Adsorptive removal of Zn (II) from aqueous solution using rice husk-based activated carbon.

By

Muhammad Zubair Bin Ghazali

Dissertation submitted in partial fulfilment
of the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

May 2012 Semester

Universiti Teknologi Petronas
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Adsorptive removal of Zn (II) from aqueous solution using rice husk-based activated carbon.

By

Muhammad Zubair Bin Ghazali

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

Approved by,

(Mohd Faisal B Taha)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
MAY 2012

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.

(Muhammad Zubair Bin Ghazali)

ABSTRACT

The study of rice husk as potential activated carbon as a low-cost adsorbent to remove zinc (Zn) from Zn(II) ion solution was investigated. Raw rice husk as an agricultural waste was chosen for this project due to its huge amount of production during milling activities. The scope of this study covers from preparation of the rice husk activated carbon (RHAC) to the experimental works for removal of Zn(II) ion from aqueous solution. The preparation involves three stages which are preparation of raw rice husk to size of 63µm, digestion and carbonization. 63µm raw rice husks were digested with 1.0 M sodium hydroxide (NaOH) solution for 24 hours. The treated rice husks were then carbonized at 500°C for 1 hour in order to remove volatile organic constituents leaving behind highly porous carbonaceous materials. Once the activated carbon was prepared, mixing process with Zn(II) ion solution at various contact time ranging from 5 to 120 minutes was carried out to study the adsorption capacity. In this study, pores development in rice husk was analyzed using FESEM for each stage. Other analyses on rice husk activated carbon were also conducted using BET Surface Area Analyzer, Fourier Transmitter Infrared Spectroscopy (FTIR), CHN Elemental Analyzer, and X-ray Diffraction (XRD) for the characterization study. The adsorption capacity towards metal ion was determined using Atomic Adsorption Spectroscopy (AAS). Isotherm models are also developed, which is Langmuir and Freundlich Isotherm. The results obtained from the adsorption study showed that rice husk has a potential to be converted to adsorbent for the removal of heave metals.

ACKNOWLEDGEMENT

In the name of ALLAH, the most merciful and compassionate, for His blessing and giving me strength and ability to complete this thesis. If not for His consent, I won't be able to finish it on time.

Firstly, I would like to acknowledge my deepest gratitude to my project supervisor, Mr. Mohd Faisal Taha for his guidance, constant attention, valuable suggestion, enthusiastic support and personal concern during the research and throughout the course of my study. Furthermore, appreciation also goes to my Co-supervisor, Dr Maizatul Shima for her attention and guidance.

Special thanks to the head of Chemical Engineering department, Dr Mohd Azmi Bustam for his permission to let me use all the brilliant facilities and equipment in completing my project. The quality leadership of him creates a healthy learning environment. My deepest gratitude to all technicians and administrative staffs of Chemical Engineering department, UTP, especially to Mr. Fadhlullah, Mr. Fazli, Mr. Fazli, Mr. Shaharudin and Ms. Azriha for helping me throughout my study.

Special thanks and appreciation goes to my loving parents for always giving me support and also to all of my colleagues that help in the process, riding along with me on my ups and downs as well as giving me the encouragement to pursue my dreams.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

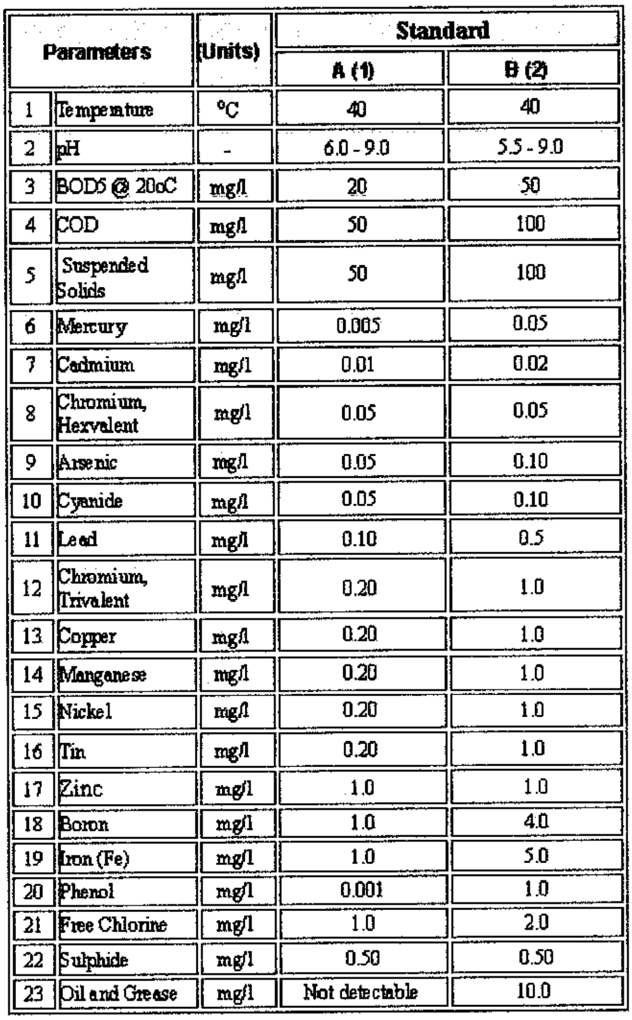
The environment has always been in danger due to the rapid growth of industrialization. One of the aspects that has been affecting heavily is the heavy metals that has been discharged into the environment without proper treatment and cleaning. Metal ions are mostly non-degradable and very toxic, and the major source is from the industrial wastewater. The contaminated wastewater can affect both surface and ground water which will affect the biological ecosystem thus resulting health hazard. The heavy metals which come with immediate concern are zinc, chromium, iron, nickel, mercury, cadmium and lead (Kadirvelu et al 2001).

Heavy metals concentration has to be reduced to some levels. Table 1.1 in the next page shows the Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, in Malaysia with selected parameter limits of effluent of heavy metals.

Zinc as the heavy metals in question mostly exhibits the environment via human activities such as mining, purifying zinc, lead and cadmium ores, steel production, coal burning, galvanizing and from the waste water of pharmaceuticals, paints, pigments, insecticides, cosmetics and industries (Bhattacharya 2006). Some of the technologies that were usually used to remove Zinc ions in wastewater are chemical precipitation, solvent extraction, reverse osmosis, ion exchange, evaporation, filtration, adsorption, oxidation and reduction. However, these methods are quite expensive and some are ineffective for low Zinc concentrations, produce toxic sludge and require the use of high reagent and energy.

Recent studies on Zinc removal has been made to search for an economically feasible method and one of the efficient and effective methods is by using adsorption with activated carbon and there were varieties of activated carbons available in the market. Though it is always available, there is still no cheap activated carbon present. Therefore, it is very necessary to find a new and inexpensive adsorbent for the removal of Zinc ions in wastewater. Some of recent studies have identified some potential in several low-cost materials among the agricultural wastes and industrial by-products that can be used to produce activated carbons.

Table 1.1: Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Malaysia: Selected parameter limits of effluent of Standards A and B (Department of Environment, DOE, Malaysia)



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

Activated carbons production are made from a material that has high carbon but low inorganic contents such as wood, lignite, peat and coal (Lua and Guo 2001). There are some agricultural waste that has been successfully converted into activated carbon such as macadamia nutshell (Ahmadpour and Do, 1996), paper mill sludge (Khalili et al, 2000) and peach stones (Arriagada et al, 1997). In Malaysia, researches with varied application have been made by using agricultural waste. Table below shows some example of activated carbon made by coconut shell and palm shell.

Table 1.2: Summary of earlier work on activated carbon using coconut shell and palm shell

Authors	Year	Rawmaterials	Method	Application
Lua and Guo	2001	Oil palm stones	CO_2 activation	SO_2 removal
Hu and Srivinasan	2001	Coconut shell and palm shell	$ZnCl_2$ activation and CO_2 activation	Phenol, methylene blue
Guo and Lua	2003	Palm shell	H_3PO_4	Ammonia adsorption
Mozammel et al.	2002	Coconut shell	$ZnCl_2$ activation	Iodine
Hu et al.	2001	Coconut shell and palm seed	$ZnCl_2$ activation	Phenol and dye
Daud and Ali	2004	Palm shell and coconut shell	Physical activation (N_2 gas)	Nitrogen adsorption

Besides above example, agricultural wastes used as activated carbon are rice husks, olive-waste cakes, palm seeds, guava seeds, and corncobs (Rahman, Ismail, & Osman, 2000). These wastes are used as it is inexpensive and they have no or low economic value. Other advantages are because of its easily prepared, requires only simple techniques and simple processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, freely available and easy regeneration (Wan Ngah & Hanafiah, 2008).

Basically, after the materials undergo proper preparation and treatment process, it will be activated first using some reagent that is acidic or basic and then carbonized in order to increase porosity. The process can be change accordingly with different properties and parameters to get the most optimized results. The main feature that is common to all activated carbon are; graphite like structures which have varied degrees of disorientation and the resulting spaces between the planes gives its porosity and this is the aim of the overall process.

One of the most potential adsorbent that is currently studied is an adsorbent from rice husks. Malaysia as one of paddy producer can produce almost 2.5 million tones of paddy every year. So, for rice husks production that takes account of 20% of paddy production can produce more than 40,000 tonnes of rice husk annually in Malaysia (Chuah Et al, 2005) and these rice husks was just considered as agricultural waste with no value.

By utilizing rice husk as an activated carbon will actually convert the waste into a value-added product. Recently, lots of studies have been focusing on the optimization of this material to be used as an activated carbon. Therefore, this research is made by manipulating the properties that is highly affecting the affectivity and the porosity of the activated carbon.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

Presence of heavy metal in wastewater has been interrupting the environment at an alarming rate. The properties of the heavy metal ions that resist to degrade into harmless compound and its affect to the biological system of surrounding environment has made it into a very dangerous substance to be present in the environment. Wastewater treatment that has been used to date is very expensive and lots of benefit based industry has neglect the use of this technology because of the high cost.

Activated carbon, as one of the most efficient method for treatment has been the targeted because there is potential for a low cost activated carbon to be produced by using agricultural waste which has no value. Rice husk as one of the agricultural waste in question is one of the by-product that has no economic value and it is usually burn in situ, resulting to more release of carbon dioxide (CO_2) and various other compound that is toxic such as carbon monoxides, volatile organic compounds, nitrogen oxides, and suspended particles which can harm the environment.

One of the heavy metals that need high attention is Zinc and this metal is very common in most wastewater. Actually, zinc is essential to the growth of plants, humans and animals but excess quantity of this metal can be very toxic. When it enters the surface or ground water, and drink by the living beings, it can cause biological disturbance and cause various random deceases such as cancer and organ failure. Hence, it is essential to remove Zinc ion and it should be removed by an effective and a low cost technology.

1.2.2 Significance of the Project

Studies on wastewater treatment have been progressing to further acknowledgement. A suitable method which is highly efficient and effective is rather in need and it has been revealed that adsorption using activated carbon meets the criteria. But still, superior activated carbon can be very expensive and this reduces the will of industrial company to a stalemate. Researchers have been studying the suitability of various agricultural wastes as a potential activated carbon and they discovers that rice husk may achieve the requirement for its availability and it is inexpensive compare to other materials such as wood that has been used to produce activated carbon. Its main component, which is carbon and silica, is an important aspect that can be look trough for the adsorption of the heavy metals.

1.3 OBJECTIVES AND SCOPE OF STUDY

The objectives of this project are listed as follows:

i. To study the capability of rice husk as and adsorbent to adsorb Zinc ion from aqueous solution
ii. To study and characterize the pore development of rice husk throughout the processes.
iii. To study the effect of mass on adsorption activities.
iv. To study the isotherm model for rice husk adsorption.

