Studies on Zn (II) Ion Adsorption by Rice Husks Digested with Nitric Acid

by

Teo Ching-synn

Dissertation in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

(Normawati Mohamad Yunus)

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TRONOH, PERAK
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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 acknowledgments, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

TEO CHING-SYNN

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ABSTRACT

The use of rice husks as activated carbon as a potential adsorbent for the removal of zinc from aqueous solution has been investigated. The objectives of this experiment are to create a highly available, effective and inexpensive adsorbent for adsorption process in removal of metal ions that present in waste water streams. Besides that, characteristics of rice husk as adsorbent are carefully studied.

Due to health, safety and environment concerns, highly toxic metals that present in waste stream are dangerous and required to be eliminated through a chemical process called adsorption. Generally, adsorption is done in the plant using adsorption column, conventional methods such as ion exchange process, and other biological processes. Since, the conventional method consumes a lot of money hence, a newer and cost effective method is applied by using agriculture wastes which face highly disposal problem or other activated carbon from a variety of materials such as peach stones, almond shells, peanut skins and others.

This laboratory scale experiment was conducted by adsorbing 25 ml of 25 ppm of Zn^{2+} solution with digested and carbonized rice husk into 500 ml conical flask. Agitation of sample was operated at 150 rpm, 2 hours at room temperature. Adsorption sample was filtered and the filtrate solution was tested on Atomic Absorption Spectrophotometer (AAS) to determine concentration left after adsorption. The AAS results were analyzed based on various factors tested. Brunauer – Emmet – Teller (BET) method was studied and Scanning Electron Micrscopy (SEM) was employed to characterize the rice husk fibrous structures.

Scopes of this experiment which are on the effects of various factors, e.g., nitric acid concentration, carbonization temperature and time, particle size of rice husk, rice husk loading, adsorption contact time and shaker speed on adsorption capacity, were quantitatively determined.

Nitric acid concentration effect at 1.0 M for acid treatment, 500 ^{0}C and 1 hour carbonization prove the highest adsorption capacity. Particle size at 0.500 mm has the greatest effect to adsorb Zn^{2+} in terms of surface area and engineering economic analysis. Higher mass loading was found to adsorb more Zn^{2+} quantity and at 30th minute, adsorption equilibrium had been achieved. During adsorption experiment, shaker speed of 200 rpm recorded the highest Zn^{2+} uptake. The two-parameter equilibrium models (Langmuir and Freundlich equations) were discussed. It was found that Freundlich best fitted on the experiment.

Overall, rice husk has a potential for removing Zn^{2+} in waste stream but is required to improve further on the rice husk preparation. Future work discussed is required to be alarmed for the betterment of this process technology.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Industrial and municipal waste water frequently contain metal ions. These metal ions in sufficient quantity can be harmful to aquatic life and human health. The accumulation of heavy metal contaminants in the environment has become a concern due to growing health risks to the public. These contaminants such as cadmium, chromium, lead and zinc, enter the environment through industrial waste, mill tailings, and landfill run off. In fact, these contaminants present which endanger living beings life have alarmed when the outbreak of Minamata disease. Minamata disease was discovered in Minamata Bay in Japan 1969. This is the result of first atomic bomb was exploded at Hiroshima, and where thousands of people suffered the hideous effects of eating fish poisoned with mercury. Since then, enactment of World Pollution Control Amendment of 1972 has raised some awareness and concern about environment and many governments have set strict legislative regulations enforcing treatment of effluents with toxic metal ions to safety level. [1]

Current methods for wastewater treatment include precipitation, coagulation/floatation, sedimentation, electrochemical techniques, ion exchange and biological process. Each method has its merits and limitations in application. The adsorption process using activated carbon is attractive to many scientists because of its effectiveness for the removal of the metal ion at trace quantities. But the process has not been used extensively, the use of the low cost materials as sorbent for metal removal from wastewater has been highlighted.

1.2 PROBLEM STATEMENT

As described in California Administrative Manual (CAM) or California Code of Regulations (CCR) Title 22, zinc (Zn) is listed as heavy metal out of 22 metals such as copper (Cu), iron (Fe), lead (Pb), mercury (Hg) and much more. [2] Exposure to heavy metal contamination has been found to cause kidney damage, liver damage, and anemia in low doses, and in high concentration, heavy metals can be carcinogenic and teratogenic if not fatal. It has been established beyond any doubt that dissolved heavy metals escaping into the environment pose a serious health hazard. They accumulate in living tissues throughout the food chain, which has humans at its top. The danger multiplies. There is a need for controlling the heavy metal emissions into the environment.

Metals with density of 5 g/cm^3 of Zn, Co, Cd, Ni are used in industrial countries. Zn is widely used for alloys like brass. It is also used to galvanize iron and for fabrication of batteries. Industrial plants producing metallic Zn by roasting or heating are always potential sources of environmental Zn contamination because the melting point of Zn is 419 °C and boiling point of 907 °C of metallic Zn is low component to other metals. Plants producing Zn by roasting are therefore also potential sources for environmental contamination with cadmium (Cd). Cadmium and solutions of its compounds are toxic. Extensive use of Zn and Cd, consequently leads to contamination of soil and fresh water habitats with the divalent cations. [3]

Industrially, the waste from the plant production is discharged in a non-environment friendly manner. This is due to expensive cost or high investment needed to be spent for discharging the effluent on conventional wastewater treatment. Conventional technologies for the removal and recovery of heavy metals from industrial wastewater include chemical precipitation, ion exchange, membrane separation and adsorption by activated carbon. [4] More recently, great effort has been contributed to develop new adsorbents to replace existing adsorbents like granular activated carbon, other adsorbents such as iron oxides, porous cellulose carrier modified with polyethyleneimine, iron coat granular, modified chitosan, etc.

In recent years, interest has been directed to the investigation of low cost materials such as agricultural byproducts, industrial wastes and biological materials as sorbents for removal of heavy metal from industrial wastewater. One of the exploitation is the use of natural wastes such as walnut waste, peanut skins, sugar cane waste skin, coffee grounds, tea leaves, apple waste, wool fiber, bark and other cellulosic material and linseed flax straw. Because of the low cost, high availability of waste materials, and no need for complicated regeneration process. The method is attractive to Scientists and Engineers. [5]

Due to this environmental impact of Zn (II) ions, a number of studies have been done for wastewater treatment by adsorption process. In this project, adsorbent material used was rice husks (agriculture waste), digested with acid to adsorb Zn (II) ion in water treatment process.

1.3 OBJECTIVES AND SCOPE OF STUDY

This work's goals are to study the possibility of the utilization of rice husks for the removal of zinc ions from aqueous solutions. In other words, we need to characterize the adsorbent materials as well. Besides that, the aim is also to develop inexpensive, highly available, effective metal ion adsorbents from natural wastes as alternatives to existing commercial adsorption.

We aim to study the dependent of adsorption activities in different experimental conditions. From here, an effective and optimum adsorption results are obtained. Isotherm model for the adsorption is required to be identified. The equilibrium adsorption isotherm is fundamentally important in the design of adsorption system.

The scopes of this experiment are listed below:

i. Effect of nitric acid concentration and carbonization temperature and time
ii. Effect of rice husk particle sizes
iii. Effect of rice husk loading
iv. Effect of adsorption contact time and shaker speed

Surface area analysis and pore volume aspects with other variable conditions in this adsorption experiment were studied. SEM and EDX analysis were done for characterization study of rice husk as adsorbent.

CHAPTER 2

LITERATURE REVIEW

2.1 ENVIRONMENTAL THREATS

By far the greatest demand for metal sequestration comes from the need of immobilizing the metals 'mobilized' by and partially lost through human technological activities. The potential health hazard which presences in concern to public by a series of heavy metals are listed in Table 2.1.

Table 2.1: Typical Waste Compounds Produced by Commercial Industrial and Agriculture Activities

Name (Metals)	Uses	Concerns
Barium	Getter alloys in vacuum tubes, deoxidizer for copper Frary's metal	Flammable at room temperature in powder form, long term increase blood pressure and nerve block
Cadmium	Electrodeposited and dipped coatings on metals, bearing and low melting alloys	Flammable in powder form, toxic by inhalation of dust concentrates in the liver, kidney, pancreas
Chromium	Alloying and plating element on metal and plastic substrates for corrosion resistance	Carcinogenic and long term skin sensitization and kidney damage
Lead	Storage batteries, gasoline additive, cable covering, ammunition	Toxic by ingestion or inhalation of dust or fumes, birth defects, long term and kidney damage
Mercury	Catalyst electrical apparatus, mercury vapor lamps, mirror coating boilers	Highly toxic by skin adsorption and inhalation of fume, birth defects

2.1.1 Environmental Pressures

The toxicology of heavy metals as promulgated by toxicologists in many of their clinical studies confirms that the metals impose dangerous impacts on human races. Due to the toxicity of these heavy metals, stricter regulations with regard to the metal discharges are being enforced particularly for industrialized countries in the developing and advanced world.

The current technologies for heavy metals removal from industrial effluents such as activated sludge, biodegradable organics, heavy metals, solved inorganic and so on appear to be inadequate and expensive. They often create secondary problems with metal-bearing sludge.

2.1.2 Metal Removal/Recovery "Priorities"

An example of the prioritization for recovery of ten metals is in Table 2.2 which may be simplistic but provides a useful direction by ranking it into 3 general priority categories:

1. Environmental risk (ER)
2. Reserve depletion rate (RDR)
3. A combination of the two factors

Environmental risk assessment could be based on a number of different factors, which could even be weighed.

The RDR category is used as an indication of probable future increase in the market price of the metal. When coupled with the ER in this example there is an indication that Cd, Pb, Hg, Zn are a high priority. However, the technological uses of Hg and PB may be considered declining, while the Cd use is on the increase. These projections and the degree of risk assessment sophistication could change the priorities among the metals considered.

