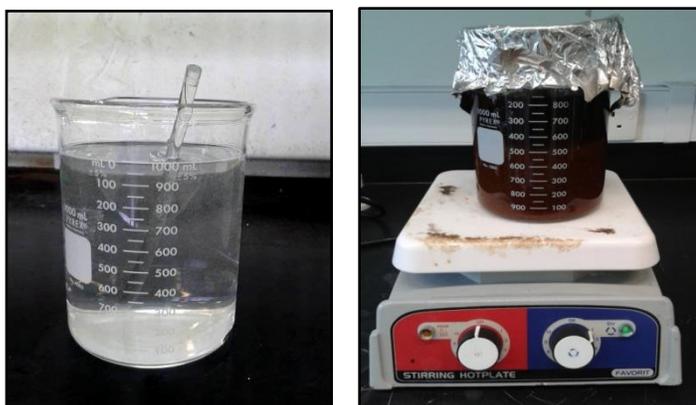


Figure 4.5: Treatment process of raw rice husk.

Sodium silicate can be easily removed from the rice husk by washing repeatedly with distilled water as it is readily soluble in water and stable in neutral and alkaline solutions. Therefore, a calibrated pH meter was used in order to ensure the pH of the filtrate in the range of 6-7. Then, TRH was dried in the oven at 80°C for 24 hours. Figure 4.6 shows the pH meter and the treated rice husk (TRH). The changes in weight of RRH after being treated with NaOH are tabulated in Table 4.1 where the yield of TRH is 75% from the initial weight. The reduction in weight was due to the lost of silica content from raw rice husk.



Figure 4.6: Calibrated pH meter and the treated rice husk (TRH)

Table 4.1: Observation data

Treatment	Colour	Weight (g)
Before	Dark brown	160
After	Light brown	120
	Total Yield (Y_T)	75 %

4.3 Carbonization of Treated Rice Husk

The carbonization process of treated rice husk (TRH) was conducted in Fixed Bed Activation Unit with the presence of nitrogen flow at 500°C for 2 hours. The total yield (Y_T) of RHAC formed is 33.33% as shown in Table 4.2. The reduction in weight was due to the lost of the volatile matters during rapid heating of carbonization process (Rahman et al., 2004).

Table 4.2: Observation data

Treatment	Colour	Weight (g)
Before	Light brown	6.0
After	Black	2.7
Total Yield (Y_T)		33.33 %



Figure 4.7: Fixed Bed Activation Unit and RHAC

4.4 Characterization of RRH, TRH and RHAC

4.4.1 CHN Elemental Analyzer

Three samples consist of RRH, TRH and RHAC were analyzed using CHN Elemental Analyzer in order to determine carbon, hydrogen and nitrogen contents.

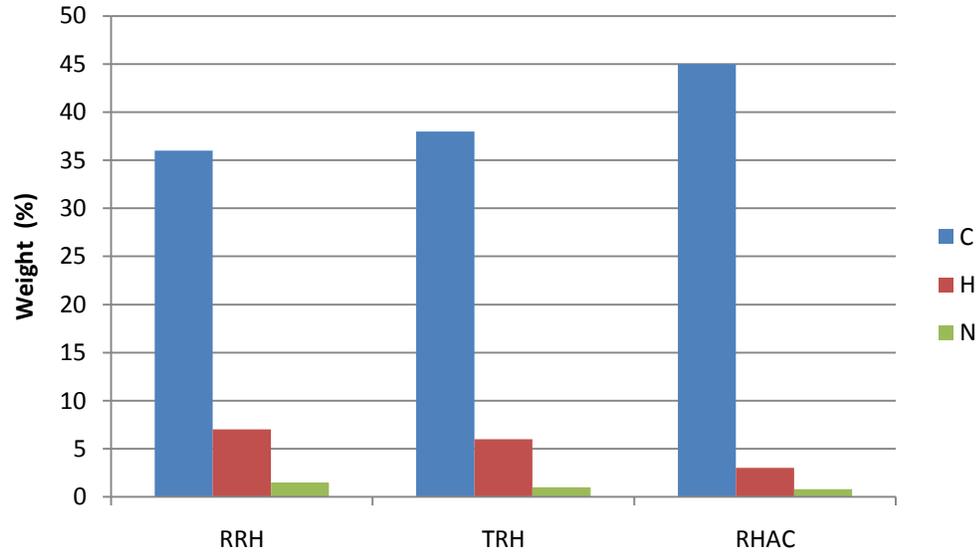


Figure 4.8: Carbon, hydrogen and nitrogen contents on RRH, TRH and RHAC

The main components of RRH, TRH and RHAC are revealed in Figure 4.8. Basically, treatment and carbonization process have increased the amount of carbon. However, hydrogen and nitrogen contents showed the opposite result. This observation can be explained due to the destruction of cellulose and hemicelluloses of rice husk especially during carbonization process that caused the vaporization of volatile matter. Previous studies have shown that carbon monoxide, CO is formed during this decomposition process where a smaller portion of CO coming from lignin by cracking of carbonyl (C-OC) and carboxyl (C=O) group in biomass (Wannapeera et al., 2008). As all the volatile matter is removed, the carbon content remains constant and leaving only the non-volatile flammable component in the RHAC (Tzong, 2004). T. H. Liou, S. J. Wu (2009) states that the decrease in hydrogen and oxygen contents may be attributed to the formation of water vapor and carbon dioxide.

4.4.2 Field Emission Scanning Electron Microscope (FESEM)

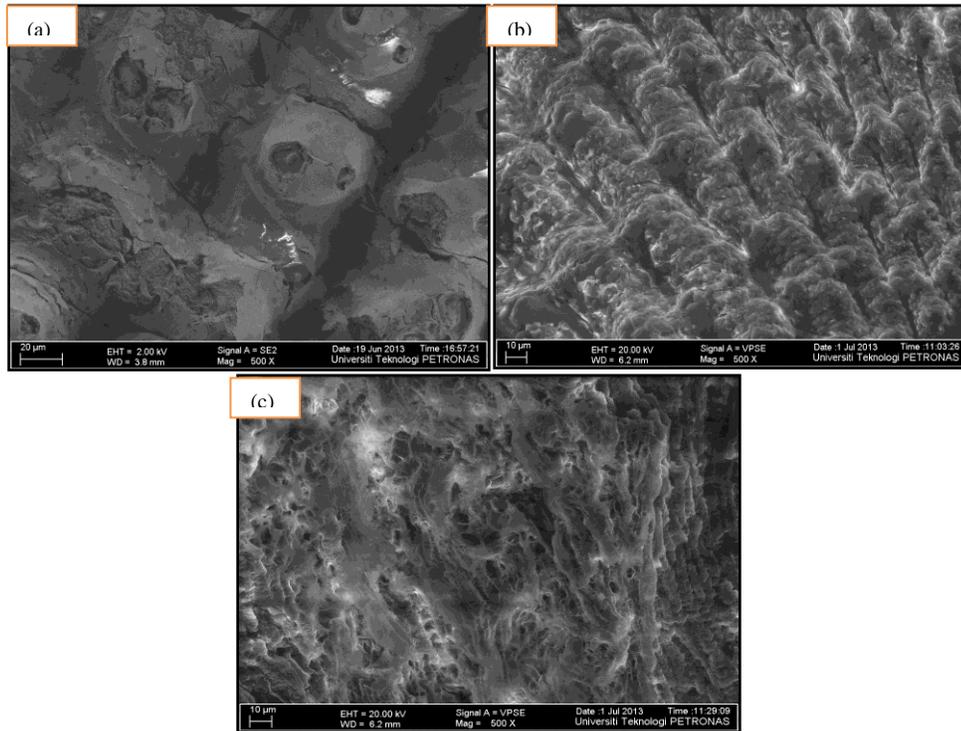


Figure 4.9: Morphology of (a) RRH, (b) TRH (c) RHAC with 500 magnification

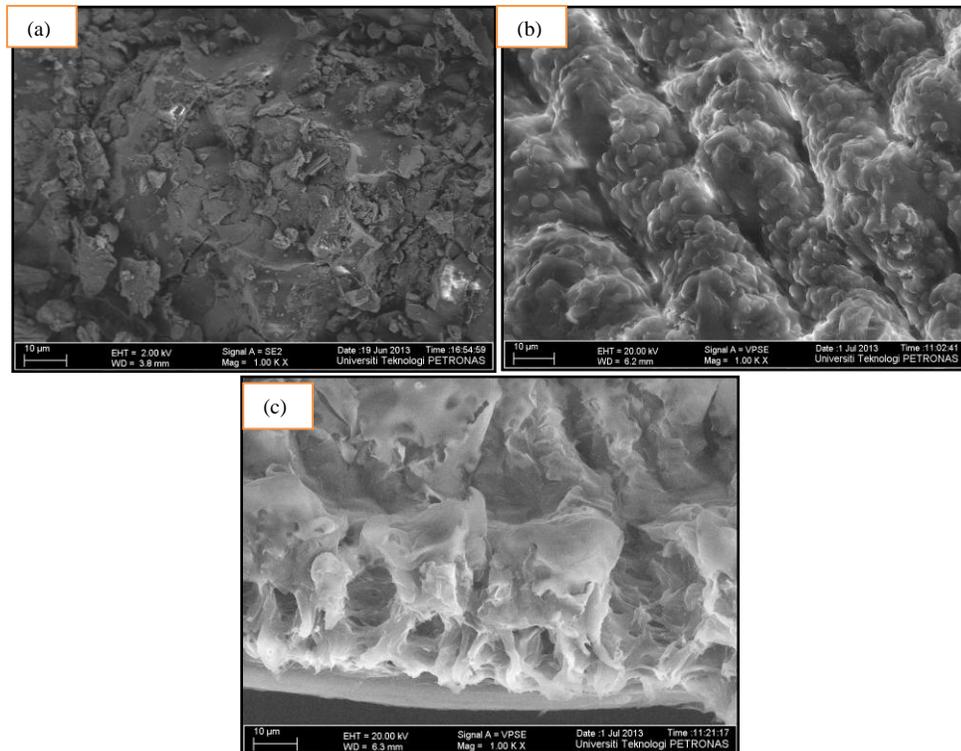


Figure 4.10: Morphology of (a) RRH, (b) TRH (c) RHAC with 1000 magnification

The morphological characteristics of RRH, TRH and RHAC were observed by using Field Emission Scanning Electron Microscope (FESEM). Figure 4.9 and 4.10 show the morphology of RRH, TRH and RHAC with different magnification respectively. FESEM micrograph of RRH shows no presence of pores, afterwards pore formation is observed in TRH that was treated chemically with NaOH. Taha et al (2011) reported that fine pores were created in the interior structure of the treated rice husk which is consistent with the theory that the chemical treatment process will produce high porous cellulose-silica material. The creation of these pores can be explained by the fact that silica reacts with activating agent, NaOH to form sodium silicate, Na_2SiO_3 . The Na_2SiO_3 is soluble in water can be removed by adequate water-washing. Besides, T.H. Liou and S. J. Wu (2009) relate that the disappearance of silica simultaneously creates more surface area and new pore structure.