1.3.1 The Relevance of the Project

Even though rice husk has not achieved the industrial requirement for activated carbon, it still serves a very high potential for an adsorbent. It still needs some tweaks to unleash its full potential in terms of its pores structure and the adsorption capability. In this project, the research is made by using the rice husk where it is easily available, laboratory process suitability, low cost and needs only a low cost technology. Thus, activated carbon from a rice husk is a good option of cheaper material and a good alternative to extract Zinc ions through adsorption process.

1.3.2 Feasibility of the Project within scope and time frame.

There are a lot of references of studies that can be used for this project as it was already developed so it is actually able to be completed in the period of one year or less. The equipments and materials needed for the project are readily available in the Chemical Engineering Laboratory as well as the chemicals involved. This project can be considered as a feasible project and can be done in the time frame as stated, so there should be no problem across.

CHAPTER 2

LITERATURE REVIEW

2.1 HEAVY METAL POLLUTION

Heavy metals are in widespread industrial use and the presence has been increasing as contaminants in the environmental system. Copper, Silver, Cadmium, Gold, Zinc, Mercury, Lead, Chromium, Iron, Nickel, Tin, Arsenic, Selenium, Cobalt, Manganese, and Aluminium are the elements that usually considered as heavy metals. Several places that have been polluted by heavy metals have turned into a land where the living organism food chain has slowly abolished and the ground and surface water is very toxic.

Zinc as one of heavy metals that is present in the natural environment has been proved to increase because of human activities such as mining, purifying zinc, lead and cadmium ores, steel production, coal burning, galvanizing and from the waste water of pharmaceuticals, paints, pigments, insecticides, cosmetics and industries (Bhattacharya 2006). As for its effects on human beings, it regularly causes irritability, muscular stiffness, loss of appetite and nausea if it is consumed more than the usual consumption. Thus, from table 1.1, the standard for zinc to be released into wastewater is set to 1 ppm only (Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Malaysia)

2.2 RICE HUSK POTENTIAL

Research on the production of a low-cost adsorbents have been carried out because of the available activated carbon are quite expensive and is in limited use in only developing countries. As a by-product or an agricultural waste for paddy production, there can be a lot of resources and it also can produce a significantly low cost activated carbon. Table 2.1 and 2.2 in the next page shows the physicochemical characteristics of rice husk as reported by Chuah et al (2005).

Table 2.1: Typical composition of rice husk

Composition	Percent
Cellulose	32.34
Hemicellulose	21.34
Lignin	21.44
Extractives	1.82
Water	8.11
Mineral Ash	15.05
Chemical composition in mineral ash	
SiO2	96.34
K2O	2.31
MgO	0.45
Fe2O3	0.41
Al2O3	0.41
CaO	0.41
K2O	0.08

Table 2.2: Reported physicochemical characteristics of rice husk

Characteristics	Values
Bulk density (g/ml)	0.73
Solid density (g/ml)	1.5
Moisture content (%)	6.62
Ash content (%)	45.97
Particle size (mesh)	200-16
Surface area (m2/g)	272.5
Surface area acidity (meq/gm)	0.1
Surface area basicity (meq/gm)	0.45

2.3. SODIUM HYDROXIDE, NAOH AS AN ACTIVATION AGENT

Base on the figure 2.1 below, the rice husk ash already has some pores developed after the carbonization. It is a carbonized rice husk without any pre-treatment with an activation agent. As to increase the pores and the surface area, we actually needed to do some pre-treatment with the raw rice husk by using an activation agent.

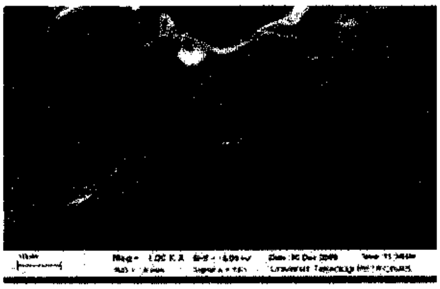


Figure 2.1: SEM for Raw Rice Husk ash (300°C, 3h), magnified 1000 times

According to Liou and Wu (2009), they say that the rice husk may be activated by using acidic solution or basic solution. Base on the results, we have decided to go on with NaOH as an activation agent because after the treatment with the alkaline solution, the silica reacts with NaOH to form sodium silicate (Na_2SiO_3). The Na_2SiO_3 is soluble in water and is removed by adequate water-washing. As a result, some large holes remain on the husks outer epidermis. Figure 2.2 below shows the pores developed after the treatment of the raw rice husk, and it shows that the rice husk have higher potential of developing more pores when treated with Sodium Hydroxide, NaOH.

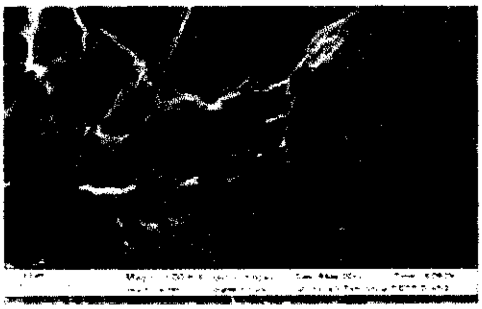


Figure 2.2: SEM for raw rice husk treated with 0.5M NaOH, magnified 1000 times

2.4 FACTORS AFFECTING ADSORPTION

For process optimization there are actually several factors that will affect the adsorption studies. That is,

i. pH
ii. Contact Time
iii. Metal Concentration
iv. Particle Size
v. Temperature

2.4.1 Particle Size

The adsorption capacity of rice husk depends very much on the surface activites, i.e., specific surface area available for solute surface interaction, which is accessible to solute. It is expected that with larger surface area, adsorption capacity will be increased because smaller particle size increases the adsorption capacity, Munaf and Zein (1997) reported that metal ions adsorbed decreases when the size of rice husk particle increases. Similar trends have been reported by Wong et al. Adsorption as surface phenomenon, smaller particle size will offer comparatively larger surface areas and higher adsorption will occur.

2.4.2 pH of Activation agent

At high pH, metal ion may be forced to bind to low affinity ligands such as hydroxyl and carboxyl group but at low pH, the binding may occur through high affinity ligands only (Michael Horsfall Jr. Et al., 2004). This is an indication that the degree of ionization on the biomass surface is pH dependent (Michael Horsfall Jr. et al., 2004) which later affect the metal adsorption activities.

Bhattacharya et al (2006) reported that removal efficiency was found to be highly dependent on hydrogen ion concentration that present in solution. At low pH, due to high positive charge density due to protons on the surface sites, electrostatic repulsion will be high during uptake of metal ions resulting in lower removal efficiency. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption. At higher pH values, OH ions compete for Zn(II) with the active sites on the surface of the adsorbents (Kalyani et al., 2003).

2.4.3 Carbonization Time of Rice Husk

It is reported that activity of adsorption decrease as carbonization time increases. This is probably due to the thermal destruction of pores structure as the carbonization time increases. It may also be due to formation of as, which may block the pores entrance (Shasankan Sekhar, 2009).

An increased in the burning time increased the amount of silica but decreased the amount of carbon content significantly. The decrease of carbon content will predictably cause the decrease of the porosity of the adsorbent. This is expected sice at longer times, more carbon are converted to silica (Daffala, Mukhtar, & Shaharun, 2010).

2.4.4 Carbonization Temperature of Rice Husk

The purpose of carbonizing the rice husk is to impart thermal decomposition to it, thus eliminating non-carbon species and fixed the carbon mass as well as the basic carbon structure. Generally, the quality and yield of the carbonized activated carbon are affected by numerous parameters which are:

- The rate of heating
- The heating final temperature
- The soaking time at the final temperature
- Nature and physical state of the raw material

Low heating rate during pyrolysis results in lower volatilization and higher char. These occur due to the increased dehydration and better stabilization of the polymeric components.

At the first stage of carbonization, the structure of the activated carbon is made of small planar aromatic rings which are randomly oriented. As the heat treatment temperature increases, the random structure will start to be arranged in parallel. The basic microstructure was formed by 500°C, although some of these pores are blocked by the pyrolysis products and could be available only when high temperature treatment is given.

2.4.5 Contact Time of Adsorption Activites

The contact time affect metal adsorption on rice husk activated carbon as the contact time increases, the metal ion adsorbed will also increase (Guo et al., 2000). About three hours of adsorption, the rate of adsorption will become constant which means the process had achieved an equilibrium condition (Mantaher et al., 2005). However, the fast kinetics between rice husk and the metal depends on the analytical speed and the removal efficiency. Therefore, this factor need to be considered and must be made constant as the effect of contact time is tested.

The project would be concentrating on the contact time, metal concentration, and also carbonization temperature as to make the project feasible because of time restrain. These factors will predetermine the properties of the activated carbon produced from the rice husk. A good activated carbon must have,

i. Large surface area
ii. Enhanced mechanical strength
iii. Favorable pore size as an access route to the internal surface
iv. Universal adsorption effect
v. A high degree of surface reactivity.

2.5 ADSORPTION ISOTHERM

The adsorption equilibrium relates q to C. The equilibrium is a function of the temperature. Therefore, the adsorption equilibrium relationship at a given temperature is typically referred to as *adsorption isotherm*, i.e.:

$$q = f(C)$$

Where:

q = mass of species adsorbed/mass of adsorbent (i.e., equilibrium concentration of adsorbable species in solid adsorbent)

C = equilibrium concentration of adsorbable species in solution

From the basic function, the isotherms that studied in this project is the Langmuir Isotherm and Freundlich Isotherm. The functions of this isotherm are as follows,

Langmuir Isotherm,

$$q = \frac{q_m K_A C}{1 + K_A C}$$

where:

qm = maximum adsorbable value of q

KA = constant (function of enthalpy of adsorption and temperature)

Freundlich Isotherm,

$$q = K_F C^{1/n}$$

where:

K_F = constant (function of energy of adsorption

and temperature)

n = constant

The Isotherm developed from the results may tell us the characteristic of the adsorption and some parameters can also be calculated.

CHAPTER 3

METHODOLOGY

3.1 PROCEDURES

There are four major parts for the project:

i. Preparation of raw rice husk
ii. Treatment of raw rice husk
iii. Carbonization of treated rice husk
iv. Adsorption study.

To maximize the capability of the activated carbon from rice husk, the preparation and treatment must be done thoroughly so that no impurities will interrupt with the carbonization process. After the rice husk is carbonized, it will be tested for its adsorption of metal ions capability. Then, from the data we can know the overall potential for rice husk as an activated carbon.

3.1.1 Preparation of Raw Rice Husk

Rice husk undergoes cleaning and drying for this process before we obtain the desired 63μm rice husk. Below are the brief descriptions of the procedures involved:

i. About 2000 g of raw rice husk was washed with distilled water for several times to make sure that there are no more adhering materials.
ii. The rice husks were dried in the oven at 80°C for 24 hours.
iii. After that, the dried rice husk were blended using blender.
iv. Then, the blended rice husk were sieved using a set of sieve trays sized 500μm, 250μm, 125μm and 63μm to obtain 63μm size of rice husk.

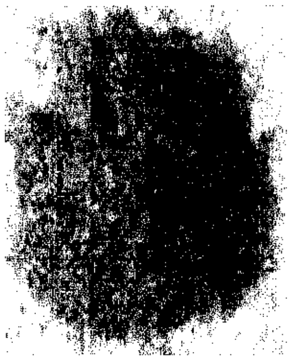


Figure 3.1: Rice husk of varying particle size

3.1.2 Treatment of Raw Rice Husk

1.0M of sodium hydroxide (NaOH) was used as an activation agent for the rice husk treatment process. The pH value is to be ranged from 6 to 8 for optimize effect of pH. The required sodium hydroxide was prepared by dissolving 40 g of NaOH pellets in 1 L of distilled water. The ratio of rice husk to the digestion agent was 1:10 where rice husk is in unit of gram (gram) while the digestion agent is in millimeter (ml).