Table 2.2: Ranking of Metal Interest Priorities

Relative Priority	Environment Risk	Reserve Depletion	Combined Factors
HIGH	Cd	Cd	Cd
	Pb	Pb	Pb
	Hg	Hg	Hg
	-	Zn	Zn
MEDIUM	Cr	-	-
	Co	Co	Co
	Cu	Cu	Cu
	Ni	Ni	Ni
	Zn	-	-
LOW	Al	-	Al
	-	Cr	Cr
	Fe	Fe	Fe

2.2 ADSORPTION

Adsorption phenomena have been known to mankind for a very long time, and they are increasingly utilized to perform desired bulk separation or purification process. The heart of an adsorption process is usually a porous solid medium. The success or failure of the process depends on how the solid performs in both equilibria and kinetics.

Adsorption equilibria information is the most important piece of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibria of pure components are the essential ingredient for the understanding of how much those component can be accommodated by a solid adsorbent. In the case of simple metal ion solutions, the adsorption equilibria data from adsorption of Zn (II) ions to be fitted in the best isotherm: Langmuir and Freundlich. Isotherm is an important tool which establishes the economic and technical feasibility of intended adsorption system design, for example: wastewater treatment system. Isotherm has a curve which relates the amount of adsorbate adsorbed per unit mass of adsorbent to the amount of unadsorbed adsorbate remaining in solutions at equilibrium point. It will assess if desired purity level can be achieved and also provides information about adsorption variables like choice of adsorbent, adsorbent dosage, temperature, pH and equilibrium time so as to operate at maximum adsorption capacity conditions.

Isotherm test can be done by treating fixed volumes of a solution with a fixed concentration of adsorbate with a series of different known weights of adsorbent or treating a series of fixed volume of solutions of different concentrations of adsorbate with a series of fixed amounts of adsorbent. Both treatments are then agitated by an appropriate device long enough to achieve equilibrium. Finally, adsorbent is separated from solutions by a filter paper or membrane filter. Therefore, concentration difference of and data obtained will be used to plot isotherm.

With this information, it can be used in the study of adsorption kinetics of a single component. Kinetic studies suggested that intraparticle diffusion occurred indicating that ion exchange between the metal ions from the solutions and protons of surface groups of adsorbents took place. Characterization results suggest that, the adsorbents were amorphous and that they contained surface groups such as –C=O, -O-H, and –Si-OH. [6]

Adsorption is also defined as a separation method in which fluid molecules, atoms/ions called adsorbates are attracted through surfaces of a solid called adsorbent through physical or chemical interactions. Physical interactions happens as a result of weak interactions like Van der Waals and dipole-dipole interactions while chemical adsorption is due to chemical bonding like covalent and hydrogen bonding. Both short range (repulsive) and longer range (attractive) forces between adsorbate and adsorbent become balanced when adsorption occurs. Some factors needed to be considered in adsorption process are as listed below:

1. Concentrations of adsorbate and adsorbent
2. Contact time for adsorbate and adsorbent
3. pH of the adsorption condition (optimum level)
4. Surface characteristics of adsorbent

Rice husks as raw materials for activated carbon (adsorbent) comprise elementary microcrystallites stacked in random orientation and are made by the thermal decomposition of various carbonaceous materials followed by an activation process. The two types of manufacturing process, are involving gas activation and chemical activation.

The gas activation process first involves heating in the absence of air at 400 – 500 °C to drive off volatile materials and to form small pores. Activation is then carried out with; for example, steam at between 800 and 1000 °C. Other gases such as carbon dioxides or flue gases can be used instead.

Chemical activation [6] can be carried out using, for example, zinc chloride or phosphoric acid to produce an activated carbon directly from the raw material, although the pores tend to be larger than with materials produced via steam activation. In this experiment, nitric acid is used.

The surface of an activated carbon adsorbent is essentially non-polar but surface oxidation may cause some slightly polarity to occur. Surface oxidation can be created, if required, by heating in air at around 300 °C or by chemical treatment with nitric acid or hydrogen peroxide. This can create some hydrophilic character which can be used to advantage in the adsorption of polar molecules but can cause difficulties in other applications such as the adsorption of organic compounds from humid gas streams. Nitric acid which contains nitrogen and oxygen atoms with lone pairs of electrons can bind metal ions through coordinate bonds. Besides that, nitric acid also acts as strong acidic ion exchanger with metal ions from solutions. In general, however, activated carbon is hydrophobic and organophilic and therefore they are used extensively for adsorbing compounds of low polarity in water treatment, decolourization, solvent recovery and air purification applications.

In this experiment, the materials for adsorbate and adsorbent are Zn (II) ion in zinc (II) nitrate and rice husks digested with nitric acid respectively. Metal Zn (II) ion which presents in wastewater, causes environmental and health effect.

2.3 RICE HUSKS AS AGRICULTURE WASTES

Rice husks are chosen because of its description as inexpensive and available waste or by-product of rice milling industry. Rice husks are capable to be prepared as adsorbent after digested with nitric acid and followed by carbonization. Its characteristics are fibrous, tough, abrasive, non digestible and high ash containing by product. Moreover, its high bulk and resistance to weathers make its disposal a problem.

Biologically, rice husks can be used as adsorbent due to its structures of silica, cellulose, hemicellulose and lignin which have adsorbent criteria to adsorb the adsorbate. Nitric acid which pretreats the rice husks to sequentially remove alkali, hemicellulose, lignin and cellulose from rice husks. The pretreatment will alter the rice husks' carbon to silica ratio and composition, which will have large a large influence on evolution of pore structure, surface area, pore volume, etc. in practical operations, maximum capacity of adsorbent cannot be fully utilized because of mass transfer effects involved in actual fluid-solid contacting processes. Table 2.3 shows the compositions of organic constituents in the activated husks compared to the raw material.

Treated and carbonized rice husk which is also considered as activated carbon, which involves in carbon adsorption whereby, is identified as a "best available technology". In carbon adsorption in this case, contaminants such as metal ions are physically attracted or adsorbed on the surface of the carbon. The adsorption capacities of carbon are high because its porosity provides a large surface area relative to its volume. [7]

Besides of rice husk characteristics in aid of adsorption, it is also most effective at removing organic compounds that have low polarity, high molecular weight, low water solubility, and a high boiling point. [7] Therefore, since zinc has high boiling temperature i.e. 907 °C, it is a suitable adsorbate for rice husk which acts as adsorbent.

Rice husks are one of the ingredients to make light weight concrete blocks in India, Pakistan and California for building material like bricks and tiles. Cellulose, one of organic constituents in rice husks is useful in producing rayon pulp for making rayon yarn. This application is widely used in Japan. Cellulose in rice husks which is heated up with sulfuric acid H_2SO_4 will produce pentosans and will convert to furfurol, a chemical used to make synthetic resins.

Meanwhile, rice husks ash which may turn to silica, substance to produce silicon to make solar cells for photovoltaic power generator. The ash which can be boiled with sodium hydroxide (NaOH) will turn silica to sodium silicate which will be used to produce detergents in soaps and adhesives. Besides that, rice husks can actually convert to fuel energy to make tar, light oil, and fuel gases. Finally, the carbon part of rice husks can be used as adsorbent, pigments, carbon papers and much more. [6]

Table2.3: Composition of Organic Constituents in the Activated Husks Compared to the Raw Material

Compositions (%)	Sample	
	Raw Rice Husks	Activated Rice Husks
Silica	16.1	74.0
Cellulose	35.5	22.8
Hemicellulose	22.3	3.1
Lignin	13.6	0.2
Soluble and Moisture	12.5	0.0
Total	100.0	100.1

CHAPTER 3

MATERIALS AND METHODS

3.1 PRETREATMENT OF RAW MATERIALS

To remove the adhering soil, rice husk was washed thoroughly with distilled water. The cleaned rice husk was dried in an oven at 35 °C for 2 days. The rice husk was thoroughly overturned frequently to ensure complete drying.

The dried rice husk was then grounded and screened through a set of sieves to get different geometrical sizes such as 0.125 mm, 0.500 mm, 1.000 mm and 2.000mm. This produced a uniform material for the complete set of sorption tests which was stored in an air-tight plastic container for all investigation.

Nitric acid (HNO_3) with 0.1 M, 0.5 M, 1.0M and 14.4 M concentrations were prepared for acid treatment procedure. The stock solutions of Zn^{2+} were prepared in distilled water using zinc nitrate ($Zn(NO_3)_2$). All working solutions were prepared by diluting the stock solution with distilled water.

Acid treatment for 19 samples of dried rice husk was done with ratio of dried rice husk to nitric acid at 1 g: 10 ml. The acid treatment samples are shown in Table 3.1. All treated samples were left overnight at the fume hood.

Table 3.1: Samples for Acid Treatment and Carbonization

Carbonization Temperature & Time	Nitric Acid Concentration (M)	Rice Husk Sizes (mm)			
		0.125	0.500	1.000	2.000
		Total Rice Husk Needed (g)			
500 °C, 1 hour	0.1	-	0.5	-	-
	0.5	-	0.5	-	-
	1.0	4.1	2.5	4.1	0.5
	14.4	-	0.5	-	-
500 °C, 2 hour	0.1	-	0.5	-	-
	0.5	-	0.5	-	-
	1.0	-	0.5	-	-
	14.4	-	0.5	-	-
900 °C, 1 hour	0.1	-	0.5	-	-
	0.5	-	0.5	-	-
	1.0	-	0.5	-	-
	14.4	-	0.5	-	-
900 °C, 2 hour	0.1	-	0.5	-	-
	0.5	-	0.5	-	-
	1.0	-	0.5	-	-
	14.4	-	0.5	-	-

Treated rice husk was washed thoroughly with excess distilled water to drain off excessive nitric acid by removing the entire remaining nitrate on its surface and to perform pH control of the samples. All samples were maintained at pH 5 by an aid of pH meter (sensION^{TM} 51935.88). Digested samples were left at fume hood for drying purpose to remove any moisture trapped.