As can be seen in the picture, carbonization process caused the formation of many fine pores in the interior structure of RHAC thereby increasing the surface area of the activated carbon. According to the micrograph, the pores were developed from the vaporization of non-carbon elements and volatile matters (such as oxygen, nitrogen and carbonate) during carbonization process with nitrogen flow at 500°C for 2 hours. Many researches shown that these well development pores can contribute to better adsorption capability of activated carbon for removal of heavy metal ions.

4.4.3 Brunauer, Emmett, Teller surface area analyzer (BET)

The BET surface area, total pore volume and average pore diameter of RHAC were found to be $354 \text{ m}^2/\text{g}$, $0.29 \text{ cm}^3/\text{g}$ and 68.39 \AA , respectively. The average pore diameter of 6.95 nm indicated that the RHAC prepared was in mesopores region.

4.4.4 Fourier Transform Infrared Spectroscopy (FTIR)

A quantitative analysis of RRH, TRH and RHAC were conducted in order to obtain infrared spectroscopy which can identify the characteristic of functional groups, an instrument in adsorption of aromatic compounds. Figure 4.11 shows differences in the FTIR spectra of the samples.

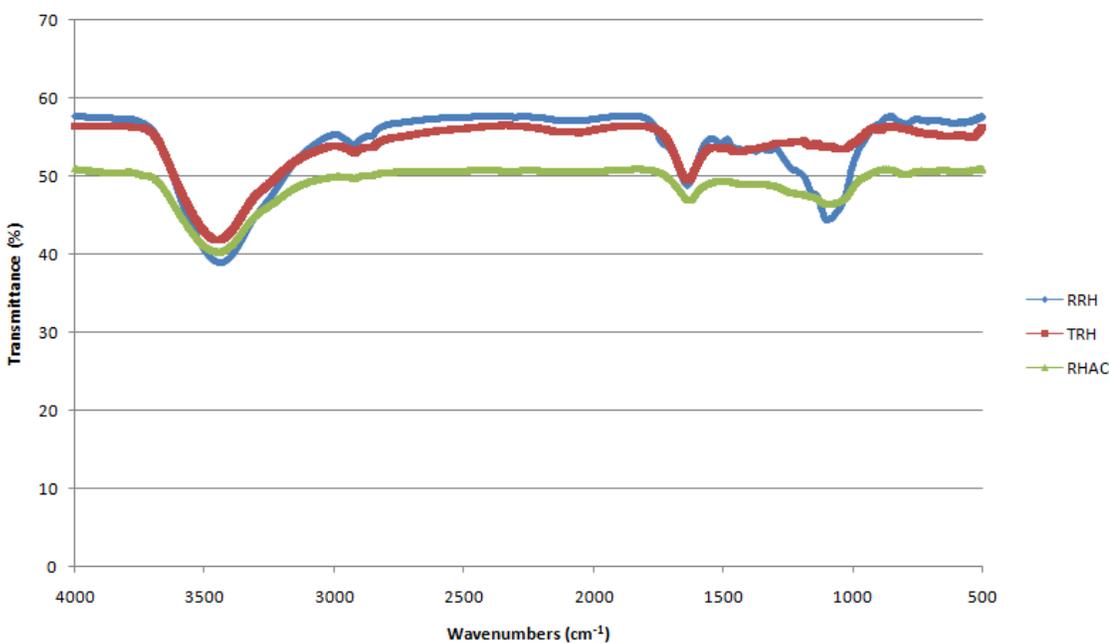


Figure 4.11: FTIR spectra of RRH, TRH and RHAC

According to FTIR spectrum, the adsorption peak around band is located at 3440cm^{-1} that indicates the existence of free O-H hydroxyl groups. In this trend, the amount of O-H hydroxyl group for RHAC is similar as RRH and TRH. This can be due to the existence of moisture that beyond human control. Besides, the C-H stretching vibration around 2900cm^{-1} indicates the presence of alkane functional group. The peak at 1640cm^{-1} corresponds to the C=O stretching that may be attributed to the hemicelluloses and lignin aromatic groups (Garg et al., 2009). The band at $1100 - 1300\text{cm}^{-1}$ may be assigned to C-O stretching vibrations in lactones. The peak around $500-800\text{cm}^{-1}$ corresponds to Si-H groups. Srivastava et al (2006) reported that the presence of polar groups on the surface is likely to provide the considerable cation exchange capacity to the adsorbent. After treating the rice husk with chemical agent, some of the functional group disappeared. This is due to the functional groups reaction with NaOH and its subsequent removal of

water. In addition, the spectrum of RHAC sample is different from the raw material after the carbonization process. Many bands disappeared after the carbonization of TRH which indicates the vaporization of organic matter. This could be explained by the fact that moisture and volatile matters were removed from the material during the carbonization process.

4.4.5 Thermogravimetric analyzer (TGA)

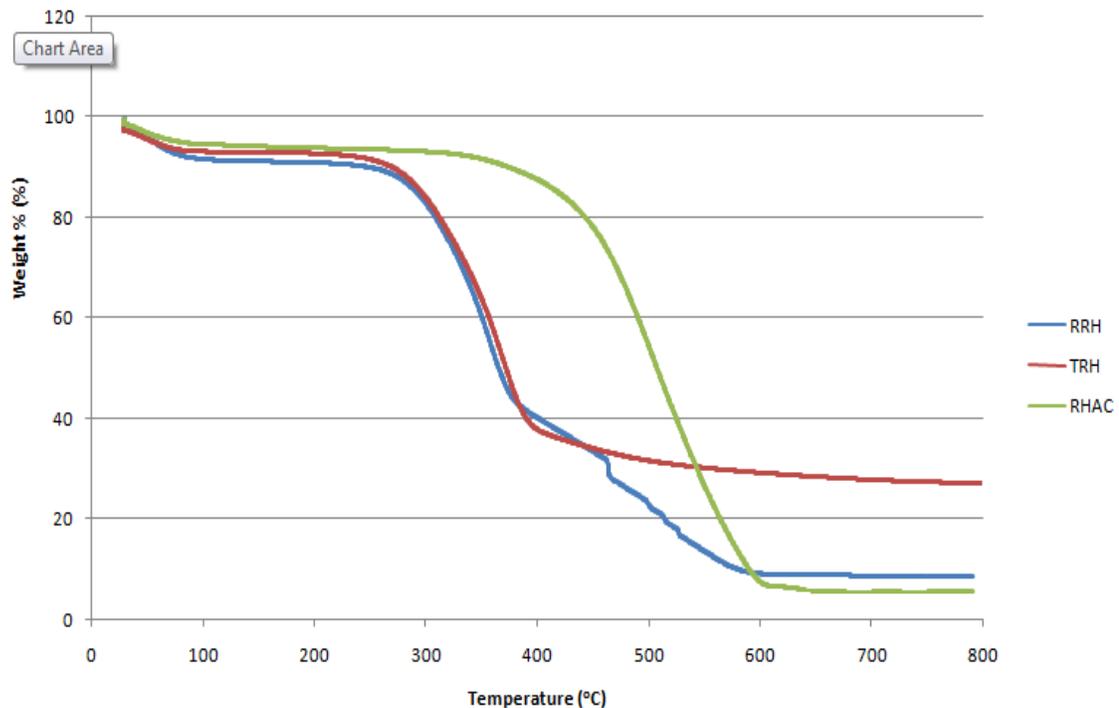


Figure 4.12: TGA analysis of RRH, TRH and RHAC

Thermogravimetric analyzer is a tool to measure the changes in weight of sample with the relation of temperature in inert or oxidative atmosphere. Figure 4.12 above shows the TGA analysis of RRH, TRH and RHAC sample that was carried out between 30 to 800°C in an inert atmosphere. Maria et al (2009) explained three stages of weight loss for activated carbon. From the researches, the weight loss over temperature indicates the composition of the sample and thermal stability. Various components of the sample decomposed with respect to temperature. The initial weight loss can be observed below 100°C due to moisture removal. The weight loss between 200 to 400°C for RRH and TRH are attributed to the decomposition of volatile materials such as cellulose,

hemicelluloses, and lignin. This statement is proved with the report from Antal (1983) that stated three major constituents (cellulose, hemicellulose, and lignin) are chemically active and decompose thermochemically between 150 and 500°C; hemicellulose mainly between 150 and 350°C, cellulose between 275 and 350°C and lignin between 250 and 500°C. Meanwhile for RHAC, the weight loss happens between 300 to 600°C. The third stage of weight loss which indicates the decomposition of pore structure occurs above 400°C (RRH and TRH) and above 600°C (RHAC).

This TGA analysis did not show a straight horizontal line in order to prove that the entire ash component has been removed. This is due to the time and temperature of the test need to be longer and higher for the straight line to appear. As a conclusion, TGA analysis shows that the activation process can be divided into three stages. For the first stage, moisture is released thereby leaving only dried component of rice husk. During the second stage, volatile elements are decomposed and removed in volatile gaseous form. The final stage is where the rice husk has fully turned into activated carbon.