The procedures for treatment of rice husk are as follows:

i. First, 1.0 M Sodium Hydroxide (NaOH) was prepared
ii. 100 g of raw rice husk 63 μm was digested with 1000 ml of 1.0 M NaOH in 1000 ml beaker.
iii. Seal the beaker containing sample using aluminum foil.
iv. After 24 hours, the digested samples filtered and washed with excessive distilled water until the filtrate is free from sodium hydroxide (pH value range from 6 to 8)
v. The samples were placed on tray for drying process in an oven at 80°C for 24 hours.
vi. Then, the samples were weight

*Preparation of sodium hydroxide, NaOH is to be conducted in fume hood for safety reason.

3.1.3 Carbonization of Treated Rice Husk

The treated rice husk are carbonized to impact thermal decomposition to it thus eliminating non-carbon species and fixed the carbon mass as well as the basic carbon structure. The details are as follows:

i. The treated rice husk was weighed.
ii. An aluminum foil was used to wrap the treated rice husk.
iii. The wrapped samples were placed into the crucible and a crucible lid was used to close crucible as to minimize the effect of oxidation.
iv. The crucible that contains rice husk was put into the furnace when the temperature reached nearly 500°C.
v. After carbonizing for 1 hour, the furnace temperature was reduced to 30°C
vi. The samples were taken out once the furnace has reached the desired temperature.
vii. Then, the samples were weighed and calculate percentage weight loss.

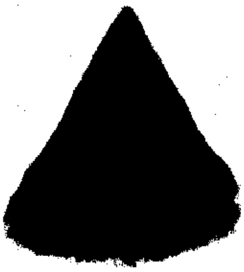


Figure 3.2: Rice husk after carbonization

3.2 ADSORPTION STUDY

To observe the adsorption activities, the sample is mixed with the metal ion solution for a specified time. After mixing, the samples are then filtered to get the filtrate before analyzed using the equipments in schedule. The metal ion concentration used is 25ml of 150ppm solution of Zinc Chloride and the rice husk activated carbon used are 0.05g, 0.1g, 0.15g, 0.2g, and 0.25g.

Below are the procedures to study the adsorption capacity of rice husk-based activated carbon using Atomic Adsorption Spectrophotometer (AAS).

i. 5 set of 25ml from the 150ppm Zinc Chloride was prepared and the solutions was mixed with 0.05, 0.1, 0.15g, 0.2g and 0.25g of rice husk activated carbon in different conical flask.
ii. The conical flasks were placed in a water bath shaker and it was left stirring at 110 rpm at room temperature for 5 minutes.
iii. Each of the solutions was filtered and then the filtrate was analyzed using AAS to check the metal concentration left in the filtrate.
iv. Steps 1 to 3 were repeated for various contact time ranging from 5, 10, 15, 20, 30, 60, 90, and 120 minutes.
v. Graph was plotte from the data to observe the effect of parameters varied on the adsorption activities.

3.3 ANALYSES

Samples before and after extraction study are analyzed using several equipments namely Field Emission Scanning Electron Microscope (FESEM), Fourier Transform Infrared (FTIR), CHN Elemental Analyzer, X-ray Diffraction (XRD), and Atomic Absorption Spectrometer (AAS). Below is the lis of samples (for reference) which were sent for analysis.

The samples also needs labelling to avoid confusion as listed in the table below,

Table 3.1: List of Samples for Analysis Study

No.	Sample Name & Description	Label
1.	Raw Rice Husk (63µm)	RRH
2.	Treated Rice Husk	TRH
3.	Carbonized Rice Husk	CRH

Then, the chemicals that are needed in this project are listed as below,

i. Sodium Hydroxide, NaOH (pellet form)
ii. Zinc Chloride, $ZnCl_2$ (adsorbate)
iii. Distilled water
iv. Deionized water

Field Emission Scanning Electron Microscope (FESEM)

The Scanning Electron Microscope (FESEM) is a microscope that uses electrons rather than light to form an image. It produces images of high resolution, which means that closely spaced features can be examined at high magnification. Preparation of the sample is relatively easy since FESEM only required the sample to be conductive. The development of pores can be easily observed due to the combination of higher magnification, larger depth of focus and great resolution.

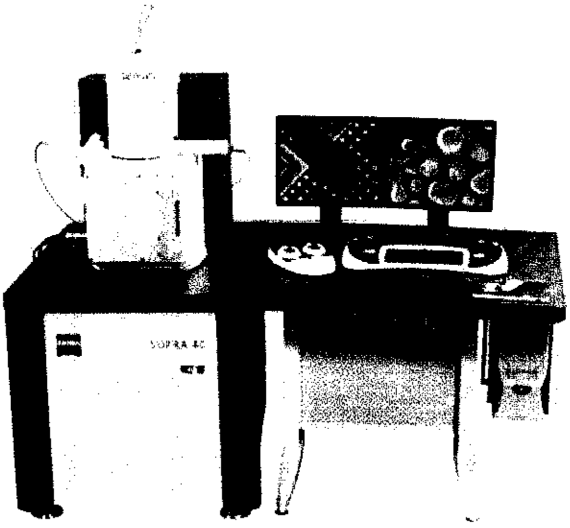


Figure 3.3: FESEM

CHN Elemental Analyzer

CHN Elemental Analyzer can provide a mean for the rapid determination of carbon, hydrogen and nitrogen in organic matrices and other types of materials. CHN Elemental Analyzer is performed to provide carbonate and organic carbon and to get some idea of the composition of the organic matter.

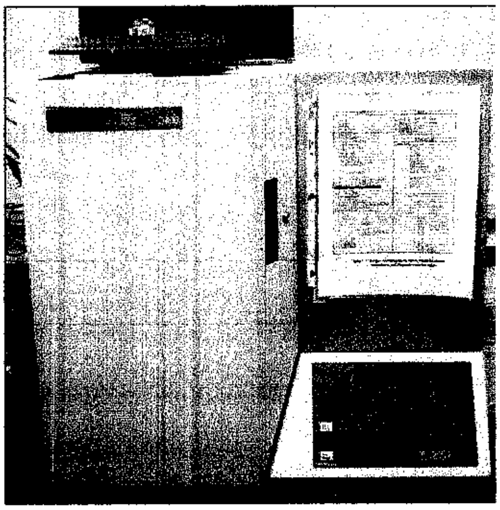
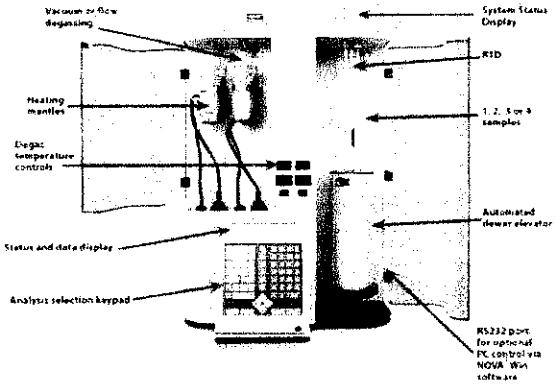


Figure: 3.4: CHN Elemental Analyzer

BET Surface Area Analyzer

BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material.



Rear of Instrument: RS 232 Port for PC Control via NOVAWin 2.0 Printer Port

Figure 3.5: BET Surface Area Analyzer

Fourier Transform Infrared (FTIR)

Fourier Transform Infrared (FTIR) is the preferred method of infrared spectroscopy. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. The size of the peaks in the spectrum is a direct indication of the amount of material present. The main purpose of performing FTIR analysis in this study is to identify the functional group of the samples.

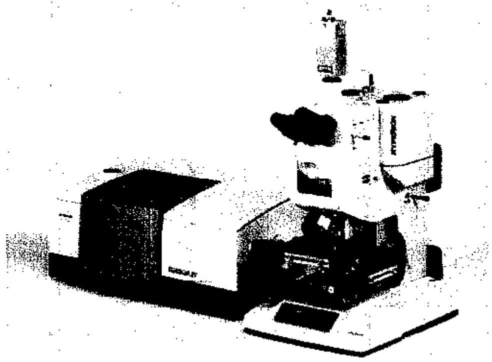


Figure 3.6: FTIR

Atomic Absorption Spectrometer (AAS)

Atomic Absorption Spectrometer (AAS) is analytical equipment used in research works as it is the only equipment that can give definite reading of the metal ions' concentration. AAS works by providing the accurate quantitative analyses for metals in water, sediment soils or rock. In this study, the purpose of using AAS is to determine the final concentration of the metal ion in the filtrate.

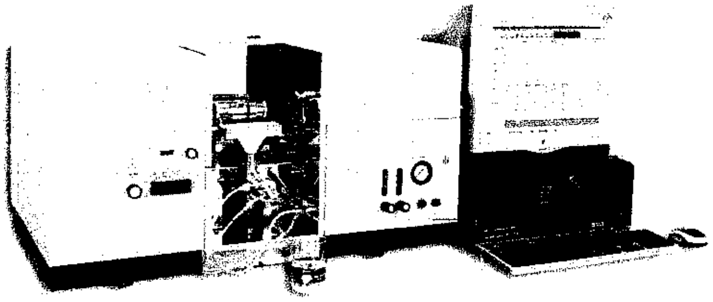


Figure 3.7: AAS

X-ray Diffraction (XRD)

The principal function of XRD is to measure the diffraction beam intensity and the d-spacings of crystalline materials, which however has been developed to determine many structural properties. In this study, XRD is conducted to investigate the crystalline and amorphous phases of the carbon samples. XRD experiments are performed with 2Ø values ranging from 2° to 80°.

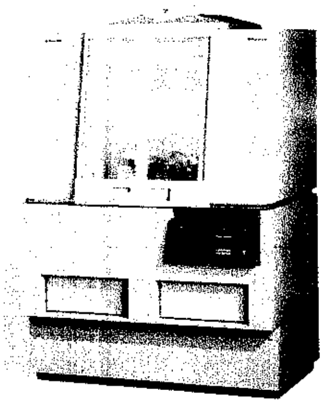


Figure 3.8: XRD

CHAPTER 4

RESULTS AND DISCUSSIONS

After the process of preparing the Rice Husk Activated Carbon, 3 samples have been sent for characterization and analysis. The 3 samples are Raw Rice Husk, Treated Rice Husk, and Carbonized Rice Husk. The data in the process are carefully recorded and will be displayed in this chapter. Then, the Carbonized Rice Husk with a quantity of 6 g has been successfully prepared and would be used for adsorption study of Zn (II) ion.

4.1 PREPARATION OF RAW RICE HUSK

The target is to prepare 6 gram of activated carbon after the carbonization process. So, some assumptions are made for calculations as to avoid repetitive actions that may cause more time to be wasted. The assumptions are,

i. 80% may be removed during the washing process after the treatment with NaOH, Sodium Hydroxide.

ii. Only 30% of the Treated Rice Husk will remain after the carbonization process. This is due to the decomposition of the rice husk structure.

So, to prepare 6 gram of Rice Husk Activated Carbon, we actually need about 100 g of Raw Rice Husk with a size of 63μm that will reduce to 20 g of Treated Rice Husk. Thus, after the carbonization process, we may eventually get 6 g of Carbonized Rice Husk. These calculations has been successfully conducted during the project and 6.13 g Carbonized Rice Husk had been produced.

Some of the observation during the preparation process, which the rice husk were cleaned using lots of distilled water, impurities and paddy remainders were floating on the water surface. Thus, the objective to remove the impurities that may contaminate the rice husk had successfully conducted. After grinding and sieving process, 103.86 g of 63μm dull brown rice husk were collected.

Figure 4.1: Raw Rice Husk (before cleaning, grinding and sieving process)

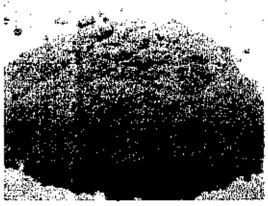


Figure 4.2: Raw Rice Husk (after cleaning, grinding and sieving process to 63μm)

4.2 TREATMENT OF RAW RICE HUSK USING ACTIVATING AGENT – NaOH (SODIUM HYDROXIDE)

As was previously mentioned in the literature review, a ratio of 1:10 is used to treat the Raw Rice Husk. So, 100 g of Raw Rice Husk were treated with 1000 ml (1L) of Sodium Hydroxide. The mixture was left overnight (24 hours) inside a 1 L beaker and was stirred with a mechanical stirrer. Table below describes the color change and the amount of rice husk lost after the treatment.