Based on Table 3.1, respective digested rice husk was kept into crucibles before carbonization was done. Respective digested rice husk was placed into a furnace for carbonization. Desired temperatures were setup and carbonization hours were first counted after the furnace had reached an equilibrium desired temperature. The furnace temperature was lowered down until 25 °C (room temperature) before taking out the carbonized samples. The carbonized samples were left to cool at desiccators.

Batch sorption experiments were performed at a constant room temperature (25 °C) on a horizontal shaker at 150 rpm using 500 ml capped conical flasks. In all sets of experiments, 0.1 g of rice husk (0.500 mm) was thoroughly mixed into 25 ml of 25 ppm Zn^{2+} solution. After shaking (agitation) the flasks for 2 hours, the reaction mixtures were filtered through filter papers to remove particulates and the filtrate was analyzed with an Atomic Absorption Spectrophotometry (AAS) (Shimadzu) for the concentrations of Zn^{2+}.

3.2 EFFECT OF HNO_3 CONCENTRATIONS AND CARBONIZED TEMPERATURE AND TIME

Batch sorption tests were done at carbonized rice husk with various nitric acid digested at different carbonized temperature and time. Each sample used an initial metal ion (Zn^{2+}) concentration of 25 ppm.

3.3 EFFECT OF RICE HUSK PARTICLE SIZES

Batch sorption experiments were carried out at the desired rice husk particle sizes (0.125 mm, 0.500 mm, 1.000 mm and 2.000 mm). Each sample used rice husk digested with 1.0 M nitric acid and carbonized at 500 °C for 1 hour, and an initial metal ion (Zn^{2+}) concentration of 25 ppm.

3.4 EFFECT OF RICE HUSK LOADING

Batch sorption tests were done for 0.125 mm and 2.000 mm carbonized rice husk (500 °C, 1 hour, HNO_3 [1.0 M]) with 0.1 g and 1.0 g loading for each size. Each sample used an initial metal ion (Zn^{2+}) concentration of 25 ppm.

3.5 EFFECT OF CONTACT TIME AND SHAKER SPEED

Batch sorption experiments were carried out at 100 rpm, 150 rpm and 200 rpm of horizontal shaker speed with interval times of 30 minutes, 60 minutes and 120 minutes. Each sample used carbonized rice husk (500 °C, 1 hour, HNO_3 [1.0 M], 0.500 mm) and an initial metal ion (Zn^{2+}) concentration of 25 ppm.

3.6 ATOMIC ABSORPTION SPECTROPHOTOMETRY (AAS)

Atomic Absorption Spectrophotometer (AAS) used in this experiment is to compare Zn^{2+} concentration absorbance to a standard. Its operating principle is based on the principle that atoms at ground state energy levels absorb electromagnetic radiation at specific wavelengths. An equation that illustrates this principle is

$$M + hv = M^* = M + hv \qquad \text{Equation 3.1}$$

Where M = neutral atom; hv = change in energy; M^* = excited atom

The main objective of an AAS is to compare an unknown sample concentration absorbance to a standard. To that end the factors that impact AAS operation include:

1. Removal or compensation for interfering ions
2. Removal of solids to prevent clogging
3. Preparation of standards similar to sample matrix

The main components of an AAS include:

1. Hollow cathode tube or electrodeless discharge lamp containing the element of interest
2. Nebulizer
3. Burner assembly
4. Monochromator
5. Detector

The element in the lamp corresponding to lead is excited by an electrical current causing light radiation to be emitted. The wavelength of the emitted light is characteristic of the element in the lamp. The nebulizer is used to aspirate the sample solution into a premixing chamber containing flow spoiler which converts large droplets into fine droplets which enter the flame through the burner head assembly. Most elements that are not refractory like lead, zinc, copper, alkali metals, use an acetylene-air flame (2100-2400 K). Elements that are refractory including silicon, aluminum, titanium, and chromium need a higher temperature flame like a nitrous oxide-acetylene source. The monochromator is used to isolate the primary wavelength of interest through a series of adjustable grating. After the monochromator the refined light bombards a photomultiplier tube (detector) which converts the light energy into electrical energy which is amplified and then readout based on a potential difference.

Two types of AAS instruments, single beam and double beam, are used. The double beam instruments used in this experiment tend to be more electronically stable since it compensates for changes in lamp intensity or variation in electronic noise or detector sensitivity. This is accomplished by comparing a sample beam to a reference beam.

Several advantages of AAS include:

1. High specificity for element desired
2. Minimal spectral interference
3. Ease of operation

Some disadvantages include:

1. Chemical interferences for elements that form stable compounds (organo-metallic ie. iron, calcium magnesium, potassium)
2. Ionization bias for elements easily ionized (alkali metals)
3. Matrix interferences caused by viscosity or specific gravity differences between standards and samples; elements analyzed one metal at a time.

The filtrate of each batch sorption was tested on AAS. Standard solutions were required to be prepared for calibration curve purpose. The preparation of standard solution was done by solving 59.99 mg, 39.995 mg, 19.995 mg and 9.9985 mg of $Zn(NO_3)_2.4H_2O$ solids with distilled water in 500 ml volumetric flask to obtain 30 ppm, 20 ppm, 10 ppm and 5 ppm of Zn^{2+} standard solution respectively.

3.7 CHARACTERIZATION OF RICE HUSK

Characterization of rice husk was determined by using BET method and through Scanning Electron Microscope (SEM).

3.7.1 BET Method (Brunauer – Emmet – Teller)

Adsorption and desorption isotherms of N_2 on rice husks were measured at 77 K using a volumetric adsorption apparatus (model). The BET method was used to evaluate the specific surface area of the rice husk from the adsorption isotherms. Batches from 3.2 to 3.5 were tested and the surface area for all samples was determined. Measuring the equilibrium volume of pure N_2 gas is adsorbed on several grams of the adsorbent at a number of different values of total pressures. In vacuum mode (5 – 250 mmHg), equation 3.2 is used:

$$\frac{P}{V(P_0-P)}=\frac{1}{V_mC}+\frac{C-1}{V_mC}\frac{P}{P_0} \qquad \text{Equation 3.2}$$

where

P = Total pressure

P_0 = Vapor pressure of adsorbate at test temperature

V = Volume of gas adsorbed at STP

V_m = Volume of monomolecular layer of gas adsorbed at STP

C = Constant

Data taken for V at each P and plot graph with Equation 3.3.

$$\frac{P}{V(P_0-P)} \text{ vs. } \frac{P}{P_0} \qquad \text{Equation 3.3}$$

Thus, values of V_m and C are determined from the graph plotted after experiment. Surface area is determined by using Equation 3.4 and 3.5.

$$S_g = \frac{\alpha V_m N_A}{V} \qquad \text{Equation 3.4}$$

$$\text{where } \alpha = 1.091\left(\frac{M}{N_A \rho_L}\right)^{2/3} \qquad \text{Equation 3.5}$$

where

N_A = 6.023 x 10^{23} molecules / mol

V = Volume of gas per mole at STP (22 400 cm^3/mol)

M = Molecular weight of adsorbate

ρ_L = Density of adsorbate in g / cm^3 at test temperature

BET works through gas absorption, measuring how much gas has been absorbed to find out the surface area. When performing BET testing, there are certain preparations to the sample that must be fulfilled.

One is that the solid sample is flat, uniform, and all of the same temperature (this is due to van der Waals forces). Second is that there's no lateral interaction between the absorbed molecules. And finally, is that after the solid has partially absorbed the gas, the remaining solid which has not absorbed gas yet must have the ability to absorb the gas or the gas must be able to be absorbed through the top layer.

3.7.2 Scanning Electron Microscopy (SEM)

SEM with the aim of investigating the surface structure of the rice husk was carried out with a scanning electron microscopy (LEO). The working principle is discussed. After the specimen is prepared and coated to make it conductive enough and vacuumed, it is placed inside the microscope vacuum column through an air tight door. After the air is evacuated, the gun starts to emit a beam of electrons.

The beam is attracted to anode, condensed by a condenser lens and forced to travel through a cylinder magnetic lens designed to focus the electrons to an extremely fine point on the sample by the objective lens.

Near the bottom, a set of scanning coils are energized by varying the voltage produced by the scan generator. If creates a magnetic field which moves the focused beam back and forth across the specimen, row by row in a controlled pattern.

The cathode-ray tube (CRT) voltage is also varied, thus it also produces a pattern of light back and forth on the surface of CRT, which has the same pattern as the moving or deflection of the electron beam. The resolution of the specimen and is decreased with an increasing working distance (spot size increase). On the other hand, the depth of the field increase with an increasing working distance (smaller divergence angle).

As the electron beams hit the each spot of sample, it produces a secondary layer of electrons on the surface. A secondary detector or a backscatter detector collects and count the electrons and sends it to an amplifier. The amplified voltage is applied to a grid in CRT and the intensity of light is changed which correspond to the topography of the sample. The image can also be photographed using Polaroid film. The mechanism of the image photographed may be different from on machine to other.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 SORPTION ISOTHERMS

Isotherms are important as it produces an isotherm that gives the Zn^{2+} storage capacity (volume) as a function of concentration. Besides that, isotherm is an indication which sorption is more favorable to some factor needs to be tested. In addition, it helps to determine the reproducibility of Zn^{2+} adsorption isotherms and to develop a standard method for measuring Zn^{2+} / rice husk adsorption isotherms. [8]

Sorption isotherms were tested on 4 batches of adsorption and fitted into Langmuir and Freundlich isotherms. Assumption is made during sorption takes place at specific homogeneous sites within sorbent, no further sorption take place thereafter. [9] In isotherm context, the rate of sorption to the surface should be proportional to a driving force which times an area. The driving force is the metal concentration in the solution, and the area is the amount of bare surfaces as usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium.