4.4.6 X-ray Diffraction (XRD)

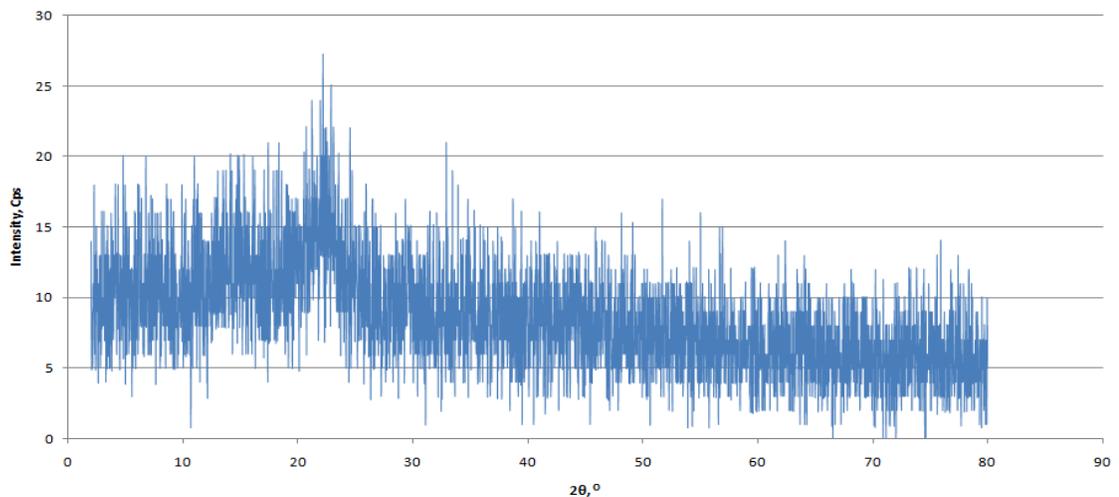


Figure 4.13: XRD curve of RRH

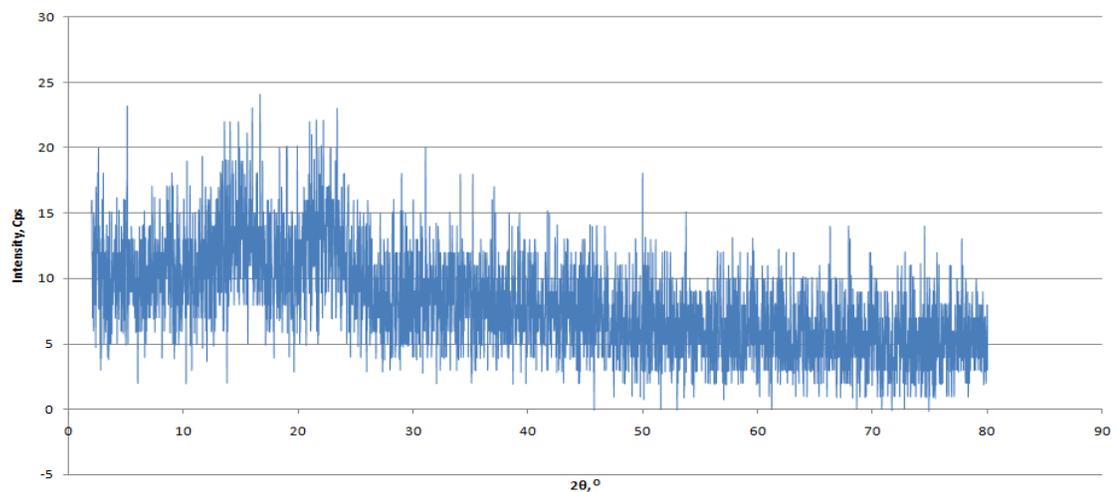


Figure 4.14: XRD curve of TRH

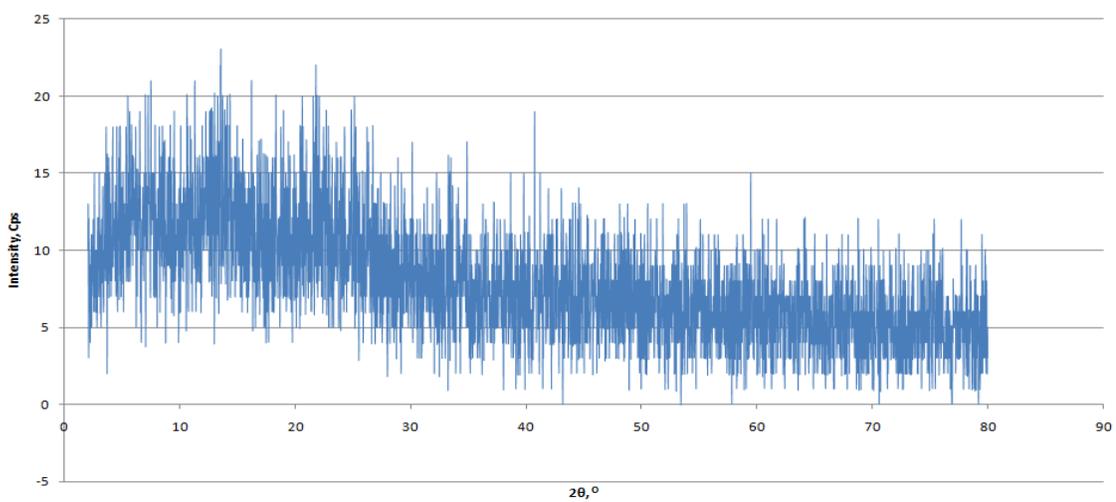


Figure 4.15: XRD curve of RHAC

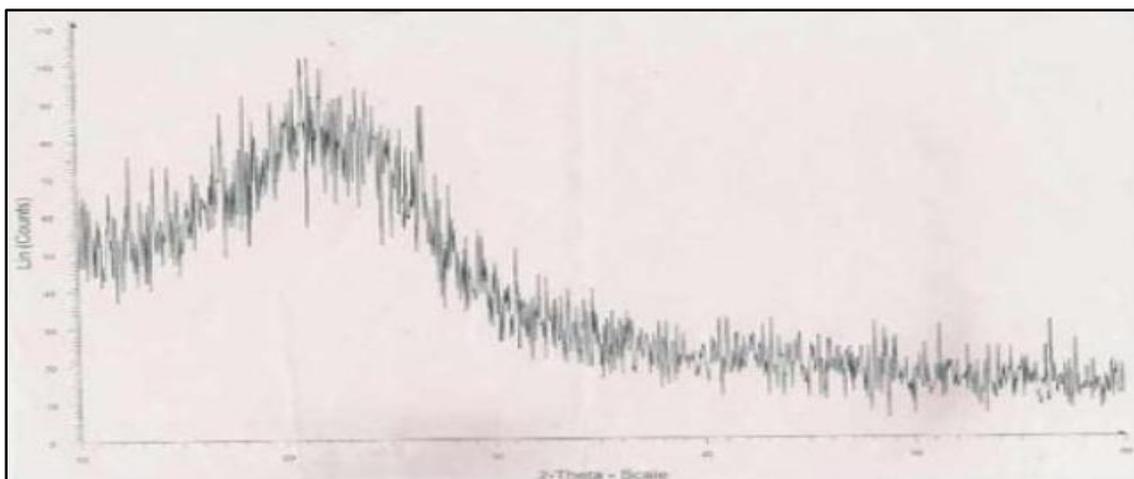


Figure 4.16: XRD curve pattern rice husk activated carbon (Chuah et al., 2005)

RRH, TRH and RHAC were analyzed using X-ray Diffraction (XRD) as a radiation source. Figure 4.13-4.15 show the XRD curves of RRH, TRH and RHAC respectively. The measurement was carried out in a scale 2θ and long duration scan 15s. XRD analysis commonly measure crystalline and amorphous phases by sharp narrow diffraction peaks and broad (halo) peak respectively. From Figure 4.13, a sharp peak is observed at $24^\circ 2\theta$ with relative intensity of 27 cps corresponds to the presence of completely crystalline silica. On the other hand, Figure 4.14 shows a broad peak at $15^\circ 2\theta$ and a sharp peak at $22^\circ 2\theta$ with the intensity of 18 and 22 cps respectively. It indicates a mixture of crystalline and amorphous phases of silica. The diffraction peak for RHAC in Figure 4.15 is around $15^\circ 2\theta$ with 23 cps intensity. This shows that the activated carbon produced in this project has similarities with the commercial activated carbon as projected in Figure 4.16.

4.5 Adsorption Studies

4.5.1 Effect of Initial Metal Ions Concentration and Contact Time

In this project, five different concentrations, 150 ppm, 200 ppm, 250 ppm, 300 ppm and 350 ppm of Pb(II), Zn(II) and Ni(II) were prepared and the dosage of adsorbent was fixed to 0.1 g. The samples were then shaken using rotary shaker from 5 minutes to 3 hours. After a certain time interval, the samples were tested using Atomic Adsorption Spectrophotometer (AAS). Figure 4.17 - 4.22 show the adsorption percentage and adsorption capacity of the metal ions.