Table 4.1: Color changes and weight difference of rice husk during and after treatment.

	Color	Weight (g)
During Treatment (mix with NaOH)	Greenish Brown	100
After Treatment	Dull Brown	18.05
	Percentage loss (%)	((100-18.05)/100)*100 = 81.95 %

Excessive amount of distilled water was used to reduce the pH of the mixture of Rice Husk and Sodium Hydroxide from 13 to 7. Some of the treated rice husks are also washed along with the distilled water. This is because, when Sodium Hydroxide reacts with silica to form sodium silicate (Na_2SiO_3), the soluble sodium silicates are also removed along with the water.

$2NaOH\ (s) + SiO_2\ (s) \rightarrow Na_2SiO_3\ (s) + H_2O\ (l)$

Final pH of the mixture was 7.27.

4.3 RICE HUSK ACTIVATED CARBON

Optimum temperature, 500^{O}C and carbonization time, 2 hours are selected based on journals. 18 grams of treated rice husk were gathered and were all used for the carbonization. There were reductions of mass after the carbonization because of some factors. The factors are the eliminations of moisture at 100^{O}C, decomposition of organic materials at 100-375^{O}C and further mass reduction at 375-800^{O}C may be attributed to further pyrolysis of the intermediate. (Reference – Tzong-Horng Liou)

Table 4.2: Observation results of carbonized rice husk

Temperature (^{O}C)	Weight (g)	
	Before Carbonization	After Carbonization
500	18.05	6.1
Percentage Weight Loss(%)	((18.05 – 6.1)/18.05)*100 = 66.2 %	

Further characterization are mentioned in the next section whereby, the characterization were made by using Thermogravimetric Analyzer (TGA), Field Emission Scanning Electron Microscopy (FESEM), CHNS Analyzer, X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Absorption Spectroscopy (AAS) for adsorption study of Zn(II) ion.

4.4 CHARACTERIZATION

4.4.1 CHNS Analyzer

This equipment was used to determine the four elements which is represents by its name, Carbon (C), Hydrogen (H), Nitrogen (N), and Sulfur (S). The weight percentage of the results is displayed in the table below. Samples are labeled likewise, Raw Rice Husk (RRH), Treated Rice Husk (TRH), and Carbonized Rice Husk (CRH).

Table 4.3: CHNS Analysis Results

Sample	Carbon %	H%	N%	S %	Total wt %
RRH	34.07	4.652	1.663	0.095	40.48
TRH	38.41	4.371	0.698	0.033	43.51
CRH	65.73	4.022	1.122	0.042	70.92

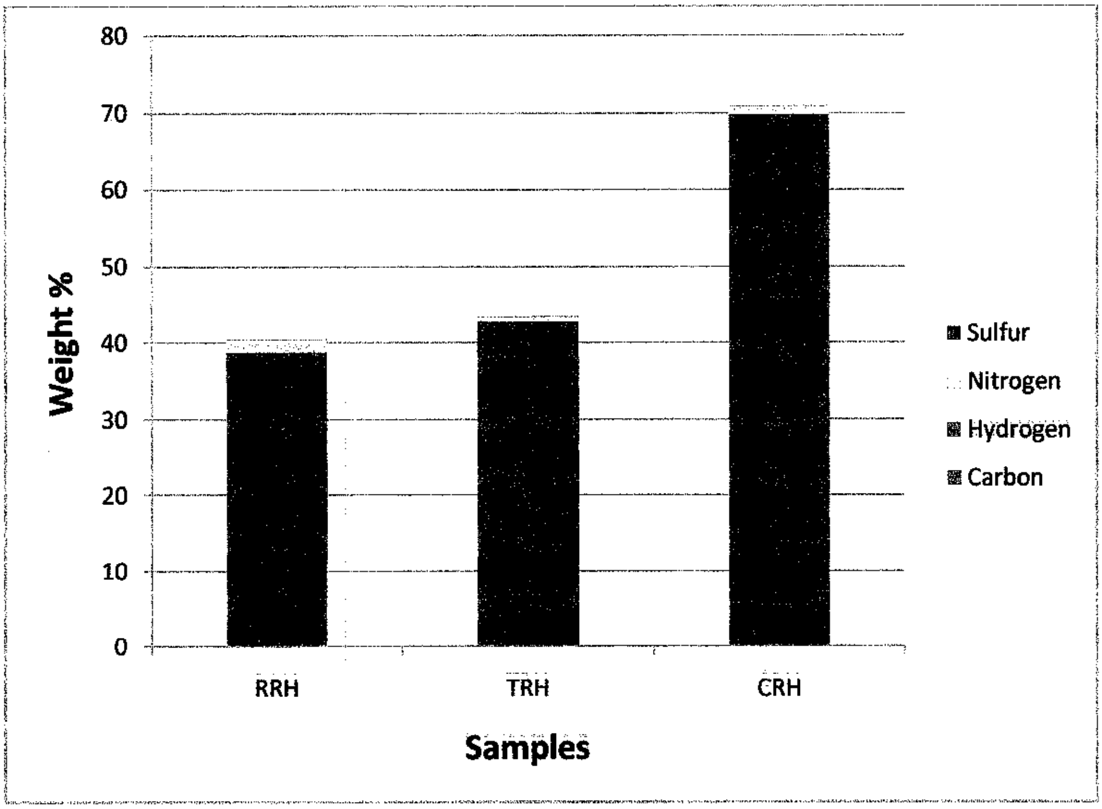


Figure 4.3: Elemental Analysis by CHNS Analyzer for RRH, TRH, and CRH

There is a significant difference of Carbon weight percentage because there are reductions of mass for other elements that made the composition of rice husk such as cellulose, hemicelluloses, lignin, water, lignin and other volatile matters. The observations that can be made are, almost seventy percent of the activated carbon produced consist carbon, an almost consistent weight percentage of nitrogen, hydrogen, carbon, and sulfur, and the percentage of sulfur in rice husk composition are insignificant and it is good as for environmental reason.

4.4.2 Field Emission Scanning Electron Microscopy (FESEM)

<u>**FESEM images**</u>

Raw Rice Husk

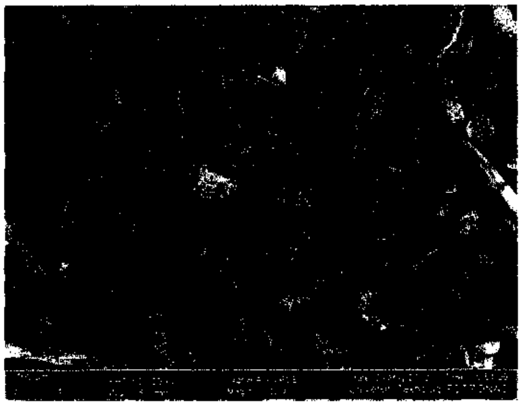


Figure 4.4: RRH Magnification: 100 x

Figure 4.5: RRH Magnification: 500 x

Figure 4.6: RRH Magnification: 1.0 K x

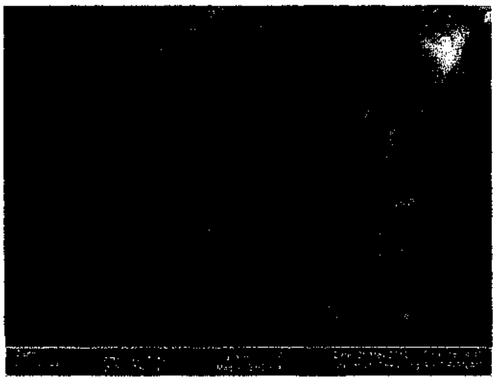


Figure 4.7: RRH Magnification: 5.0 K x

Raw Rice Husk that has been washed with distilled water and blended to 63μm has a microstructure with a lot of surface area. Unfortunately, during this stage, there is no evidence of pores, so it is still not suitable for adsorption process.

Treated Rice Husk

Figure 4.8: TRH Magnification: 100 x

Figure 4.9: TRH Magnification: 500 x

Figure 4.10: TRH Magnification 1.0 K x

Figure 4.11: TRH Magnification: 5.0 K x

Treated Rice Husk that has been treated with Sodium Hydroxide and washed with distilled water has a smoother microstructure where the sodium silicate that has been produce by the reaction of sodium hydroxide and the silica on the rice husk and it has been washed by distilled water. The Treated Rice Husk is ready for carbonization to develop more pores.

Carbonized Rice Husk

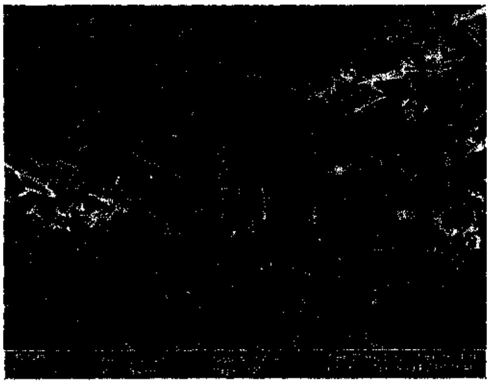


Figure 4.12: Magnification: 100 x

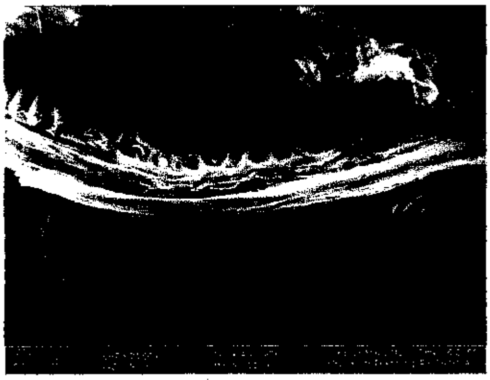


Figure 4.13: Magnification: 500 x

Figure 4.14: Magnification: 1.0 K x

Figure 4.15: Magnification: 5.0 K x

Treated Rice Husk that has been carbonized is turned into an activated carbon by applying high temperature (500°C) on it in a furnace with a nitrogen flow. We can actually see from this Carbonized Rice Husk, that it has pores developed. These many pores are important for metal ion adsorption. The pores opening in the surface must be due to the extraction of some materials such, e.g., dissolution of lignins and other mineral components from the husk during treatment process (L. John Kennedy et al. 2004). Metal ions would be attracted to the pores due to the adsorption kinetics called London Dispersion Forces, a type of Van de Waals Force which exists between molecules.

Along with images, FESEM results also came with EDX Spectrum that shows the elements in the samples. Below are the list and the spectrum of the elements.