The relationship between the quantity of adsorbate per unit of adsorbent, q_e, and the equilibrium concentration of adsorbate in solution, C_e, is called an adsorption isotherm. Thus if C_0 is the initial concentration and C_e is the concentration of solute after equilibrium and m is the mass of adsorbent present, then amount of solute adsorbed per unit weight of adsorbent is given as: [10]

$$q_e = \frac{(C_o - C_e)xV}{m} \qquad \text{Equation 4.1}$$

4.1.1 Langmuir Isotherm

The equilibrium data of the sorption of Zn^{2+} in $Zn(NO_3)_2$ solutions were fitted into rearranged Langmuir equation (Equation 4.2).

$$\frac{1}{q_e} = \frac{1}{q_o b C_e} + \frac{1}{q_o}$$ Equation 4.2

where

q_o = q_o corresponds to the surface concentration at monolayer coverage and represents the maximum value of q_e that can be achieved as C_e is increased

b = b (constant) is related to the energy of adsorption and increases as the strength of the adsorption bond increases.

Linear plots with high correlation coefficients (Figure 4.1 – 4.4) were obtained and maximum sorption capacities of rice husk for Zn^{2+} were calculated from the slopes and shown in Table 4.1.

In fact, from the calculations, adsorption capacity due to monolayer coverage of rice husks. If experiment were tested on more than one metal ion, this isotherm can determine the difference in sorption capacities of rice husk for other metal ions. As example, two metal ions were competing for the same sorption sites contribute to depreciation of q_o when both metals were present compared with those in single metal solution. From this data, it confirms the ion can affect the ability activated carbon to remove metal ion.

4.1.2 Freundlich Isotherms

The equilibrium data of the sorption of Zn (II) in $Zn(NO_3)_2$ solutions were fitted into rearranged Freundlich equation (Equation 4.3).

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad \text{Equation 4.3}$$

where

K_F = A constant, a relative measure of adsorption capacity for the adsorbate

n = A constant indicates affinity on interaction energy (strength) between adsorbent and adsorbate

The effect of isotherm shape can be used to predict whether a sorption system is 'favorable' or 'unfavorable'.

If $\frac{1}{n} = 1$, rate of change of concentration of adsorbed substance in adsorbent is equal to the rate of change in solution.

If $\frac{1}{n} < 1$, rate of change of concentration is favorable, of adsorbed substance is smaller, than the rate of change in solution.

Meanwhile, if $\frac{1}{n} > 1$, it is unfavorable, because of rate of change of concentration of adsorbed substance is higher than the rate of change in solution.

The constants of model was calculated from the slopes and intercepts of (Figure 4.5 – 4.8) and listed in Table 4.1. The highest correlation is being obtained with the Freundlich Isotherm.

Table 4.1: Langmuir and Freundlich Isotherms Coefficients of Zn^{2+} Adsorption on Rice Husk

Sorption Batches	Langmuir Coefficients			Freundlich Coefficients		
	q_o	b (1/Ce)	R^2	$\left(\frac{1}{n}\right)$	K_F	R^2
Batch 1						
500 °C, 1 hour	0.3522	-0.0768	0.9886	-3.0097	10165	0.9918
500 °C, 2 hours	0.3750	-0.0721	0.9658	-3.0097	10165	0.9918
900 °C,1 hour	0.1062	-0.0530	0.9908	-6.6411	1.63 x 10^{-9}	0.9978
900 °C, 2 hours	0.0828	-0.0511	0.9986	-7.6807	1.53 x10^{10}	0.9996

Langmuir and Freundlich models can be used to describe the sorption isotherms of metal ions, which indicated that the biosorption of metals can be a monolayer sorption without interaction between adsorbed metal ions.[9] Freundlich isotherm which characterized most adsorption processes rather well under conditions present in most waste water systems. One problem with this isotherm, however is its failure to consider that there may be limited amount of adsorption sites on the surface of the solid; the lack of further sites may prevent adsorption under conditions in which equilibrium is reached. The Langmuir isotherm was developed to represent this site limitation, and it does a better job at describing adsorption under some conditions, particularly as the solid becomes saturated and solute molecules have trouble finding adsorption sites.

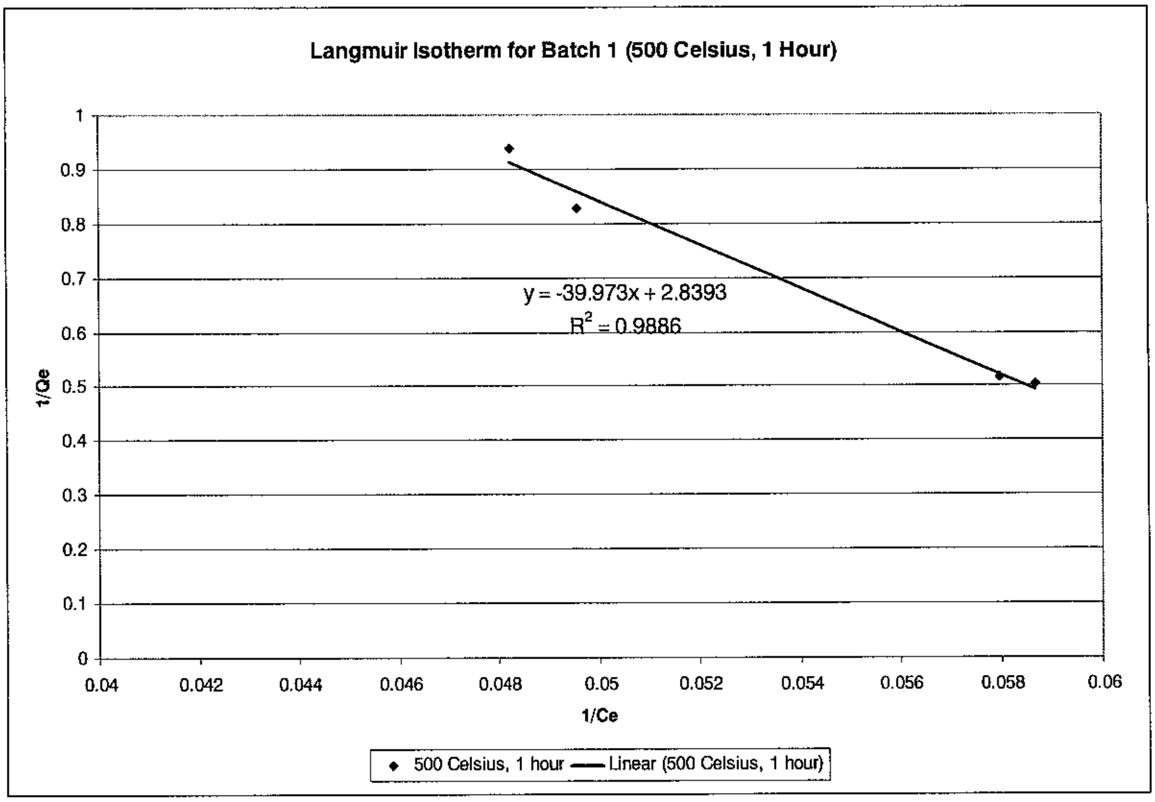

Figure 4.1: Langmuir Isotherm for Batch 1 (500 °C, 1 Hour)

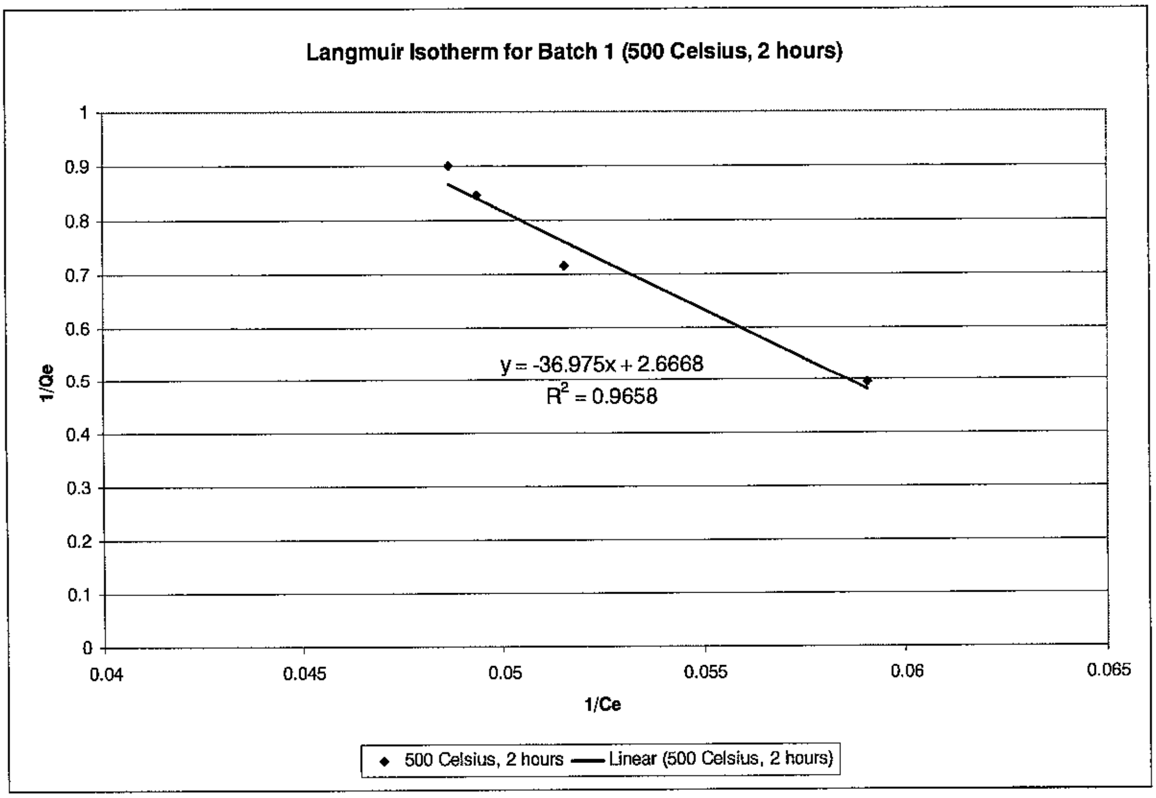

Figure 4.2: Langmuir Isotherm for Batch 1 (500 °C, 2 Hours)