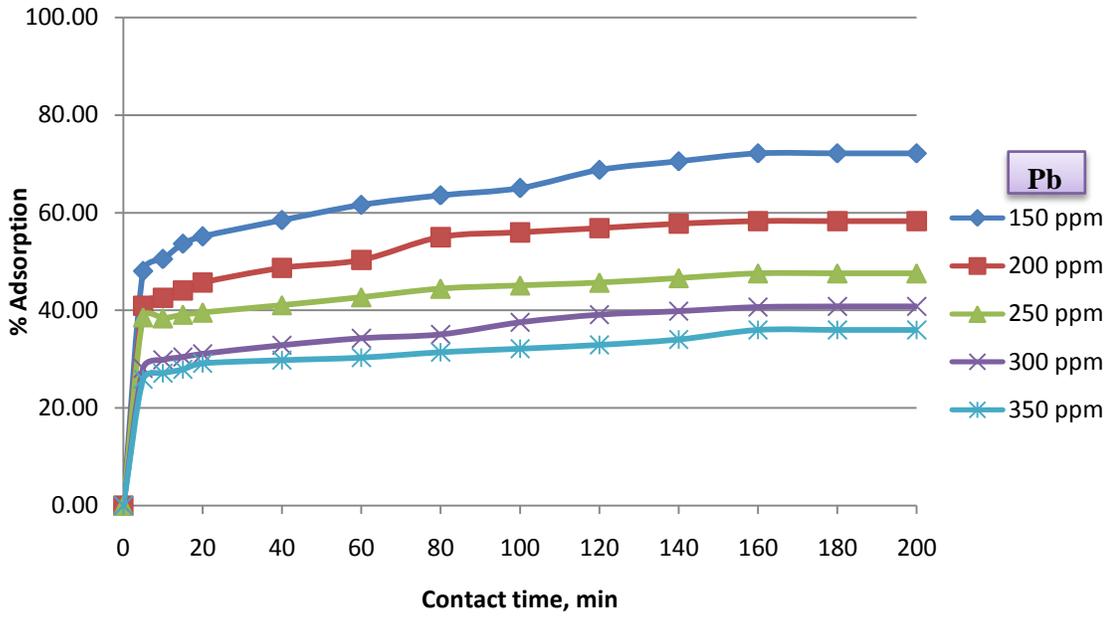


Figure 4.17: Adsorption percentage of Pb(II) ion

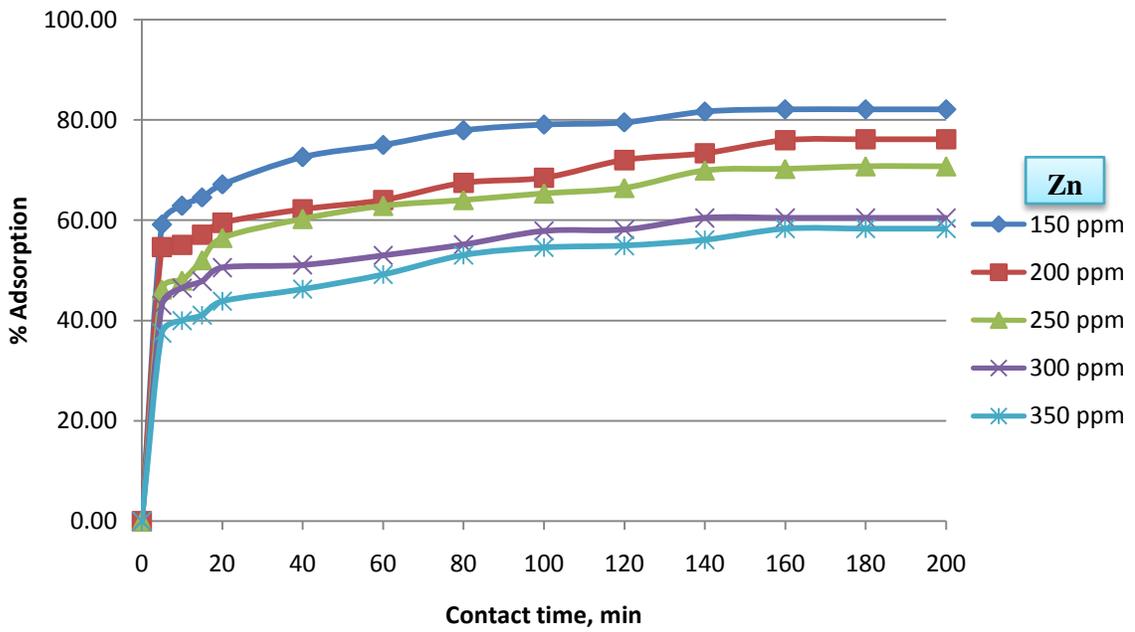


Figure 4.18: Adsorption percentage of Zn(II) ion

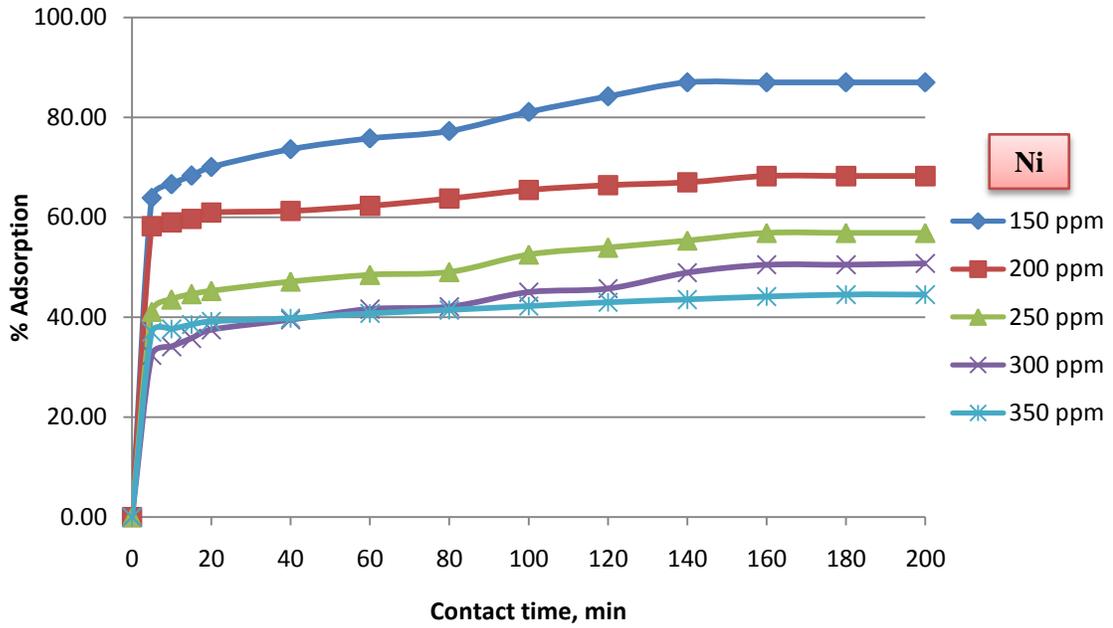


Figure 4.19: Adsorption percentage of Ni(II) ion

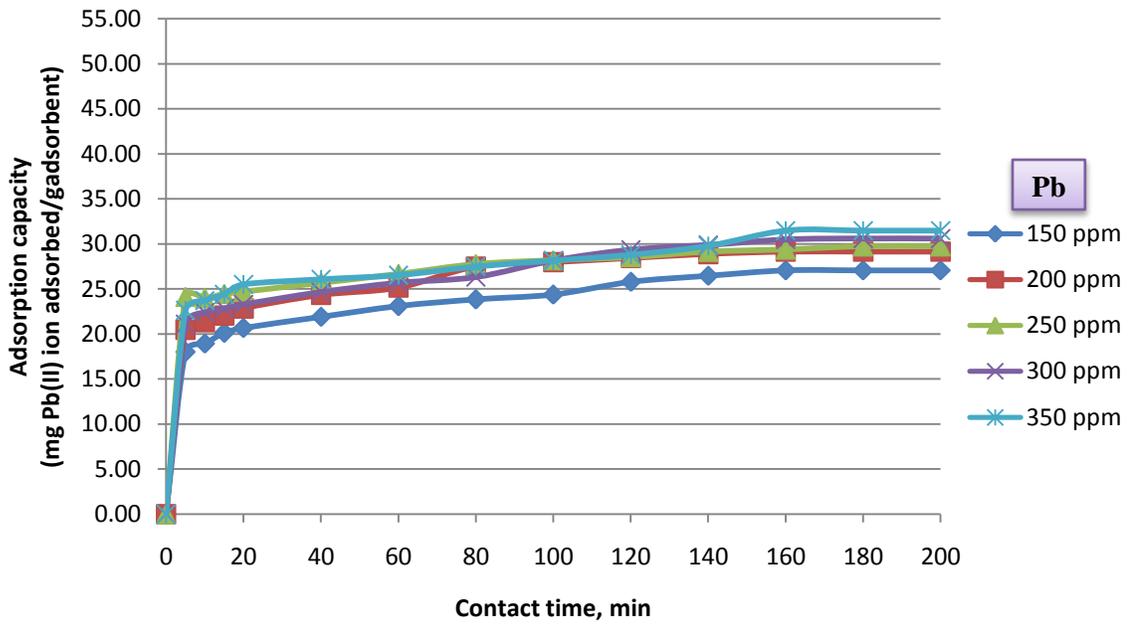


Figure 4.20: Adsorption capacity of RHAC towards Pb(II) ion

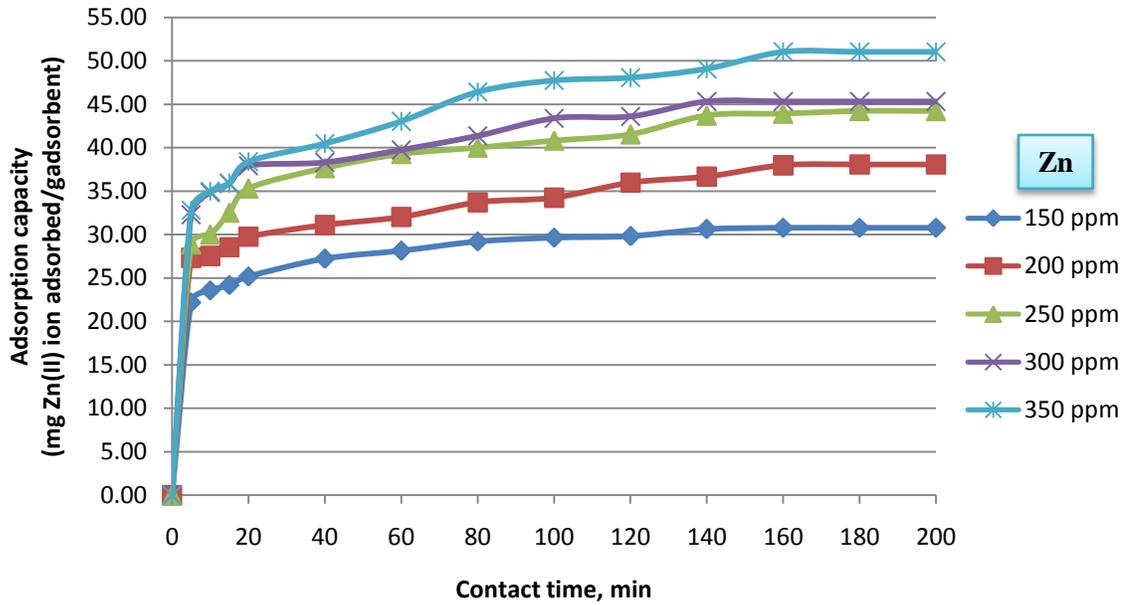


Figure 4.21: Adsorption capacity of RHAC towards Zn(II) ion

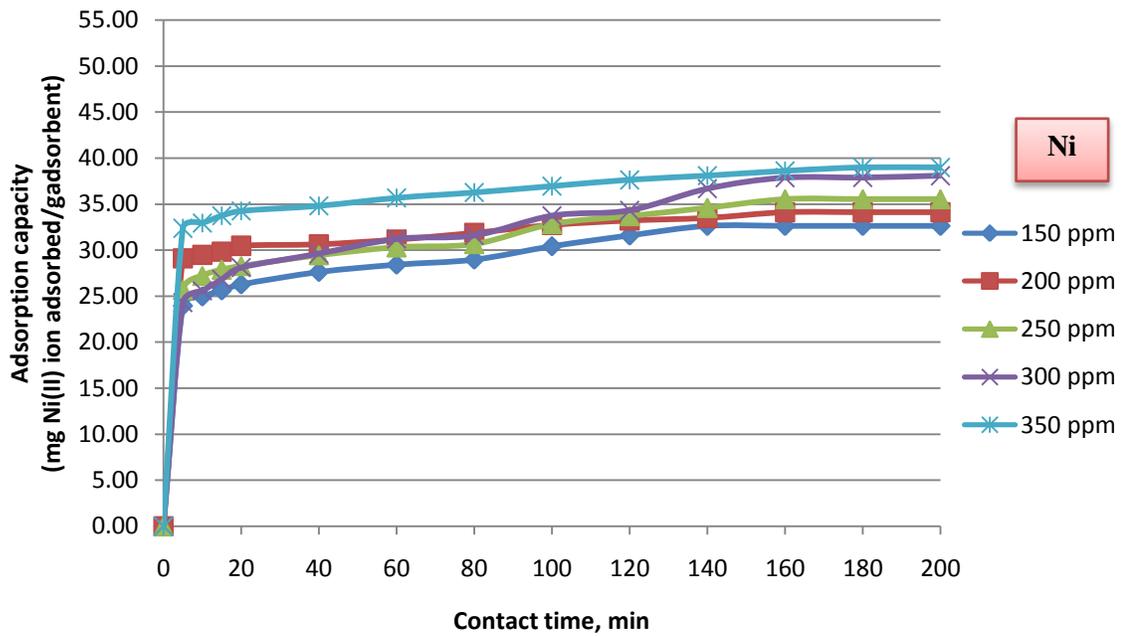


Figure 4.22: Adsorption capacity of RHAC towards Ni(II) ion

From those plots, it is found that adsorption percentage of Pb(II), Zn(II) and Ni(II) ions increases with increasing contact time at each initial metal ions concentration. However, when the contact time reaches the threshold of 160 minutes, any increment in contact time then would not have significant improvement in adsorption ratio. Hence it can be deduced that the equilibrium time for adsorption within the same scenario is 160 minutes regardless of the concentration of metal ions solution. The pattern also showed that the percentage removal increases with decrease in the concentration of metal ions. The increase in percentage adsorption with dilution is explained on the basis of availability of larger number of surface sites of the adsorbent for a relatively small number of adsorbing species at high dilution (Parekh et al., 2002).

From the adsorption capacity graphs, it was observed that the amount of metal ion uptake, q_t is increased with increase in initial metal ion concentration. At lower concentration, lead ion in the solution would interact with the binding sites and thus facilitated almost 100% adsorption while at higher concentration, more lead are left un-adsorbed in the solution due to saturation of the binding sites. This adsorption behavior indicates that rice husk-based activated carbon (RHAC) has a potential as metal extraction agent for Pb(II), Zn(II) and Ni(II) from single aqueous solution. The result obtained shows that the adsorption capacity of Pb(II), Zn(II) and Ni(II) are 31.48 mg/g, 51.04 mg/g and 38.97 mg/g respectively. Thus, RHAC has the ability to remove Zn(II) ion better than Pb(II) and Ni(II). Thus, further study has been conducted in order to investigate the selectivity of RHAC towards Pb(II), Zn(II) and Ni(II) ions when these metal ions are mixed together in an aqueous solution. Figure 4.23 - 4.24 shows the adsorption percentage for the mixture of metal ions at 150 ppm.