Sample: Raw Rice Husk
Standard:
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
Mg MgO 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
P GaP 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM

Table 4.4: Composition of Raw Rice Husk

Element	Weight%	Atomic%
C K	51.71	59.62
O K	44.67	38.67
Mg K	0.26	0.15
Si K	2.43	1.20
P K	0.30	0.14
K K	0.62	0.22
Totals	100.00	

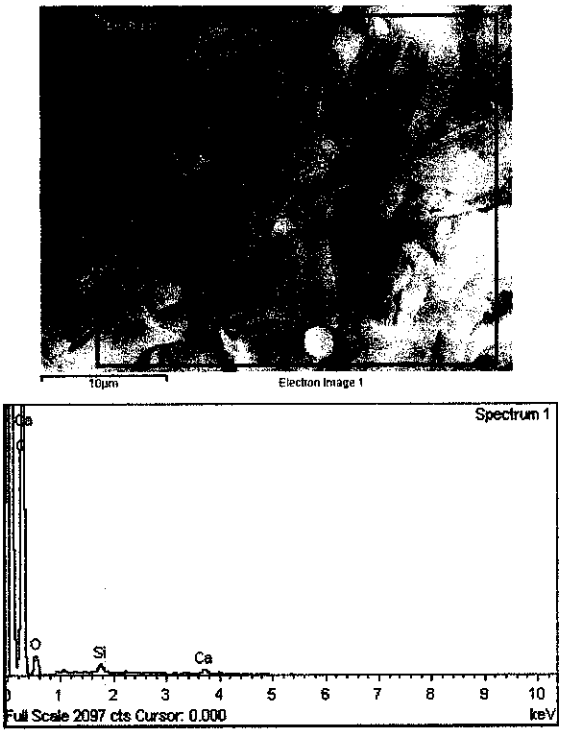


Figure 4.16: Raw rice husk image and spectrum

Sample: Treated Rice Husk

Standard:

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

Table 4.5: Composition of Treated Rice Husk

Element	Weight%	Atomic%
C K	50.99	58.09
O K	49.01	41.91
Totals	100.00	

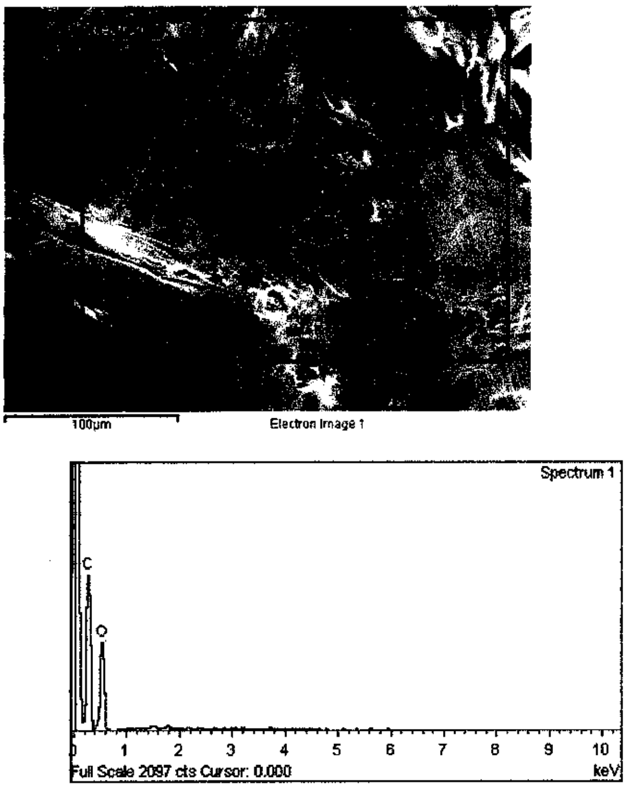


Figure 4.17: Treated rice husk image and spectrum

Sample: Carbonized Rice Husk

Standard:

C CaCO3 1-Jun-1999 12:00 AM

O SiO2 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

Ca Wollastonite 1-Jun-1999 12:00 AM

Table 4.6: Composition of Carbonized Rice Husk

Element	Weight%	Atomic%
C K	79.74	84.43
O K	18.98	15.09
Si K	0.53	0.24
Ca K	0.75	0.24
Totals	100.00	

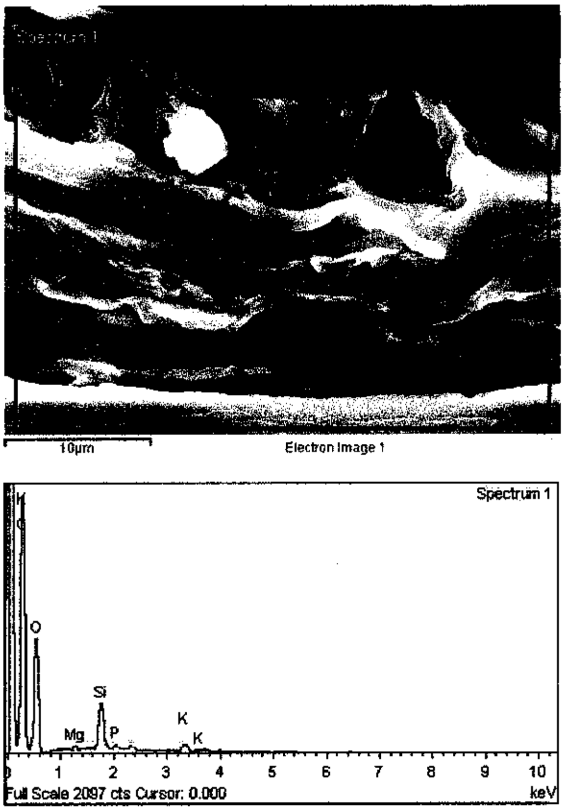


Figure 4.18: Carbonized rice husk image and spectrum

4.4.3 Fourier Transform Infrared (FTIR)

The function of FTIR is to obtain the infrared spectrum which measures intensity over a narrow range of wavelengths at a time. It detects the functional group of an organic compound and delivers a peak for the dominant functional group. Below are the figures which represent the data for the 3 samples.

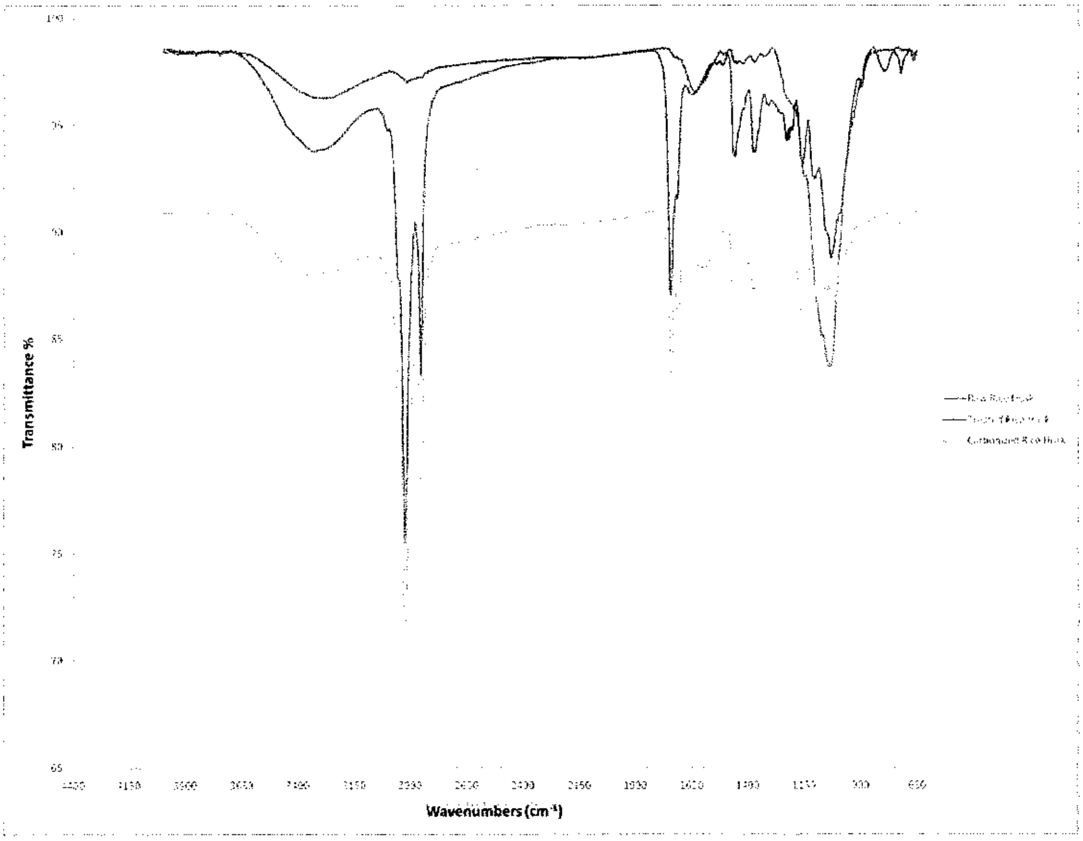


Figure 4.19: FTIR spectra of samples; Blue line (RRH), Red line (TRH), Green line (CRH)

The comparative study that can be made for these three spectra is of their functional groups. The functional groups identified for these two spectra are listed in the table 4.7. There are some obvious differences of the spectra before and after the treatment with Sodium Hydroxide, NaOH that will be discussed afterwards. The peak after the carbonization process also has slight changes.

Table 4.7: Peak identified in Raw Rice Husk and Treated Rice Husk spectra

Wavenumbers (cm^{-1})	Functional Group	Comparison for RRH, TRH, and CRH
3284	-OH and Si-OH	Peak is wide. RRH has the lowest transmittance peak.
2850-2930	C-H stretching of alkanes	Almost none of the peak for RRH. Peak developed for TRH and CRH.
1712-1743	C=O stretching of aromatic groups	Almost none for RRH. Peak developed for TRH and CRH.
1598	C=O stretching of aromatic groups	Almost no change
1456	CH2 and CH3	Peak developed for TRH and CRH. Almost none for RRH.
1377	Aromatic CH and carboxyl-carbonate	Peak developed for TRH and CRH. Almost none for RRH.
1233	CHOH stretching of alcohol group	Peak developed for TRH and CRH. Almost none for RRH.
1158	CO group in lactones	Peak developed for TRH and CRH. Almost none for RRH.
1035	Si-O-Si	Peak is very wide and steep for RRH. Gradually decreasing for TRH and CRH.
797	Si-H	Almost no change

The functional groups identified above are relevant with the functional groups identified by S.B. Daffalla et al, 2010 and Tzong-Horn Liou et al, 2009. We can conclude from the graph where the stretching at 1035 cm^{-1} suddenly decrease because the functional group of silicon, Si-O is removed. It is stated before that, when sodium hydroxide reacts with the silica in the rice husk, it forms sodium silicate that is soluble in water. So it is washed away after the treatment process.

Then, the Si-OH bond is formed where the stretch is wide at 3284 cm^{-1} because of the reaction.

$2NaOH (s) + SiO_2 (s) \rightarrow Na_2SiO_3 (s) + H_2O (l)$ (reaction of sodium hydroxide with water)

Other significant comparison that can be made, is that there is a reduction of peak at 900-1700 cm^{-1} that indicates the removal of ash in carbons after the activation and carbonization process and there are also some other bands that disappear because of the vaporization of organic matter. The difference of intensity that happens between Treated Rice Husk and Carbonized Rice Husk where the intensity decrease for Carbonized Rice Husk is because of the proportion of carbon content increases at high temperatures (Tzong-Horng Liou et al, 2009).

4.4.4 THERMOGRAVIMETRIC ANALYZER (TGA)

This equipment analyzes the change of mass while the samples are subjected to a uniform rate of temperature programmed. When heats are applied to the samples, some of the components in it may burn off, thus resulting weight loss. The weight loses are recorded and then be displayed, while there are some changes in the mass, it actually indicates the composition of the sample and its thermal stability.