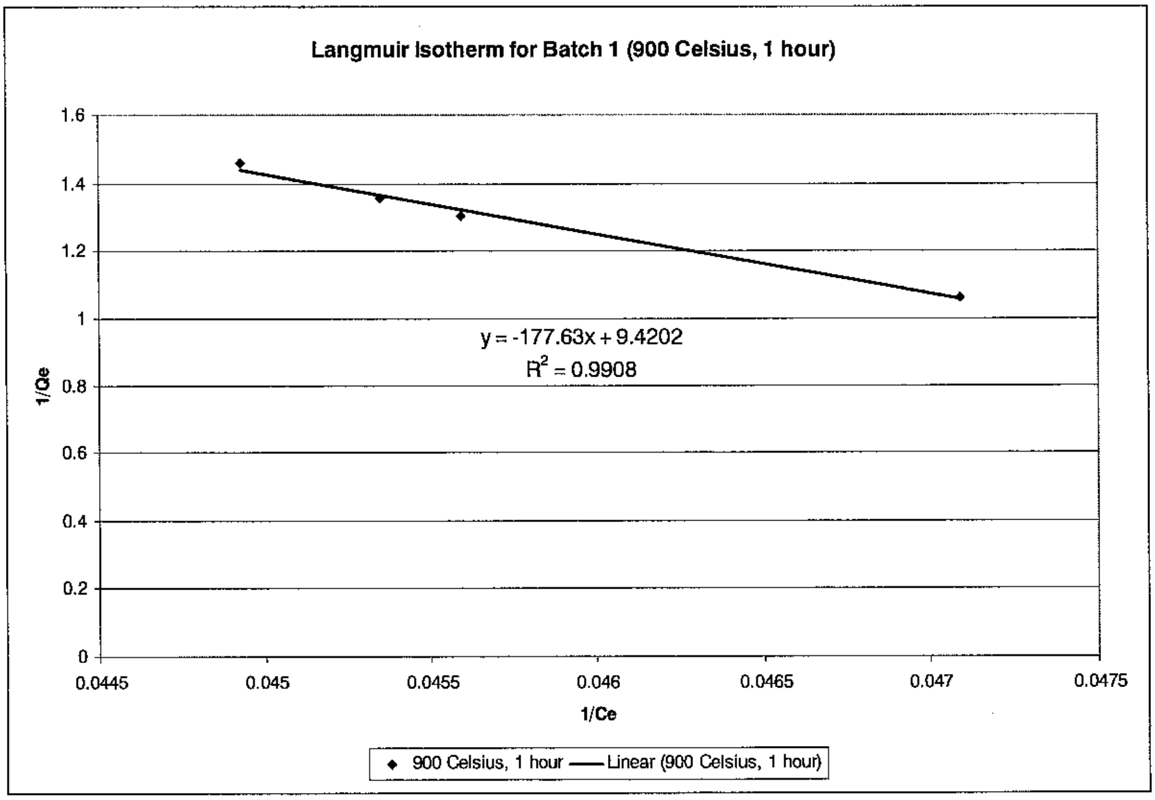

Figure 4.3: Langmuir Isotherm for Batch 1 (900 °C, 1 Hour)

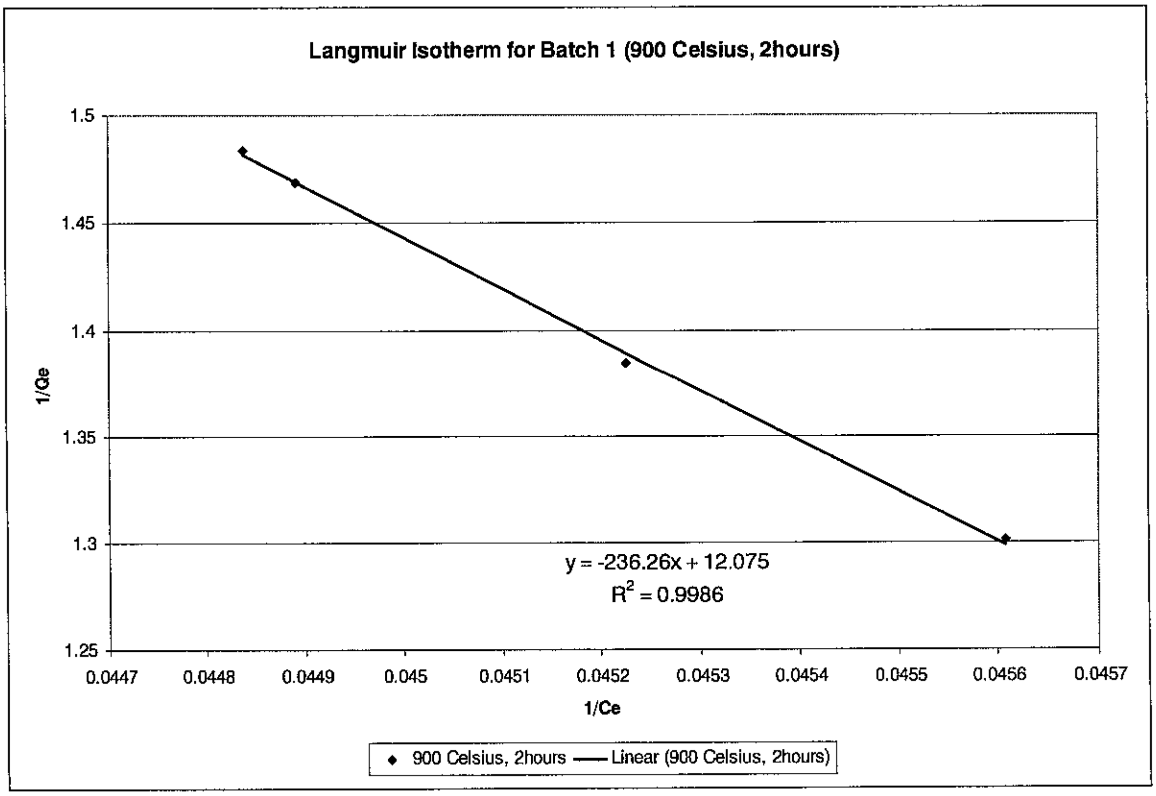

Figure 4.4: Langmuir Isotherm for Batch 1 (900 °C, 2 Hours)

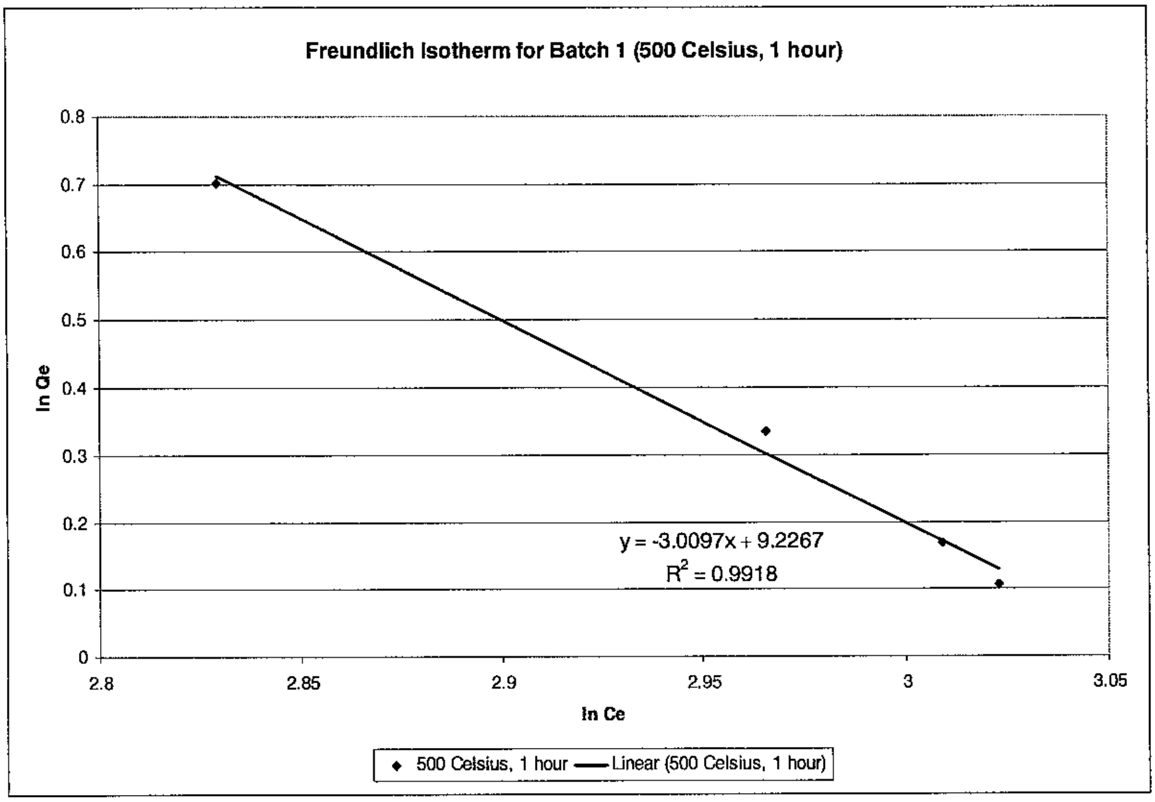

Figure 4.5: Freundlich Isotherm for Batch 1 (500 °C, 1 Hour)