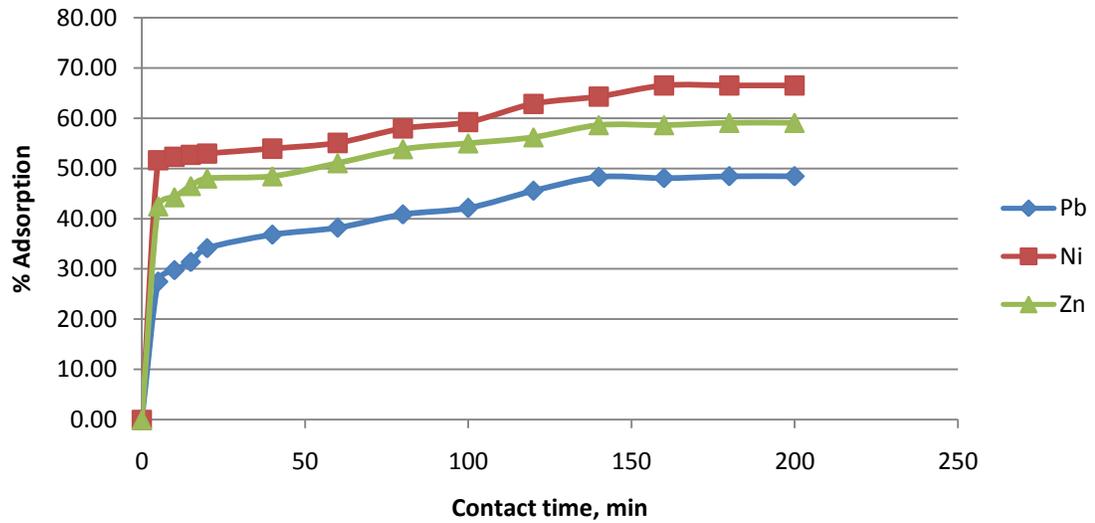


Figure 4.23: Adsorption percentage for the mixture of metal ions at 150 ppm.

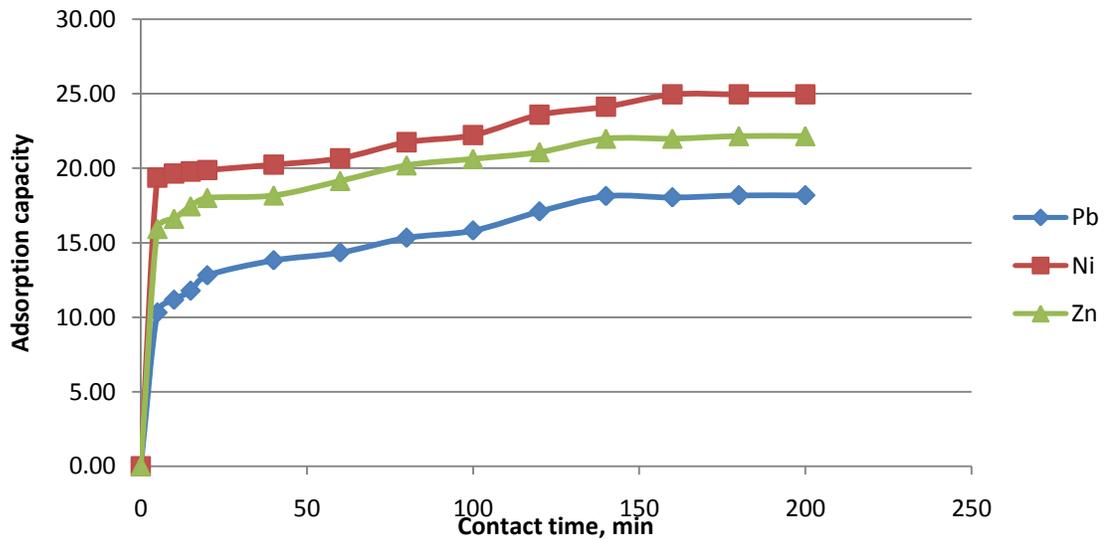


Figure 4.24: Adsorption capacity for the mixture of metal ions at 150 ppm.

From the graph, it is proven that the adsorption towards Ni(II) ions is higher than Pb(II) and Zn(II) ions when these metals are present together in a solution. The adsorption capacity of Ni(II) is 24.95 mg/g compared to Pb(II) and Zn(II) ions which are 18.04 mg/g and 22.99 mg/g. In addition, the adsorption capacities of Pb(II), Zn(II) and Ni(II) ions are relatively smaller as compared to their adsorption capacity in single aqueous solution. According to Yue, the sorption capacities should be taken as the values that can be achieved under a specific set of conditions and not as maximum sorption capacities.

4.5.2 Isotherm Experiment

The adsorption isotherm for the removal of metal ions were studied using initial concentration of between 150 ppm and 350 ppm at an adsorbent dosage level of 0.1g for Pb(II), Zn(II) and Ni(II). The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e .

Adsorption equilibrium data or isotherms are required in designing an adsorption system. The measured adsorption equilibrium data are fitted with Langmuir and Freundlich adsorption isotherm. These isotherms are useful in determining the total amount of adsorbent needed to adsorb a required amount of metal ions from aqueous solution as well as to diagnose the nature of adsorption. Linear regression was frequently used to determine the most fitted isotherm (Sen et al., 2008).

Langmuir isotherm assumes uniform energies of monolayer adsorption onto surface and without transmigration of adsorbate in the plane of the surface (Gupta et al., 2006). The linearized form of Langmuir can be written as

$$\frac{1}{q_e} = \left(\frac{1}{bq_m} \right) \frac{1}{C_e} + \frac{1}{q_m} \quad (5)$$

Where q_e is the amount of metal ions adsorbed on RHAC at equilibrium (mg/g), C_e is the equilibrium concentration of metal ion (mg/L). q_m and b are the Langmuir constants related to the maximum adsorption capacity and energy of adsorption respectively.