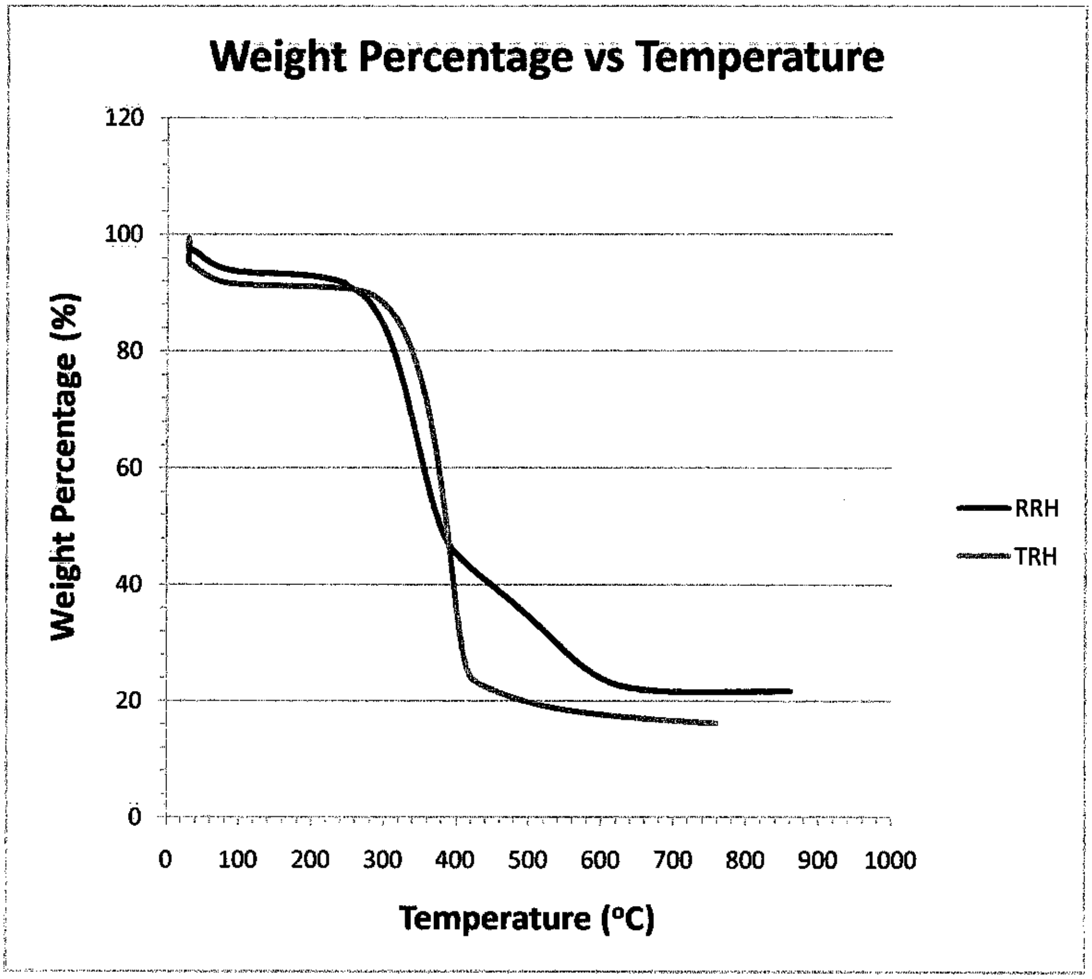


Figure 4.20: TGA Result Comparison for RRH and TRH

From the figure 4.20, it actually means that there are three stages that we can divide into three distinct temperature zones. Base on it, the first small mass loss for both samples is at 100°C – 120°C, which is the stage of moisture elimination and moisture accumulates around 5-7 percent of the samples composition. Second stage of mass loss, which is also the major part of it, is at 300-450°C where the burning and the decomposition of organic materials occurred. Afterwards, during the third stage, which is at 450°C-800°C, the weight lost is lessening and this shows that the structure achieve structure stability at that temperature.

Carbonized Rice Husk is also sent for sample analyzing, and it shows a stable weight loss. The result is as shown in the figure below.

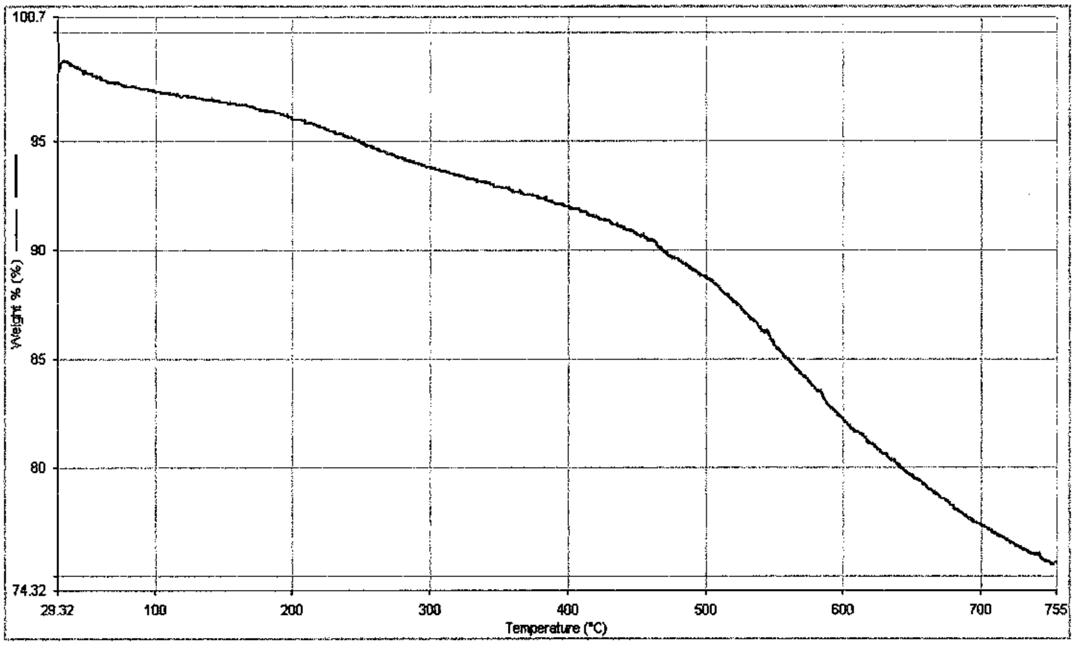


Figure 4.21: TGA result for CRH

From the graph, we can also determine the ash content in samples by the straight line when the samples are gradually heated. For raw rice husk, the ash content is 20-22%, and for treated rice husk the ash content can be approximately to be 18-20%.

4.4.5 X-Ray Diffraction (XRD)

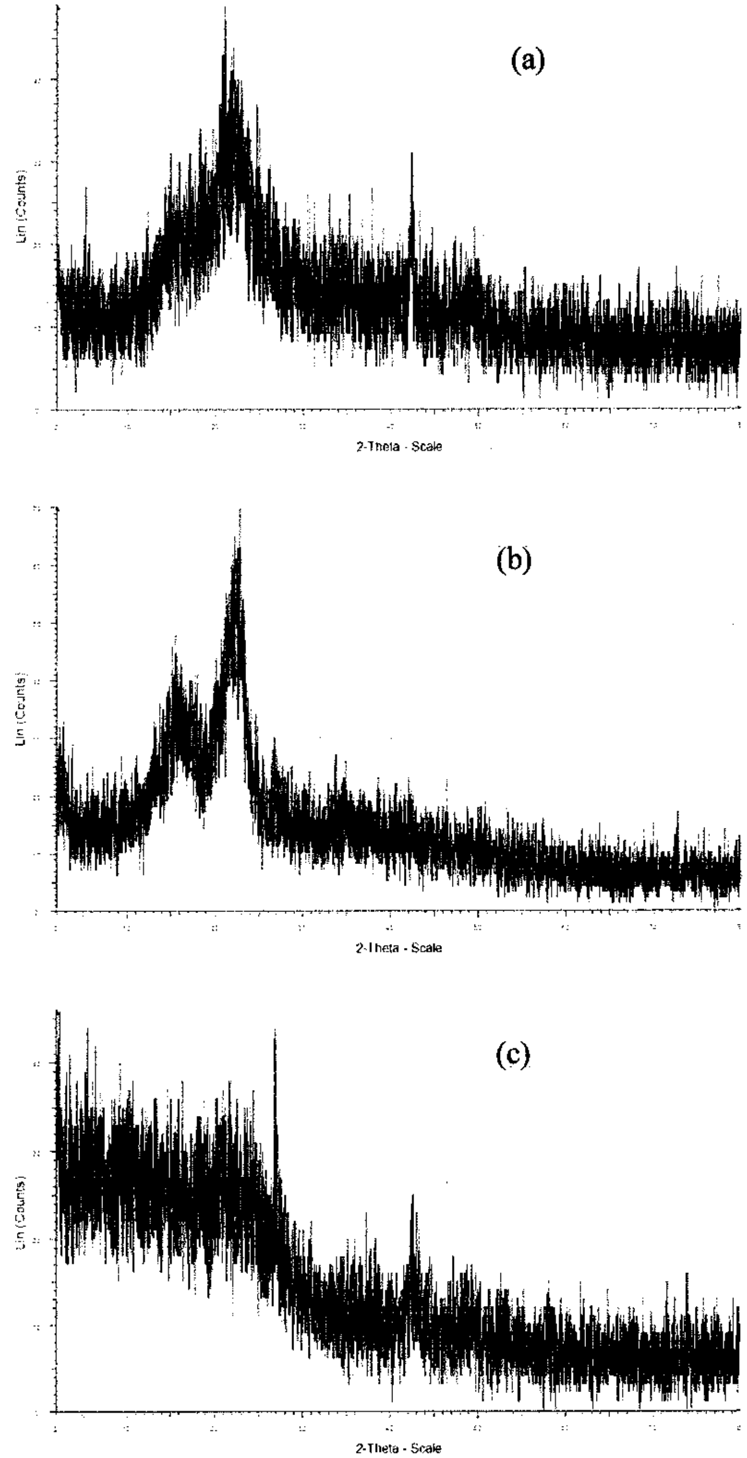


Figure 4.22: XRD curves of (a) RRH, (b) TRH, and (c) CRH.

Figure 4.22 has shown the x-ray diffraction curves of the samples and it provides the information on the crystallinity of a compound. From the results obtained, we can determine whether the compound has a crystallinity component or amorphous component. Crystallinity component gives sharp and narrow diffraction peaks and amorphous component gives a very broad peak. Based on the figure X raw rice husk and treated rice husk has a mixture of amorphous and crystalline phases of silica with a peak centered at 2Θ angle of 22°. Somehow, there suppose to be dual peak for raw rice husk as there is in treated rice husk if we refer to the Tzong Horng Liou et al, 2009 but it may be caused equipment error. It is known that the crystalline phases of silica are identified as crystobalite and tridymite (Yalcin N. & Sevinc V., 2001). Then, by looking at the figure 4.22(c), the diffractions are very wide from the peak at the 2Θ angle of 2° to 28°. This broad peak signifies the amorphous component of the CRH.

4.5 ADSORPTION STUDY

4.5.1 ATOMIC ABSORPTION SPECTROPHOTOMETER (AAS)

The objective of the project is to investigate the adsorption of Zinc (II) metal ion and from the data obtained; isotherms are determined to characterize the adsorption rice husk. A set of contact times are made for the adsorption study, that is from 5, 10, 15, 20, 30, 60, and 120 minutes with a variation of the activated carbon mass (0.05g, 0.1g, 0.15g, 0.2g, 0.25g). Before the process of concentration measurement, standard solutions of Zn (II) with different concentrations have to be prepared for 1ppm, 2ppm, and 4ppm.

Table 4.8: Concentration of Zinc after adsorption

Weight	Adsorption contact time	Initial Conc., CO (ppm)	Final Conc., Ce (ppm)	Percent Metal Uptake (% Removal)	Adsorption Capacity, (mg Zn(II) ion adsorbed/g adsorbent)
0.05	0	0	0	0	0
	5	150	133.13	11.25	8.435
	10	150	126.00	16.00	12
	15	150	122.25	18.50	13.875
	20	150	120.38	19.75	14.8125
	30	150	119.25	20.50	15.375
	60	150	115.50	23.00	17.25
	90	150	114.75	23.50	17.625
	120	150	114.00	24.00	18
0.10	0	0	0	0	0
	5	150	126.00	16.00	6
	10	150	122.63	18.25	6.84375
	15	150	118.13	21.25	7.96875
	20	150	114.75	23.50	8.8125
	30	150	112.50	25.00	9.375
	60	150	98.00	34.67	13
	90	150	94.13	37.25	13.9675
	120	150	92.80	38.13	14.3

0.15	0	0	0	0	0
	5	150	127.88	14.75	3.6875
	10	150	123.38	17.75	4.4375
	15	150	120.38	19.75	4.9375
	20	150	120.00	20.00	5
	30	150	116.25	22.50	5.625
	60	150	93.00	38.00	9.5
	90	150	83.34	44.44	11.11
	120	150	81.10	45.93	11.48333333
0.20	0	0	0	0	0
	5	150	133.13	11.25	2.109375
	10	150	126.00	16.00	3
	15	150	120.00	20.00	3.75
	20	150	117.00	22.00	4.125
	30	150	114.00	24.00	4.5
	60	150	89.75	40.17	7.53125
	90	150	78.00	48.00	9
	120	150	63.00	58.00	10.875
0.25	0	0	0	0	0
	5	150	129.38	13.75	2.0625
	10	150	121.50	19.00	2.85
	15	150	118.88	20.75	3.1125
	20	150	115.00	23.33	3.5
	30	150	112.75	24.83	3.725
	60	150	92.00	38.67	5.8
	90	150	71.35	52.43	7.865
	120	150	58.00	61.33	9.2

A pattern of adsorption can be observed from the data in the table 4.8. This data is then was analyzed for adsorption study and also is used to develop the Isotherm whether Langmuir Isotherm or Freundlich Isotherm.