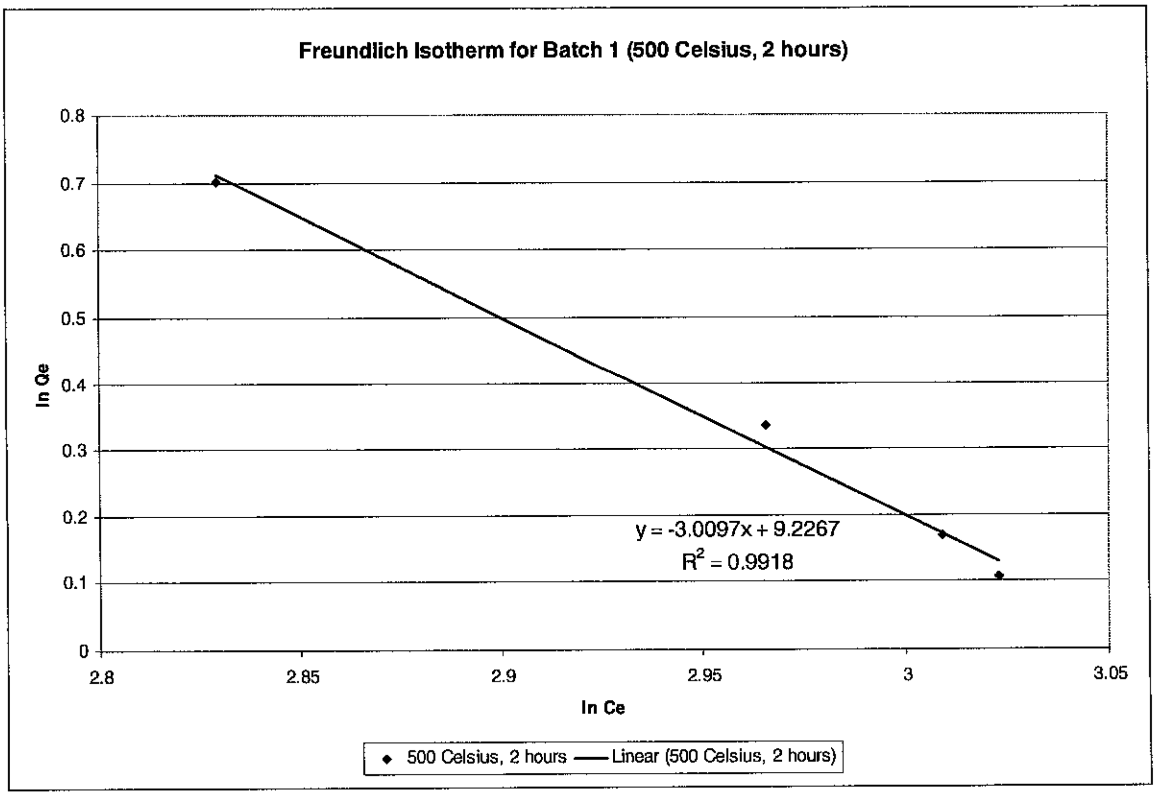

Figure 4.6: Freundlich Isotherm for Batch 1 (500 °C, 2 Hours)

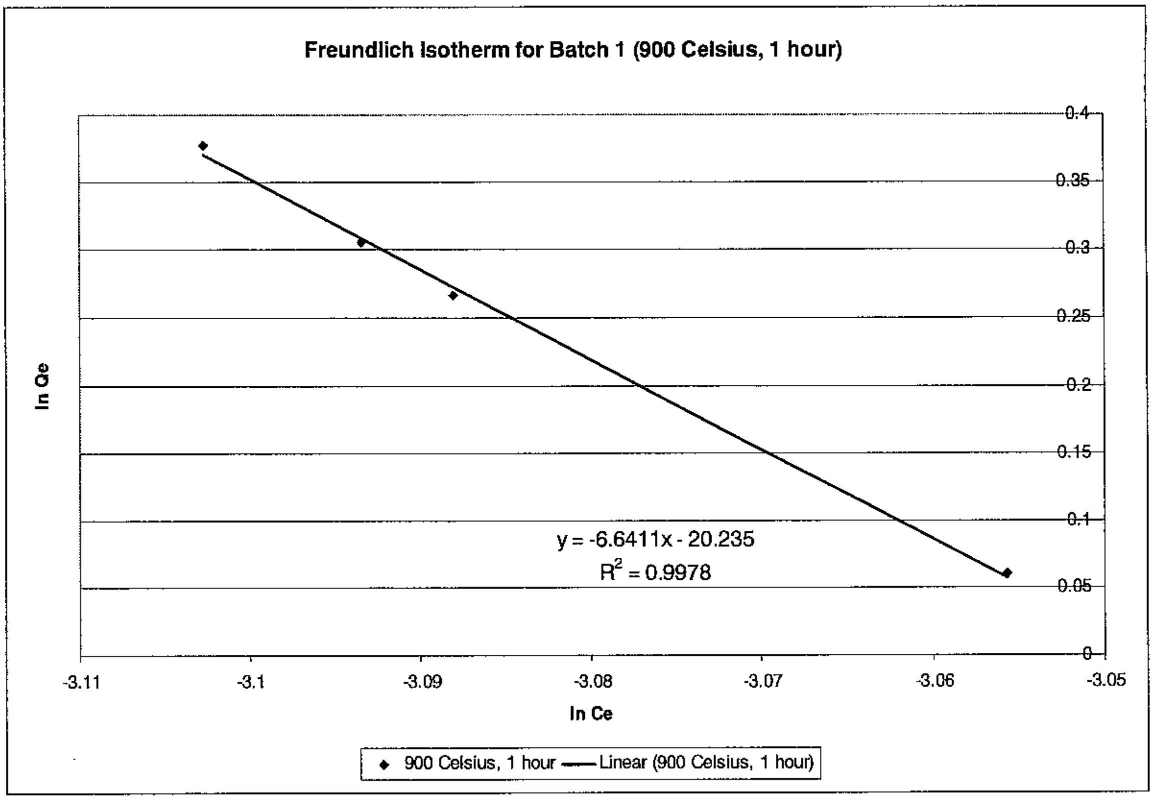

Figure 4.7: Freundlich Isotherm for Batch 1 (900 °C, 1 Hour)

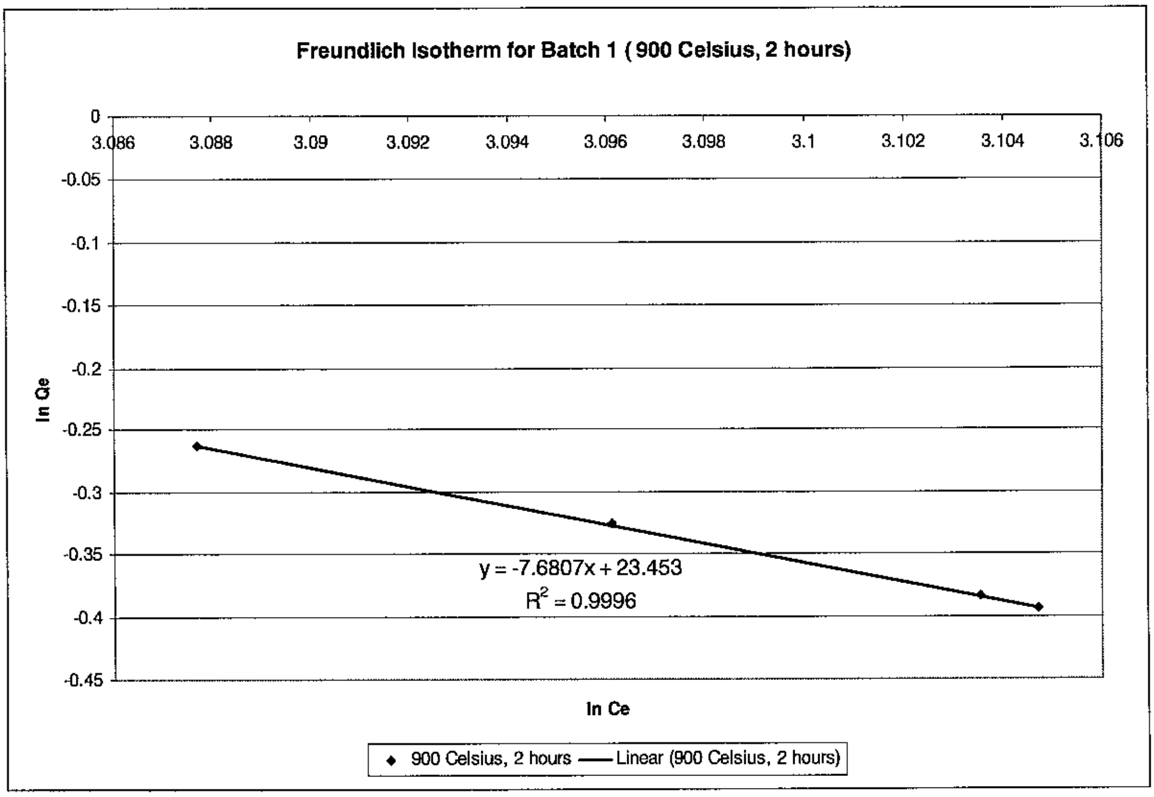

Figure 4.8: Freundlich Isotherm for Batch 1 (900 °C, 2 Hours)

4.2 EFFECT OF HNO_3 CONCENTRATION AND CARBONIZED TEMPERATURE AND TIME

4.2.1 500 °C, 1 Hour vs. 900 °C, 1 Hour

Adsorption performance differs from nitric acid concentration and also temperature and time of carbonization. Figure 4.9 shows the comparison of carbonized samples with temperature between 500 °C and 900 °C at 1 hour in Zn^{2+} uptake. Overall, 500 °C carbonized sample shows better adsorption capability as compared to 900 °C carbonized sample. As for 500 °C carbonized sample managed to adsorb Zn^{2+} at the range of 4 – 8 ppm but 900 °C carbonized sample covers lower Zn^{2+} uptake region, from 2 – 3 ppm.