The Freundlich adsorption isotherm, which assumes that adsorption takes place on heterogeneous surfaces, can be expressed as

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_f \quad (6)$$

Where q_e is the amount of metal ions adsorbed on RHAC at equilibrium (mg/g), C_e is the equilibrium concentration of metal ion (mg/L). K_f and $1/n$ are Freundlich constants which

indicate the capacity and the intensity of the adsorption, respectively. The linearized Langmuir and Freundlich adsorption isotherms of Pb(II), Zn(II) and Ni(II) are shown in Figure 4.25 - 4.30.

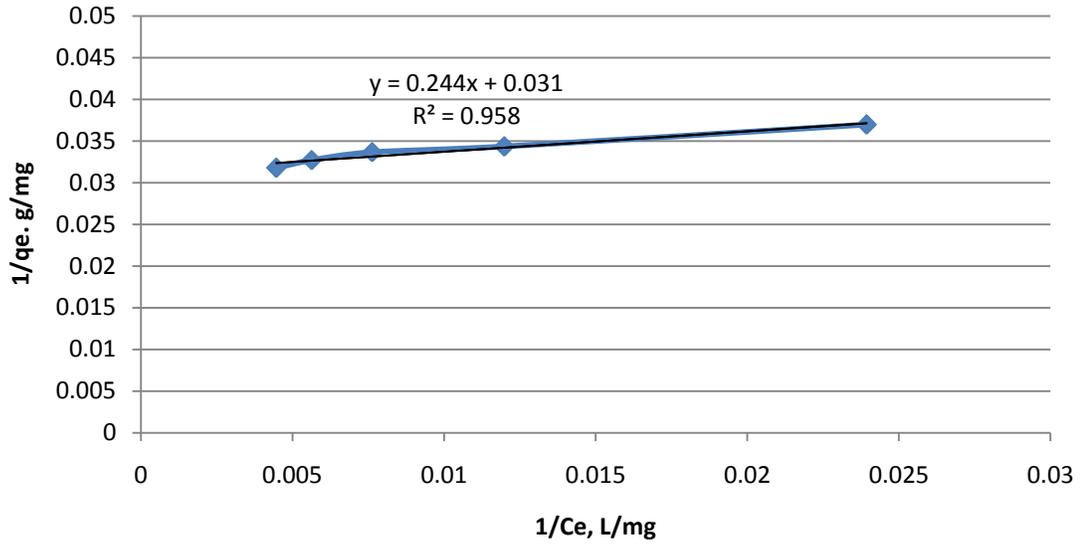


Figure 4.25: Langmuir isotherm for adsorption of Pb(II) ion on RHAC

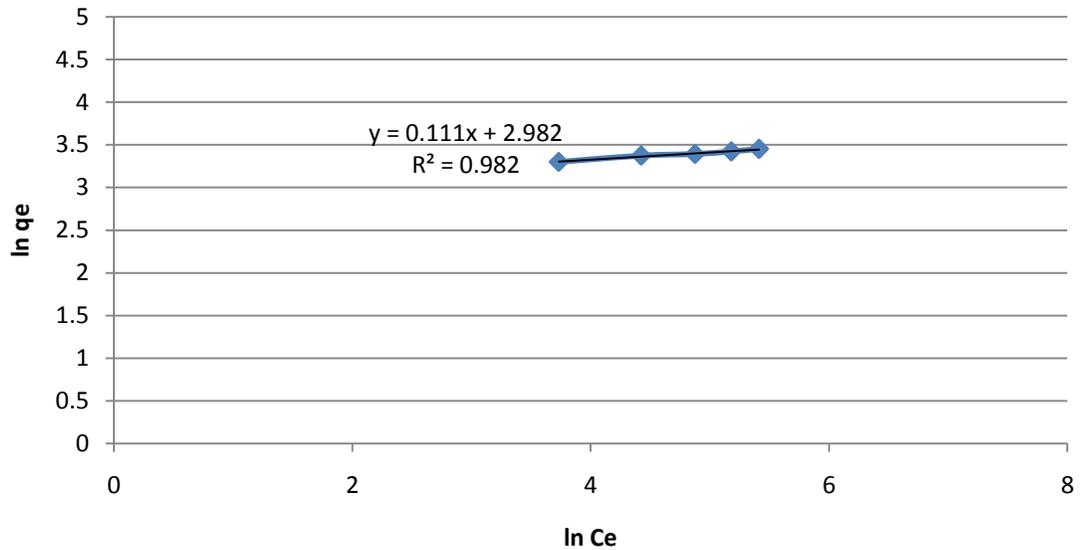


Figure 4.26: Freundlich isotherm for adsorption of Pb(II) ion on RHAC

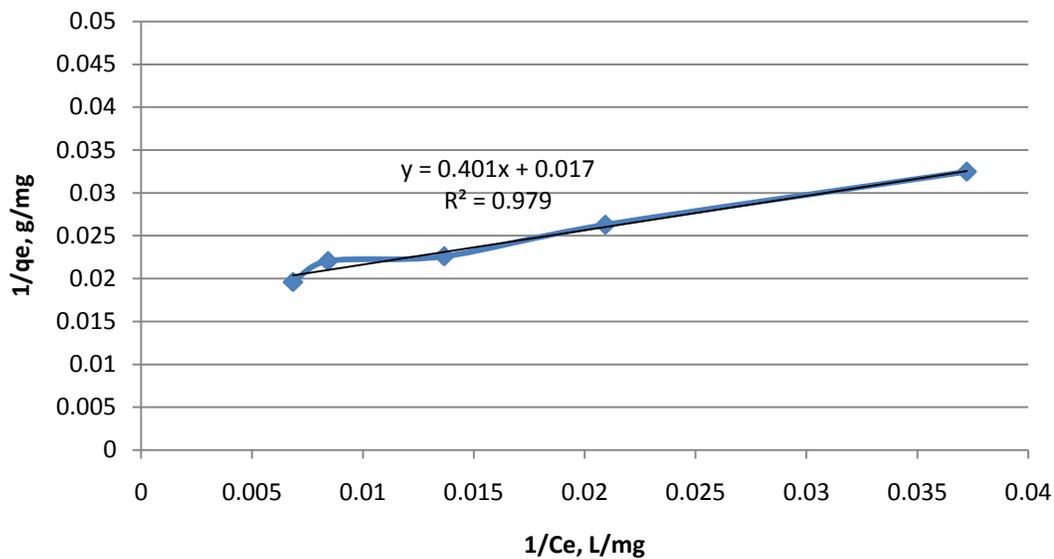


Figure 4.27: Langmuir isotherm for adsorption of Zn(II) ion on RHAC

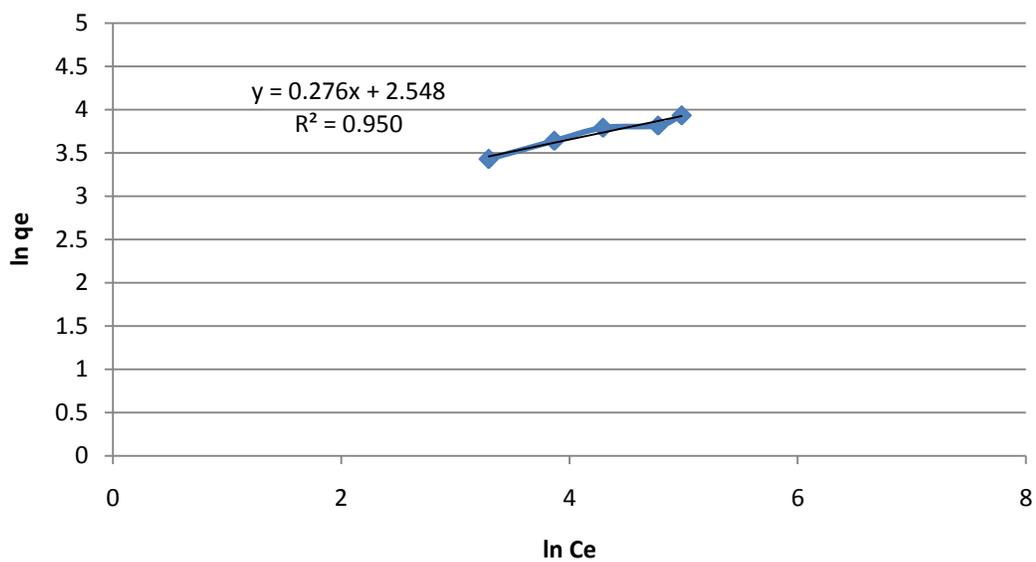


Figure 4.28: Freundlich isotherm for adsorption of Zn(II) ion on RHAC

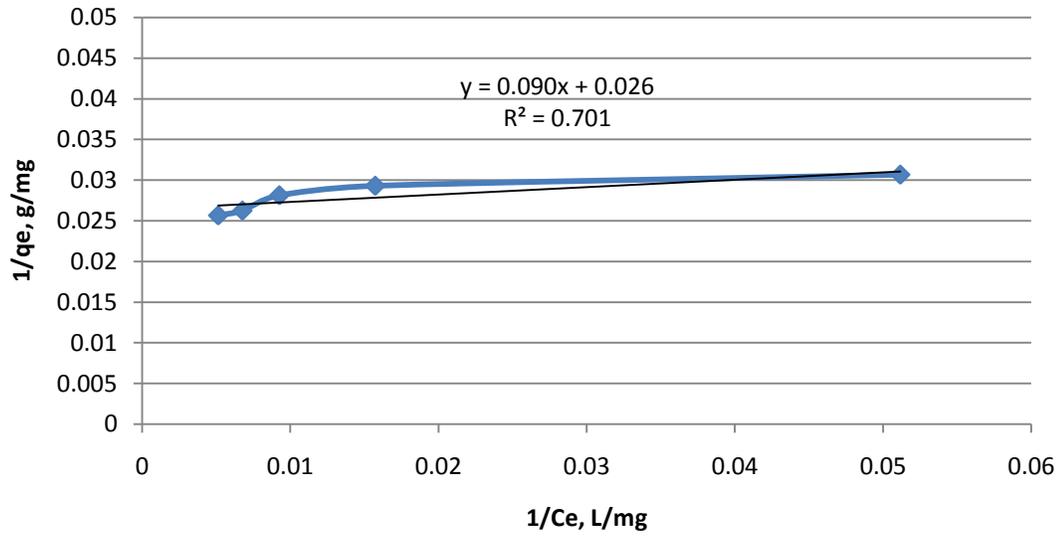


Figure 4.29: Langmuir isotherm for adsorption of Ni(II) ion on RHAC

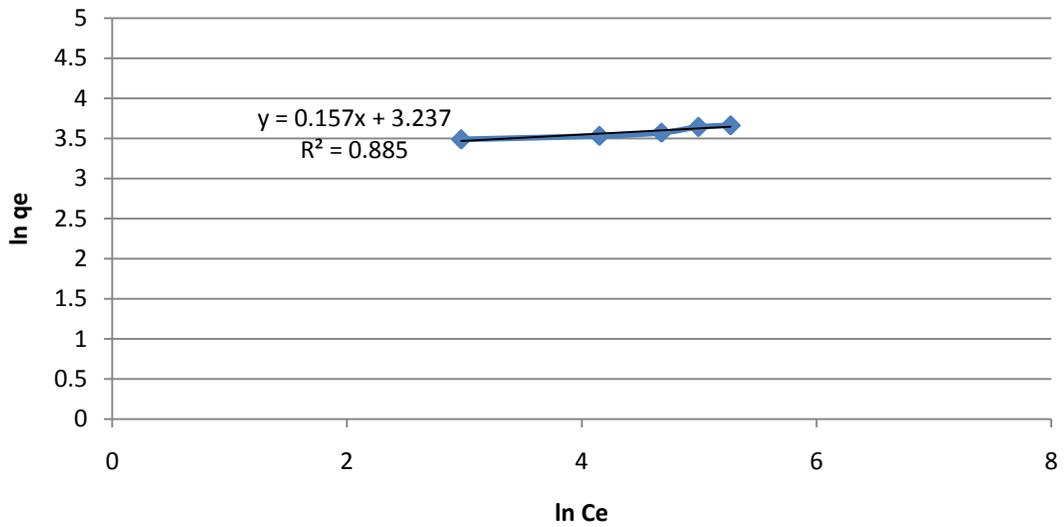


Figure 4.30: Freundlich isotherm for adsorption of Ni(II) ion on RHAC

The values of adsorption isotherm for Pb(II), Zn(II) and Ni(II) are tabulated in Table 4.3. Comparing to the R^2 values, the adsorption data fits Freundlich isotherm well compared to Langmuir isotherm. It shows the heterogeneity of the material as well as the possibility of monolayer adsorption. Besides, the values of $1 < n < 10$ indicate the effectiveness of the adsorbent towards the removal of metal ions (Ramadevi et al., 2005). In industry, Freundlich isotherm is used most commonly to describe adsorption characteristics of the activated carbon used in water and wastewater treatment.

Table 4.3: Langmuir and Freundlich isotherm constants for adsorption of Pb(II), Zn(II) and Ni(II) ions on RHAC

Metal ions	Langmuir Constants			Freundlich Constants		
	$Q_m(\text{mg/g})$	$b(\text{mg/L})$	R^2	K_f	n	R^2
Pb(II)	32.25806	0.127049	0.958	19.72723168	9.01	0.982
Zn(II)	58.82353	0.042394	0.979	12.78152	3.62	0.950
Ni(II)	38.46154	0.288889	0.701	25.45724	6.37	0.885

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In conclusion, this project serves to enhance the research and development of low-cost commercial activated carbon. In this context, rice husk is selected as an alternative source due to the high production of rice husk globally. Rice husk-based activated carbon is synthesized through the treatment of raw rice husk and carbonization process of treated rice husk at 500°C for 2 hours. The characterization of raw rice husk (RRH), treated rice husk (TRH) and rice husk-based activated carbon (RHAC) was carried out by using CHN Elemental Analyzer, FESEM, BET, FTIR, TGA and XRD. Based on the result obtained, the carbon content is increased whereby the nitrogen and hydrogen content showed the opposite trend. From the morphology analysis, RHAC showed better evolution on the development of pores as compared to RRH and TRH that would give RHAC a better adsorption capacity for the removal of Pb(II), Zn(II) and Ni(II) ions from aqueous solution. The surface area, pore volume and average pore diameter of RHAC are 354m²/g, 0.29 cm³/g and 6.84 nm respectively. Adsorption studies have revealed that the initial metal uptake was rapid and equilibrium was attained in 160 minutes. Zn(II) has the highest adsorption capacity (51.04 mg/g) compared to other metal ions in a single aqueous solution. Besides, experimental results have proved that Ni(II) has the highest adsorption selectivity compared to other metal ions where they are mixed together in an aqueous solution with the value of 24.95 mg/g. Isothermal study indicated that adsorption data correlated well with Freundlich isotherm model.