4.5.2 EFFECT OF MASS ON THE METAL UPTAKE OF ZN (II)

Table 4.8 has shown the percentage of metal uptake versus the contact time suggested. According to the data, the activated carbon has successfully adsorbed a portion of the 150ppm Zinc (II) ion. By means, the final adsorption capacity that have been observed for each set of activated carbon mass are 18 for 0.05g, 14.3 for 0.1g, and 11.5 for 0.15g. This set of activated carbon has successfully achieved equilibrium as shown in the figure 4.23. As for 0.2g and 0.25g, the activated carbon tested did not achieve the equilibrium points and still adsorbing through the contact time suggested.

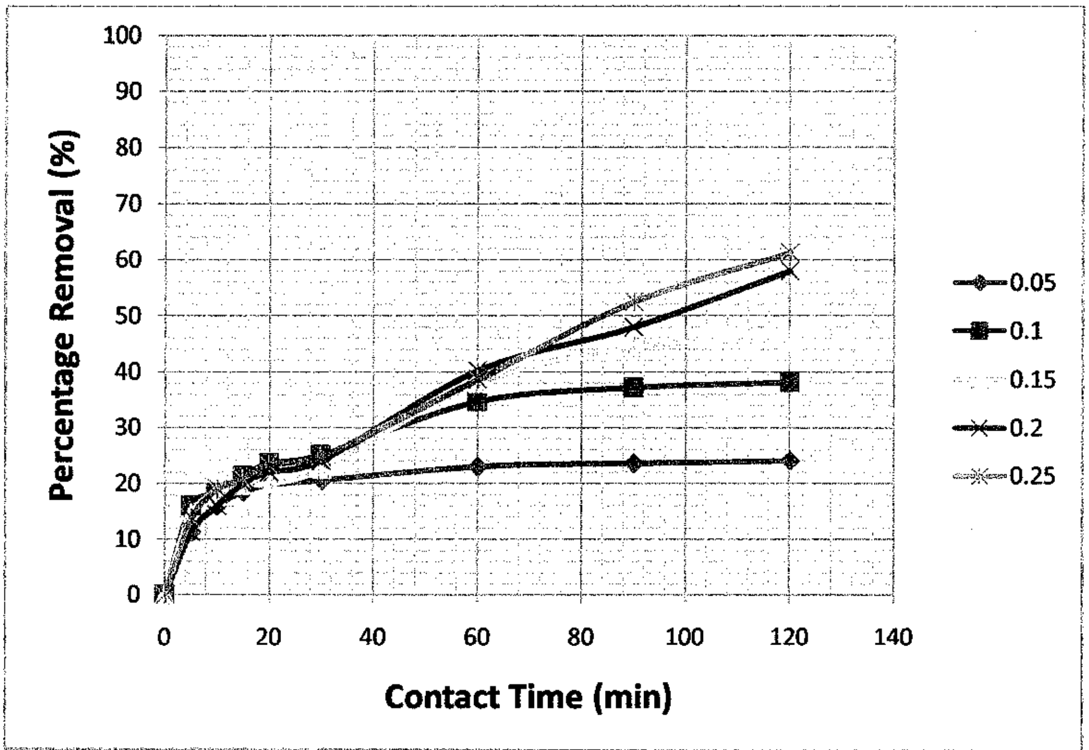


Figure 4.23: Percentage Removal versus Contact Time

During the adsorption of the Zn (II) metal ion, the colorless aqueous solution is put into a water bath shaker to maximize the adsorption as stirring or shaking may results for more contact of the adsorbent pores with the metal ion. During the first 30 minutes, the adsorption occurs steadily until it reaches 90 minutes where for 0.05, 0.1 and 0.15g of activated carbon slowly reach equilibrium. Finally, when the time reach 100-120 minutes, the adsorption stops, but for 0.2g and 0.25g, adsorption is still happening so it needs to be lengthen a little bit for the adsorption process to reach equilibrium. So, the data to plot the isotherms will be taken for 0.05, 0.1 and 0.15g only as the others didn't yet achieve equilibrium. The metal uptake also increases with the increasing quantity of activated carbon used.

The equilibrium concentration for the three sets are recorded and tabulated in the table below.

Table 4.9: Equilibrium Concentration for 0.05, 0.1, and 0.15g (plot by graph)

Weight	Equilibrium Concentration, C (ppm)	Time to reach Equilibrium (minute)	mg Zn(II) ion adsorbed/g adsorbent
0.05	114	100	18
0.1	93	110	14.25
0.15	81	120	11.5

4.5.3 EFFECT OF MASS WITH ADSORPTION CAPACITY

As you can see from the data in table 4.24, the adsorption capacity of the activated carbon is inversely proportional to the increasing quantity or mass of the activated carbon. This can be proved by looking at the equations used to calculate the adsorption capacity.

$$\frac{mg\ Zn\ (II) ion\ adsorbed}{g\ adsorbent} = \frac{[Initial\ ppm\left(\frac{mg}{L}\right) - Final\ ppm\ \left(\frac{mg}{L}\right)] \times volume\ (L)}{g\ adsorbent}$$

So, as the mass increase, the adsorption capacity drops for the 25 ml of Zinc (II) ion solution used. This relationship can easily be displayed as in the figure below. The increase of mass of the activated carbon actually made the activated carbon accumulates more volume so the crowded volume of solution has less efficiency for adsorption. So, to have better adsorption is to increase the volume for the adsorption to occur.

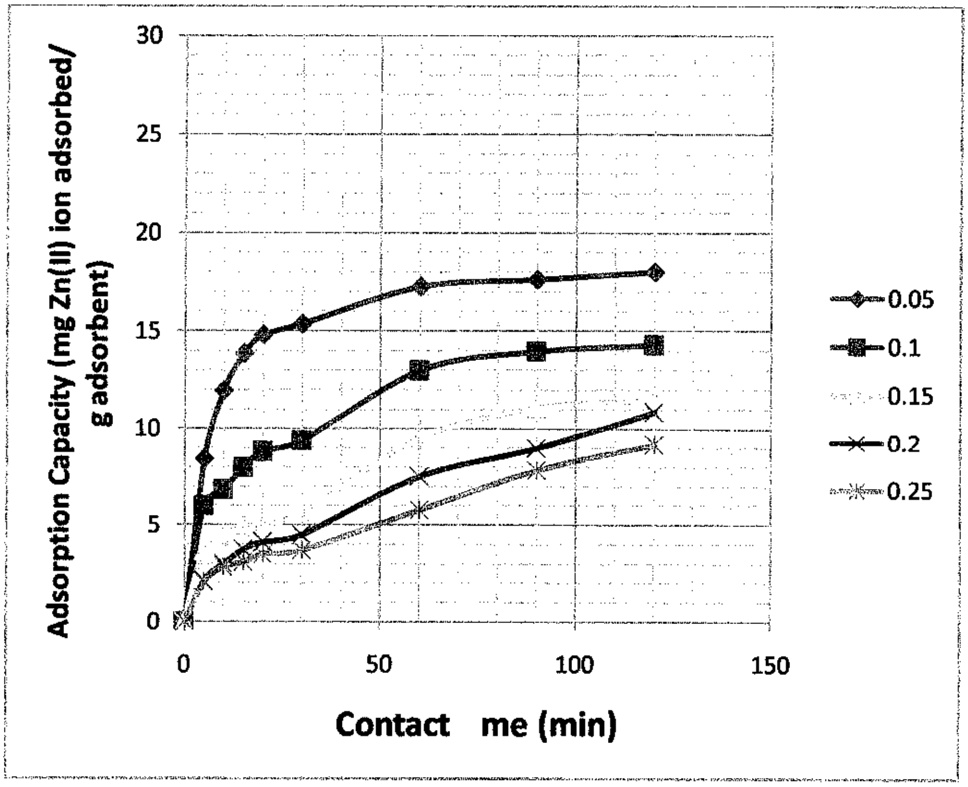


Figure 4.24: Adsorption capacity vs Contact time

4.5.4 LANGMUIR ISOTHERM AND FREUNDLICH ISOTHERM

To plot the isotherm, some variable has to be clarified based on the results from table X. The variables need to be clarify are;

$q = \frac{mass\ of\ species\ adsorbed}{mass\ of\ adsorbent}$

(i.e., equilibrium concentration of adsorbable species in solid adsorbent)

c = equilibrium concentration of adsorbable species in solution

Then, the isotherms that will be investigated are the Langmuir Isotherm and the Freundlich Isotherm. This is determined by the graph function, whereby the graph with R^2 that have the value nearest to 1. After the isotherm is determined, we can determine the parameters related base on the basic function, Y=mX + C. Below are the functions of the isotherm with the parameter.

Langmuir Isotherm, $\frac{C}{q} = \frac{1}{K_A q_m} + \frac{1}{q_m} C$

Accordingly, a plot of C/Q vs. C will give:

Slope = $\frac{1}{K_A q_m}$

Intercept = $\frac{1}{q_m}$

Freundlich Isotherm, $\log q = logK_F + \frac{1}{n} logC$

Accordingly, a plot of log q vs. log C will give:

Slope = $\frac{1}{n}$

Intercept = $logK_F$

So, the variable for 0.05g, 0.1g, and 0.15g are listed as follow:

Table 4.10: Parameters for developing Isotherm

Weight, g	mg adsorbate/g adsorbent, q	Log q	Equilibrium concentration of adsorbable species in solution, C	Log C	C/q
0.05	18	1.255	114	2.057	6.333
0.10	14.25	1.154	93	1.968	6.526
0.15	11.5	1.061	81	1.908	7.043

Below, the graphs for the Langmuir and Freundlich are displayed. The nearest value of R^2 for any of the isotherms to 1 will be selected and the parameters will be calculated based on the functions.