According to the results obtained, Zn^{2+} uptake decreases at higher nitric acid concentration for 500 °C carbonized sample. In contrast, Zn^{2+} uptake increases at higher nitric acid concentration for 900 °C carbonized sample.

Zn^{2+} uptake is at the peak at the lower nitric acid concentration during acid treatment (0.1 M) for 500 °C carbonized sample. The uptake reads at 7.958 ppm of Zn^{2+}.

This case does not apply in 900 °C carbonized sample. Acid concentration at 0.1 M shows the lowest Zn^{2+} uptake which is 2.0481 ppm. At 900 °C carbonized sample with 14.4 M nitric acid concentration adsorbed at the higher Zn^{2+} concentration which is 3.765 ppm.

Generally, 500 °C, 1 hour carbonized sample is better than 900 °C, 1 hour carbonized sample. It is more favorable to optimize the nitric acid concentration at 1.0 M for 500 °C, 1 hour as it shows high Zn^{2+} uptake. Even though, 0.1 M nitric acid of 500 °C, 1 hour carbonized sample shows at high Zn^{2+} uptake but, too little acid for chemical treatment (acid treatment) is insufficient because it is not enough to create some hydrophilic character which can be used to advantage in the adsorption as its surface indicates nonpolar and hydrophobic character. [11] Nitric acid helps because it contains nitrogen and oxygen atoms with lone pairs of electrons to bind metal ions through coordinate bonds. Besides that, nitric acid also acts as strong acidic ion exchanger with metal ions from solutions. In addition, more acidic surface functional groups of HNO_3 oxidized fibers to provide spaces for adsorption. In carbon adsorption, more H^+ dissociations are preferred and with acid treatment, silica content in rice husk can be increased as shown in Table 2.3. Therefore, it is more favorable to choose at higher nitric acid concentration for acid treatment.[12]

In fact, too excessive HNO_3 (14.4 M) concentration does not uptake Zn^{2+} at high values, because it is too acidic which will destroy the functional group such as silica, hemicellulose, etc. or porosity structure in rice husk. Therefore, 14.4 M HNO_3 will perform badly in Zn^{2+} uptake. Detailed discussion on adsorbent choice is discussed in section 4.2.5.

4.2.2 500 °C, 2 Hours vs. 900 °C, 2 Hours

Figure 4.10 shows the comparison of carbonized samples with temperature between 500 °C and 900 °C at 2 hours in Zn^{2+} uptake. Overall, similar to 4.3.1, 500 °C carbonized samples show better adsorption capability than 900 °C carbonized sample. Results in this section gives almost reliable results as it agrees with theory found.

As mentioned in 4.2.1, at low nitric acid concentration does not accelerate Zn^{2+} uptake. Results show that for both 500 °C and 900 °C carbonized samples at 1 M nitric acid concentration adsorbed Zn^{2+} more than at lower nitric acid concentration. Zn^{2+} uptake for 1 M acid treated 500 °C carbonized sample is 5.5936 ppm and at 900 °C carbonized sample is 2.8881 ppm. Overall, it is favourable to choose 500 °C, 2 hours carbonized sample with 1 M nitric acid concentration treatment.

4.2.3 500 °C, 1 Hour vs. 500 °C, 2 Hours

According to Figure 4.11, 0.5 M for both 500 °C, 1 hour and 500 °C, 2 hours carbonized samples adsorbed at almost the same Zn^{2+} ions concentration which is from region of 4.7355 to 4.8329 ppm. These Zn^{2+} uptake values are comparatively low if compared with 1 M of nitric acid treated 500 °C, 1 hour and 2 hours carbonized samples adsorbed 7.7575 and 5.5936 ppm, respectively. Surface area of rice husk can increase as much as 10-fold during nitric acid oxidation or also known as acid treatment. The increased in acidic surface functional groups of nitric acid oxidized fibers reported above must be due to an increase in surface area. In addition, the surface area is expected to increase with oxidation time. [10]

Overall, 500 °C at any hours of carbonization shows better Zn^{2+} adsorption at 1 M nitric acid treated samples than 0.5 M nitric acid treated samples. Based on these results, it is proven that higher acid concentration sample for acid treatment shows higher acid adsorption compared with lower acid concentration treatment. This is because at low acid concentration, less hydrophilic character is created in adsorbent. Hydrophilic character can be used as an advantage in adsorption. In addition, pore development of mesopores or micropores by nitric acid activation reactions is governed by the diffusivity and reactivity of the activation agents and to produce reactive sites on the adsorbent. With this knowledge acquired, activation conditions and to deduce methods for developing many pores in activated carbons can be decided. [13]

By referring to Figure 4.11 again, there is an intersection point for 500 °C, 1 hour and 500 °C, 2 hours carbonized samples at approximately 6.4 M nitric acid. This may result that at 6.4 M nitric acid treated samples may performed at high Zn^{2+} uptake for both 500 °C, 1hour and 2 hours carbonized samples. The Zn^{2+} uptake reads approximately 6.6 ppm and it falls in high region of Zn^{2+} uptake. This part of observation is proposed for future work for rice husk preparation for an optimum Zn^{2+} uptake.

In addition, oxidation time or also known as acid treatment effect on adsorption capacity is required to be studied in future work.

4.2.4 900 °C, 1 Hour vs. 900 °C, 2 Hours

Generally, 900 °C carbonized samples were tested to prove that Zn^{2+} uptake performance is low and it is unsuitable for Zn^{2+} adsorption (Figure 4.12). This case can be seen that at 900 °C, 1 hour and 2 hours show low Zn^{2+} uptake. This may due to the fact that too high temperature which destroys the porosity structure of rice husk and hence will reduce the adsorption capability.

Meanwhile, it is seen that at 900 °C, 1 hour carbonized sample shows better Zn^{2+} uptake at 0.5 M nitric acid treated than that of 1.0 M nitric acid treated. At 900 °C, 1 hour carbonized sample, 0.5 M nitric acid treated ones was able to adsorb 3.0661 ppm Zn^{2+} but 2.7420 ppm Zn^{2+} only for 1.0 M nitric acid treated samples.

As compared between 900 °C, 1 hour and 900 °C, 2hours, it is more suitable to choose 900 °C, 1 hour as it shows better overall adsorption capability than 900 °C, 2 hours. Treated samples of 900 °C, 1 hour at 0.5 M nitric acid are better than at 1.0 M nitric acid treated samples.

4.2.5 Choice of Adsorbate and Adsorbent

Adsorbate used in this experiment was Zn^{2+} in $Zn(NO_3)_2.4H_2O$ solution. The concentration used for Zn^{2+} was 25 ppm. The concentration for Zn^{2+} in this experiment is favorable at lower concentration. This is because the adsorbate could occupy the active sites on the carbon surface sufficiently. But with the increase in adsorbate concentration, the number of active adsorption sites is not enough to accommodate adsorbate ions. In addition, the limit of pore size dimension and the electrostatic repulsion between negative charge of adsorbate ions results in the decrease of adsorption percentage. [14] Even at commercial Zn^{2+} concentration ranges from 25 – 460 mg/L, [4] it is suitable and viable to choose lower Zn^{2+} concentration in this laboratory scale experiment.

The rest of the experiment used 500 °C, 1 hour at 1.0 M HNO_3 treated samples with the rice husk particle size of 0.500 mm. Based on Figure 4.13, 500 °C, 1 hour carbonized sample is better than 900 °C, 1 hour carbonized sample in Zn^{2+} uptake with 1.0 M HNO_3 concentration. Figure 4.13 shows a decrement in Zn^{2+} uptake at higher carbonized temperature. That is why, 500 °C, 1 hour at 1.0 M HNO_3 treated samples are widely used for all batches. Interestingly, rice husk as activated carbon is known to have a heterogeneous physical and chemical structure. It is characterized by the existence of micropores, mesopores and macropores of different sizes. [11] On the other hand, silica percentage that present in rice husk would be higher (~ 74.0 %) after it is activated with nitric acid which silica helps in adsorption performance.

The pH of this experiment is maintained at 5 and the effect of pH is not tested here. With reference, at higher pH values, an important decrease of the adsorption capacity was observed likely due to the increase of the concentration of the ionized organic form which is adsorbed to a lower extent because of its higher solubility in water. On the other hand, at very low pH, higher solubility of metal occurred.

Both anions and cations may be removed from waters by adsorption process onto activated carbon (rice husk). The most preferred ion in carbon adsorption is reported to be H^+. Hence, it is not surprising that pH heavily influences the adsorption process because low pH will provide a high number of the preferred H^+ ion which may take the space of other ions on potential adsorption sites. [10]

Besides conducting sorption batch of studying particle sizes effect, 0.500 mm rice husk size was used throughout the sorption batches. It is recommended to use 0.500 mm of rice husk size for adsorption experiment because of its small size which contribute to larger number surface area of adsorption size in rice husk than 1.000 mm or 2.000 mm rice husks. As compared to 0.125 mm and 0.500 mm, it is clearly seen that larger number surface area for 0.125 mm rice husk size is higher than 0.500 mm. In terms of costs spent for using more energy to grind the rice husks into 0.125 mm, it is not suitable to use 0.125 mm although in theory, it gives better adsorption capability. 1.000 mm and 2.000 mm of rice husks are not favorable for the choice of adsorbent particle size because these sizes will have smaller number surface area for Zn^{2+} adsorption, though grinding energy cost is saved.

It is proposed that engineering economic analysis is carried out in future work of this experiment.