There are several recommendation have been identified in order to improve the current project. Adsorption studies can be investigated by using industrial wastewater in order to test the capability of rice husk based activated carbon for the removal of heavy metals. Besides, adsorption studies can be carried out by varying the adsorbent dose, carbonization temperature as well as the pH of initial metal ion solution.

CHAPTER 6

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CHAPTER 7

APPENDICES

APPENDIX I

Calculation of 500 ppm of Pb(II) ion solution.

In order to minimize error, the solution prepared is started from 50 ppm Pb(NO₃)₂:

$$500 \text{ ppm by mass} = \frac{500 \text{ mg Pb(II)}}{1 \text{ kg of water}}$$

Given the molar mass: Pb – 207.2 g/mol Pb(NO₃)₂ – 331.2 g/mol

Assuming 1.0 mol of Pb(NO₃)₂, thus having 1.0 mol of Pb(II)

$$\begin{aligned} \text{Mass of Pb(II) ions} &= \frac{207.2 \text{ g Pb(II)}}{1 \text{ mol of Pb(II)}} \times 1 \text{ mol of Pb(II)} \\ &= 207.2 \text{ g Pb(II)} \end{aligned}$$

$$\begin{aligned} \text{Mass of Pb(NO}_3)_2 \text{ ions} &= \frac{331.2 \text{ g Pb(NO}_3)_2}{1 \text{ mol of Pb(NO}_3)_2} \times 1 \text{ mol of Pb(NO}_3)_2 \\ &= 331.2 \text{ g Pb(NO}_3)_2 \end{aligned}$$

$$\begin{aligned} \text{Percent mass of Pb(II) ions} &= \frac{207.2 \text{ g Pb(II)}}{331.2 \text{ g Pb(NO}_3)_2} \\ &= 0.626 \text{ g} \frac{\text{Pb(II)}}{\text{Pb(NO}_3)_2} \end{aligned}$$

Then 500 mg of Pb(II) in Pb(NO₃)₂ :

$$500 \times 10^{-3} \text{ g Pb(II)} \times \frac{1 \text{ g Pb(NO}_3)_2}{0.626 \text{ Pb(II)}} = 0.799 \text{ g Pb(NO}_3)_2$$

By using dilution formula, $M_1V_1 = M_2V_2$

$$500V_1 = 150(1000\text{ml})$$

$$V_1 = 300 \text{ ml}$$

Therefore, **300 ml of 500 ppm of Pb(II) ion solution** is diluted to prepare 150 ppm of Pb(II).

APPENDIX II

Calculation for Percentage Adsorption and Adsorption capacity

The calculation for percentage adsorption and adsorption capacity are such as below:

$$\text{Percentage adsorption} = \frac{(C_i - C_t)}{C_i} \times 100$$

$$\text{Adsorption capacity, } q_t = \left[\frac{(C_i - C_t)}{W} \right] \times V$$

Where:

C_i = Initial metal ion concentration

C_t = Metal ion concentration at time t

W = Dry weight of adsorbent used, g

V = Volume of metal ion solution, L

APPENDIX III

Adsorption Studies: Effect of Initial Metal Ions Concentration and Contact Time

Volume of solution, $V = 25\text{mL} = 0.025\text{ L}$

Amount of adsorbent, $m = 0.1\text{ g}$

Table A.1: Effect of Initial Pb(II) Ion Concentration

Sample ID	Time(min)	Initial concentration, C_i (ppm)	Final concentration, C_f (ppm)	Adsorption %	Adsorption capacity, qt (mg/g)
1	0	150	150.00	0.00	0
2	5	150	77.99	48.01	18.00375
3	10	150	74.30	50.47	18.92625
4	15	150	69.53	53.65	20.11875
5	20	150	67.34	55.11	20.66625
6	40	150	62.36	58.43	21.91125
7	60	150	57.65	61.57	23.08875
8	80	150	54.69	63.54	23.8275
9	100	150	52.47	65.02	24.3825
10	120	150	46.89	68.74	25.7775
11	140	150	44.19	70.54	26.4525
12	160	150	41.78	72.15	27.05625
13	180	150	41.78	72.15	27.05625
14	200	150	41.78	72.15	27.05625
15	0	200	200.00	0.00	0
16	5	200	118.10	40.95	20.475
17	10	200	114.84	42.58	21.29
18	15	200	111.86	44.07	22.035
19	20	200	108.64	45.68	22.84
20	40	200	102.64	48.68	24.34
21	60	200	99.36	50.32	25.16
22	80	200	90.04	54.98	27.49
23	100	200	88.10	55.95	27.975
24	120	200	86.3	56.85	28.425
25	140	200	84.48	57.76	28.88
26	160	200	83.45	58.275	29.1375
27	180	200	83.45	58.275	29.1375
28	200	200	83.45	58.275	29.1375
29	0	250	250.00	0.00	0
30	5	250	153.49	38.604	24.1275
31	10	250	154.11	38.356	23.9725