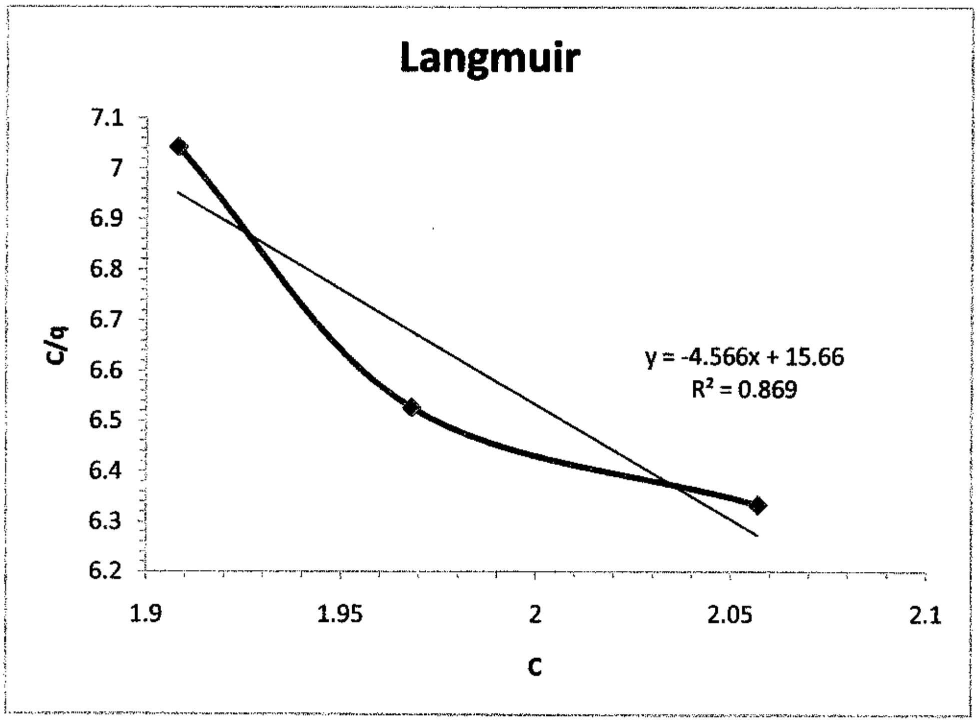


Figure 4.25: Langmuir Isotherm plotted for 0.05, 0.1, and 0.15g

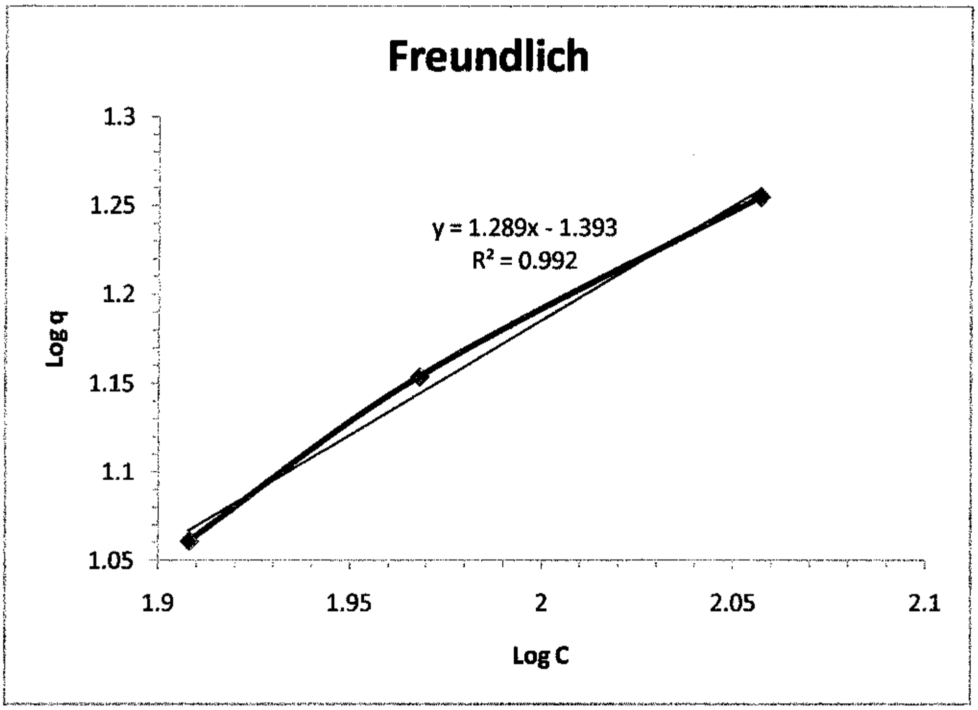


Figure 4.26: Freundlich Isotherm plotted for 0.05, 0.1, and 0.15g

As the R^2 for the plotted Freundlich Isotherm has the value nearest to 1 that is 0.992; it will be selected as the isotherm model for this adsorption. Thus, the function of the graph, $y = 1.289x - 1.393$ would be used to determine the 1/n (constant) and K_f(constant, function of energy of adsorption and temperature).

So the intercept is,

$x=0$, $y= -1.393 = \log K_f$

$K_f= 10^{-1.393} = 0.0405$

And the slope is equal to 1.289 and also equal to 1/n. So, n equals to 0.7758.

Thus, we can conclude that rice husk develops Freundlich Isotherm's adsorption. Freundlich Isotherm represents an empirical model and no assumption can be made for the adsorption characteristic. Freundlich isotherm also can be used for mixtures of compound rather than Langmuir Isotherm that represents data only for single components.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

From the results obtained, several conclusions can be made as the followings:

1. The characterization of rice husk as an activated carbon proves that it can be made into a good adsorbent after it has gone through careful preparation with activated agent (Sodium Hydroxide), optimize particle size (63μm), optimize carbonization temperature (500°C), and are highly porous cellulose-silica.
2. As the mass is increased, the metal uptake also increases. But the adsorption capacity decrease with mass, which can be fixed by increasing the volume of the adsorption to avoid crowded ion adsorption on the activated carbon.
3. Rice Husk adsorption develops an adsorption with Freundlich Isotherm. The value for K_f and 1/n are also determined in the process, that is 0.0405 (K_f) and 0.7758 (n). This value is subject to error, as there may be some error in the production and error from the equipment.
4. Rice husk has high potential to substitute current adsorbents as a low-cost activated carbon to remove Zn (II) and can be utilized for water treatment management.

5.2 RECOMMENDATIONS

The study on rice husk as a potential adsorbent has not finish yet. There are lots of are of improvement to be made so that it will be fully capable for industrial use. Thus, below are the recommendations for further development of rice husk.

1. To relate rice husk with other isotherms, such as Brunauer-Emmet-Teller (BET) isotherm and Kisliuk Isotherm so that we can determine other attributes of rice husk adsorption.
2. To study on the effect of batch adsorption and continuous flow adsorption.
3. To study the adsorption activities for complex ion, which wastewater usually have complex mixture of ion.

REFERENCES

1. Bhattacharya, A.K., Mandal, S.N., Das, S.K., (2006). Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chemical Engineering Journal, 123, 43-51.

2. Kadirvelu, K., Thamaraiselvi, K., Namasivayam, C., (2001a). Removal of Heavy metal from industrial waste water by Adsorption onto activated Carbon prepared from agricultural solid waste. Bioresour. Technol., 76, 63-65.

3. Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Malaysia: Selected parameter limits of effluent of Standards A and B (Department of Environment, DOE, Malaysia)

4. Rahman, I., A., Ismail, J., & Osman, H. (2000). Studies of Zn(II) ion adsorption by rice husk digested with nitric acid. *Malaysia Journal of Chemistry* 2(1), 012-015.

5. Lua, A.C. and J. Guo, 2001. Preparation and characterization of activated carbons from oil-palm stones for gas-phase adsorption. Coll. Surfaces A: Physicochem. Eng. Aspects, 179: 151-162.

6. Ahmadpour, A., Do, D.D., 1996. The preparation of active carbons from coal by chemical and physical activation. Carbon 34, 471-479.

7. N.R. Khalili, H. Arastoopour, L. Wolhof, (2000) IITPatent # 6,030,922 ..

8. Arriagada, R., R. Garcia, M. Molina-Sabio, and F. Rodriguez-Reinoso, "Effect of Steam Activation on the Porosity and Chemical Nature of Activated Carbons from Eucalyptus Globulus and Peach Stones," Micropor. Mater., 8, 123 (1997).

9. Wan Ngah, W. S., & Hanafiah, M. A. K. M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Bioresource Technology, 99(10), 3935-3948.

10. Chuah, T. G., Jumasiah, A., Azni, I., Katayon, S., & Thomas Choong, S. Y. (2005). Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: An overview. Desalination, 175(3), 305-316.

11. Neeta Sharma and Jatinder Singh: Removal of Zn^{+2} Ions from Aqueous Solution Using Rice (*Oryza sativa*) Husk in a Sequential Bed Adsorption Column.

12. Nasehir, K. E. M. Y., M. Faizal, Pakir. M. L., Ismail, A., Olugbenga, S. B., M. Azmier, A., (2010) Process optimization for Zn (II) removal by activated carbon prepared from rice husk using chemical activation. International Journal of Basic & Applied Sciences IJBAS-IJENS Vol: 10 No: 06.

13. Tzong-Horng Liou*, Shao-Jung Wu, 2009, "Characteristics of microporous/mesoporous carbons prepared from rice husk under bas- and acid-treated conditions," Journal of Hazardous materials 171:693-703.

14. Yalcin N., Sevinc V., 2001, "Studies on silica obtained from rice husks," Ceram. Int. 27:219-224

15. S.B. Daffalla, H. Mukhtar, M.S. Shaharun, 2010, "Characterization of Adsorbent Developed from Rice Husk: Effect of Surface Functional Group on Phenol Adsorption," Journal of Applied Sciences 10(12): 1060-1067

16. T.G. Chuah[a*], A. Jumaisiah a, I. Azni a, S. Katayon b, S.Y. Thomas Choong[a], 2004 "Rice Husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview".

APPENDICES

APPENDIX I

Calculation of 150 ppm of Zn (II) ion solution

In order to minimize error, the solution prepared is started from 500 ppm $ZnCl_2$.

$$500\ ppm\ by\ mass = \frac{500\ mg\ Zn^{2+}}{1\ kg\ of\ water}$$

Given the molar mass: Zn – 65.38 g/mol; $ZnCl_2$ – 136.28 g/mol

Assuming 1.0 mol of ZnCl2, thus having 1.0 mol of Zn^{2+}

$$Mass\ of\ ion\ Zn^{2+} = \frac{65.38\ g\ Zn^{2+}}{1\ mol\ of\ Zn^{2+}} \times 1\ mol\ of\ Zn^{2+}$$

$$Mass\ of\ ZnCl_2 = \frac{136.28\ g\ ZnCl_2}{1\ mol\ of\ ZnCl_2} \times 1\ mol\ of\ ZnCl_2$$

$$\therefore\ Percent\ mass\ of\ ion\ \ of\ Zn^{2+} = \frac{65.38\ g\ Zn^{2+}}{136.28\ g\ ZnCl_2} = \frac{0.4797\ g\ Zn^{2+}}{1.000\ g\ ZnCl_2}$$

Then 500 mg of Zn^{2+} in $ZnCl_2$:

$$500\ \times 10^{-3}\ g\ of\ Zn^{2+} \times \frac{1.000\ g\ ZnCl_2}{0.4797 g\ Zn^{2+}} = 1.042\ g\ ZnCl_2$$

By using dilution formula M1V1 = M2V2

$$500\ V_1 = 150\ (1000 ml)$$

$$\therefore\ V_1 = 300 ml$$

Therefore, 300 ml of 500 ppm of Zn (II) ion solution is diluted to prepare 150 ppm of Zn^{2+}

APPENDIX II

Calculation for Percent Metal Uptake

The calculation for metal uptake is shown as below:

$$\frac{Initial\ concentration - Final\ Concentration}{Initial\ Concentration} \times 100\%$$

For example, the initial concentration is 150 ppm and the final concentration is 114 ppm, therefore the percent metal uptake is;

$$\frac{150\ ppm - 114\ ppm}{150\ ppm} \times 100\%$$

= 24% metal ion uptake

Calculation for Adsorption Capacity

The calculation for adsorption capacity is such as below:

$$\frac{Initial\ concentration - Final\ Concentration}{Weight\ of\ rice\ husk\ in\ gram\ (g)} \times Volume\ of\ solution\ in\ litre(L)$$

For example, the initial concentration is 150 ppm and the final concentration is 114 ppm, volume of solution is 0.025 L and weight of the rice husk used is 0.1 g, therefore the adsorption capacity is;

$$\frac{150\ ppm - 114\ ppm}{0.1\ g\ rice\ husk} \times 0.015\ L$$

= 14.63 mg Zn (II)/ g rice husk

APPENDIX V

Timelines for FYP 1

No.	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	■	■						Mid-semester break							
2	Preliminary Research Work		■	■	■	■										
3	Submission of Extended Proposal Defence						●									
4	Proposal Defence									■	■					
5	Project work continues											■	■	■		
6	Submission of Interim Draft Report														●	
10	Submission of Interim Report															●

● Suggested milestone

■ Process

Figure 4.27: Timeline for FYP 1

Timelines for FYP 2

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■	Mid-Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									■	■	■	■	■			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

● Suggested milestone

■ Process

App

Figure 4.28: Timeline for FYP 2