32	15	250	152.23	39.11	24.44375
33	20	250	151.20	39.52	24.7
34	40	250	147.30	41.08	25.675
35	60	250	143.33	42.67	26.66875
36	80	250	138.98	44.41	27.75625
37	100	250	137.23	45.11	28.19375
38	120	250	135.88	45.648	28.53
39	140	250	133.5	46.6	29.125
40	160	250	132.5	47.56	29.375
41	180	250	131.1	47.56	29.725
42	200	250	131.1	47.56	29.725
43	0	300	300.00	0.00	0
44	5	300	215.61	28.13	21.0975
45	10	300	210.45	29.85	22.3875
46	15	300	208.68	30.44	22.83
47	20	300	206.85	31.05	23.2875
48	40	300	201.39	32.87	24.6525
49	60	300	197.25	34.25	25.6875
50	80	300	194.76	35.08	26.31
51	100	300	187.38	37.54	28.155
52	120	300	182.67	39.11	29.3325
53	140	300	180.56	39.81	29.86
54	160	300	178.05	40.65	30.4875
55	180	300	177.63	40.79	30.5925
56	200	300	177.63	40.79	30.5925
57	0	350	350.00	0.00	0
58	5	350	259.48	25.86285714	22.63
59	10	350	255.15	27.1	23.7125
60	15	350	252.4	27.88571429	24.4
61	20	350	248.01	29.14	25.4975
62	40	350	245.74	29.78857143	26.065
63	60	350	243.88	30.32	26.53
64	80	350	240.11	31.39714286	27.4725
65	100	350	237.48	32.14857143	28.13
66	120	350	234.84	32.90285714	28.79
67	140	350	230.90	34.03	29.77625
68	160	350	224.07	35.98	31.4825
69	180	350	224.07	35.98	31.4825
70	200	350	224.07	35.98	31.4825

Table A.2: Effect of Initial Zn(II) Ion Concentration

Sample ID	Time(min)	Initial concentration, C_i (ppm)	Final concentration, C_t (ppm)	Adsorption %	Adsorption capacity, qt (mg/g)
1	0	150	150	0.00	0
2	5	150	61.29	59.14	22.1775
3	10	150	55.725	62.85	23.56875
4	15	150	53.22	64.52	24.195
5	20	150	49.29	67.14	25.1775
6	40	150	41.16	72.56	27.21
7	60	150	37.485	75.01	28.12875
8	80	150	33.195	77.87	29.20125
9	100	150	31.44	79.04	29.64
10	120	150	30.78	79.48	29.805
11	140	150	27.525	81.65	30.61875
12	160	150	26.865	82.09	30.78375
13	180	150	26.865	82.09	30.78375
14	200	150	26.865	82.09	30.78375
15	0	200	200.00	0.00	0
16	5	200	90.74	54.63	27.315
17	10	200	89.82	55.09	27.545
18	15	200	85.78	57.11	28.555
19	20	200	81.02	59.49	29.745
20	40	200	75.64	62.18	31.09
21	60	200	71.92	64.04	32.02
22	80	200	65.12	67.44	33.72
23	100	200	63.04	68.48	34.24
24	120	200	56.06	71.97	35.985
25	140	200	53.30	73.35	36.675
26	160	200	48.10	75.95	37.975
27	180	200	47.76	76.12	38.06
28	200	200	47.76	76.12	38.06
29	0	250	250.00	0.00	0
30	5	250	134.45	46.22	28.8875
31	10	250	130.05	47.98	29.9875
32	15	250	119.88	52.05	32.53125
33	20	250	108.80	56.48	35.3
34	40	250	99.40	60.24	37.65
35	60	250	92.90	62.84	39.275

36	80	250	89.98	64.01	40.00625
37	100	250	86.70	65.32	40.825
38	120	250	83.88	66.45	41.53125
39	140	250	75.225	69.91	43.69375
40	160	250	74.38	70.25	43.90625
41	180	250	73.13	70.75	44.21875
42	200	250	73.13	70.75	44.21875
43	0	300	300.00	0.00	0
44	5	300	170.85	43.05	32.2875
45	10	300	160.62	46.46	34.845
46	15	300	156.57	47.81	35.8575
47	20	300	148.35	50.55	37.9125
48	40	300	146.79	51.07	38.3025
49	60	300	141.06	52.98	39.735
50	80	300	134.55	55.15	41.3625
51	100	300	126.45	57.85	43.3875
52	120	300	125.64	58.12	43.59
53	140	300	118.68	60.44	45.33
54	160	300	118.68	60.44	45.33
55	180	300	118.68	60.44	45.33
56	200	300	118.68	60.44	45.33
57	0	350	350.00	0.00	0
58	5	350	218.82	37.48	32.795
59	10	350	210.04	39.99	34.99125
60	15	350	206.29	41.06	35.9275
61	20	350	196.46	43.87	38.38625
62	40	350	188.09	46.26	40.4775
63	60	350	177.87	49.18	43.0325
64	80	350	164.33	53.05	46.41875
65	100	350	159.08	54.55	47.73125
66	120	350	157.78	54.92	48.055
67	140	350	153.72	56.08	49.07
68	160	350	145.85	58.33	51.03875
69	180	350	145.85	58.33	51.03875
70	200	350	145.85	58.33	51.03875

Table A.3: Effect of Initial Ni(II) Ion Concentration

Sample ID	Time(min)	Initial concentration, C_i (ppm)	Final concentration, C_f (ppm)	Adsorption %	Adsorption capacity, qt (mg/g)
1	0	150	150.00	0.00	0
2	5	150	54.20	63.87	23.95125
3	10	150	50.13	66.58	24.9675
4	15	150	47.54	68.31	25.61625
5	20	150	44.93	70.05	26.26875
6	40	150	39.56	73.63	27.61125
7	60	150	36.33	75.78	28.4175
8	80	150	34.16	77.23	28.96125
9	100	150	28.37	81.09	30.40875
10	120	150	23.69	84.21	31.57875
11	140	150	19.55	86.97	32.61375
12	160	150	19.55	86.97	32.61375
13	180	150	19.55	86.97	32.61375
14	200	150	19.55	86.97	32.61375
15	0	200	200.00	0.00	0
16	5	200	83.55	58.23	29.1125
17	10	200	82.04	58.98	29.49
18	15	200	80.65	59.68	29.8375
19	20	200	78.11	60.95	30.4725
20	40	200	77.45	61.28	30.6375
21	60	200	75.39	62.31	31.1525
22	80	200	72.48	63.76	31.88
23	100	200	69.04	65.48	32.74
24	120	200	67.14	66.43	33.215
25	140	200	65.98	67.01	33.505
26	160	200	63.54	68.23	34.115
27	180	200	63.54	68.23	34.115
28	200	200	63.54	68.23	34.115
29	0	250	250.00	0.00	0
30	5	250	147.28	41.09	25.68125
31	10	250	141.15	43.54	27.2125
32	15	250	138.48	44.61	27.88125
33	20	250	136.88	45.25	28.28125
34	40	250	132.23	47.11	29.44375
35	60	250	128.80	48.48	30.3
36	80	250	127.40	49.04	30.65
37	100	250	118.65	52.54	32.8375

38	120	250	115.23	53.91	33.69375
39	140	250	111.65	55.34	34.5875
40	160	250	107.83	56.87	35.54375
41	180	250	107.83	56.87	35.54375
42	200	250	107.83	56.87	35.54375
43	0	300	300.00	0.00	0
44	5	300	202.80	32.40	24.3
45	10	300	197.67	34.11	25.5825
46	15	300	192.69	35.77	26.8275
47	20	300	187.56	37.48	28.11
48	40	300	181.59	39.47	29.6025
49	60	300	175.14	41.62	31.215
50	80	300	173.64	42.12	31.59
51	100	300	165.03	44.99	33.7425
52	120	300	162.78	45.74	34.305
53	140	300	153.27	48.91	36.6825
54	160	300	148.53	50.49	37.8675
55	180	300	148.47	50.51	37.8825
56	200	300	147.69	50.77	38.0775
57	0	350	350.00	0.00	0
58	5	350	220.49	37.00	32.3775
59	10	350	218.19	37.66	32.9525
60	15	350	215.09	38.55	33.7275
61	20	350	212.97	39.15	34.2575
62	40	350	210.78	39.78	34.805
63	60	350	207.31	40.77	35.6725
64	80	350	204.98	41.43	36.255
65	100	350	202.22	42.22	36.945
66	120	350	199.48	43.01	37.63
67	140	350	197.64	43.53	38.09
68	160	350	195.54	44.13	38.615
69	180	350	194.11	44.54	38.9725
70	200	350	194.11	44.54	38.9725

Table A.4: Selectivity of Pb(II), Zn(II) and Ni(II) in an aqueous solution at 150 ppm

ID	Time (min)	Initial concentration, C_i (ppm)	Final Concentration, C_t (ppm)			% Adsorption			Adsorption capacity, q_t (mg/g)		
			Pb	Zn	Ni	Pb	Zn	Ni	Pb	Zn	Ni
1	0	150	150	150	150	0	0.00	0	0	0	0
2	5	150	108.75	86.265	72.525	27.5	42.49	51.65	10.3125	15.93375	19.36875
3	10	150	105.33	83.535	71.46	29.78	44.31	52.36	11.1675	16.61625	19.635
4	15	150	102.9	80.175	70.89	31.4	46.55	52.74	11.775	17.45625	19.7775
5	20	150	98.775	77.94	70.485	34.15	48.04	53.01	12.80625	18.015	19.87875
6	40	150	94.725	77.28	69.045	36.85	48.48	53.97	13.81875	18.18	20.23875
7	60	150	92.64	73.38	67.335	38.24	51.08	55.11	14.34	19.155	20.66625
8	80	150	88.68	69.195	63.03	40.88	53.87	57.98	15.33	20.20125	21.7425
9	100	150	86.745	67.455	61.125	42.17	55.03	59.25	15.81375	20.63625	22.21875
10	120	150	81.615	65.64	55.665	45.59	56.24	62.89	17.09625	21.09	23.58375
11	140	150	77.49	62.025	53.505	48.34	58.65	64.33	18.1275	21.99375	24.12375
12	160	150	77.835	62.025	50.19	48.11	58.65	66.54	18.04125	22.9948	24.9525