Table 4.2: AAS Data on Effect of HNO_3 Concentration and Carbonized Temperature and Time

25 ml Zn(II) Uptake	Carbonization temperature & time		HNO_3 concentration; 0.1g rice husk; 0.500 mm size			
			150 rpm, 2 hours contact			
			0.1 M	0.5 M	1.0 M	14.4 M
	500 °C	1hr	7.9580	4.8329	7.7575	4.2671
		2hrs	4.4507	4.7355	5.5936	8.0667
	900 °C	1hr	2.0481	3.0661	2.7420	3.7650
		2hrs	2.6970	2.7233	2.8881	3.0736

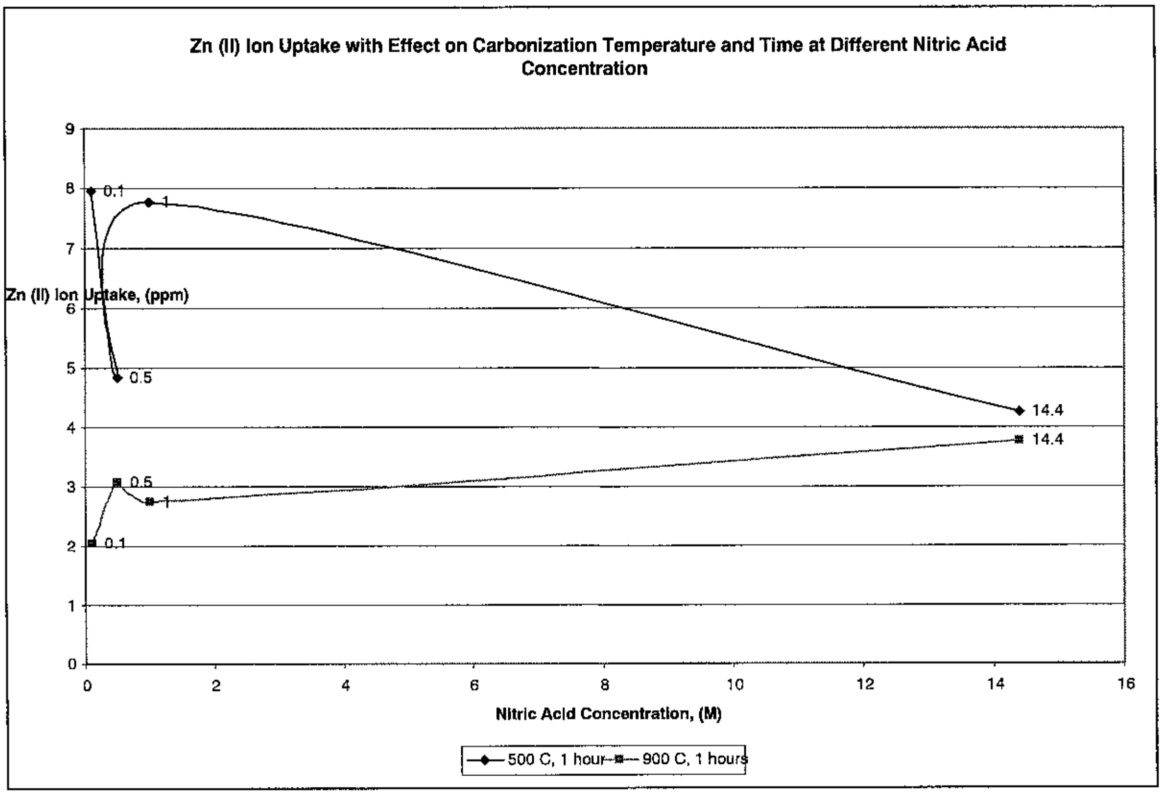

Figure 4.9: Comparison of Zn^{2+} Uptake at 500 °C and 900 °C (1 hour)

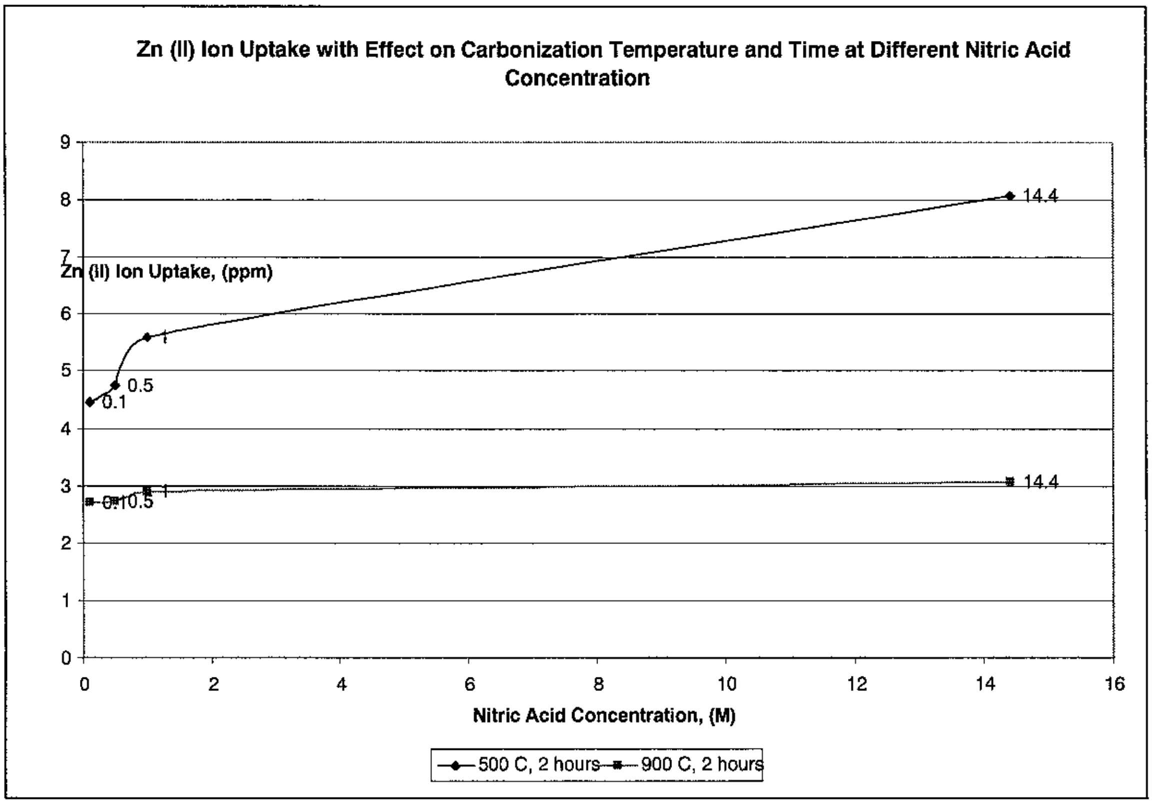

Figure 4.10: Comparison of Zn^{2+} Uptake at 500 °C and 900 °C (2 hours)

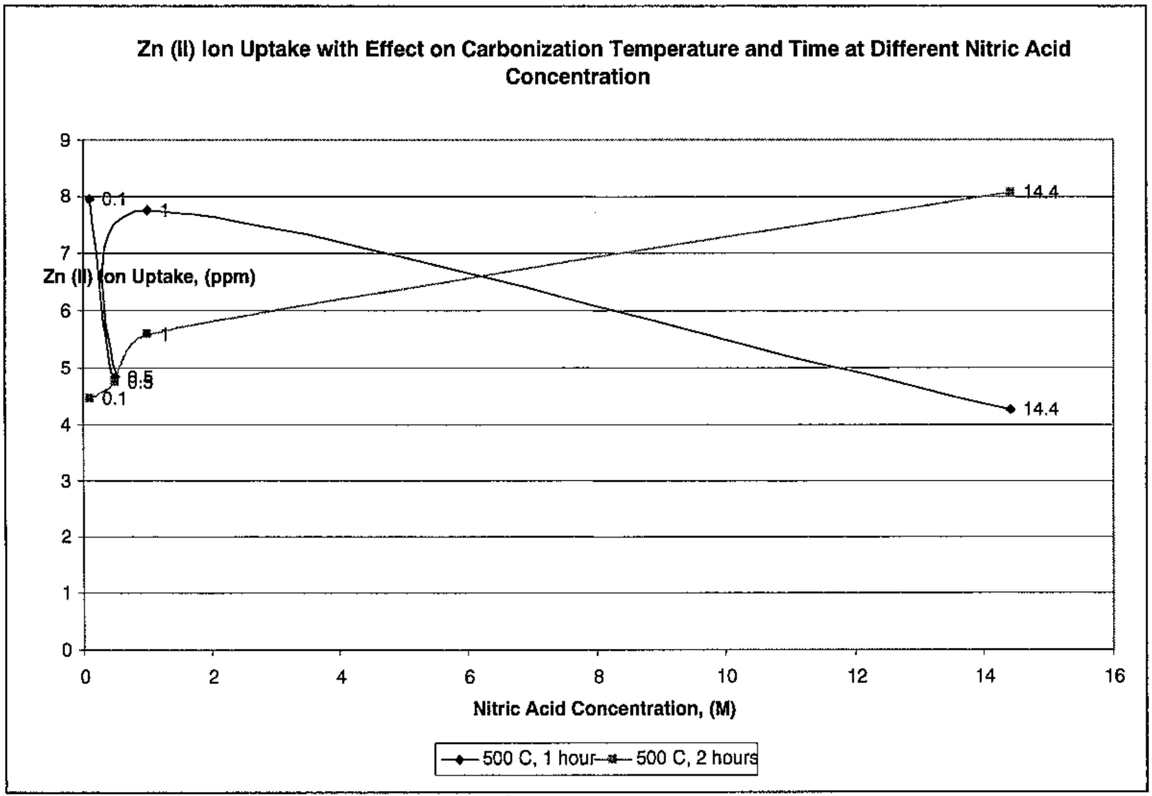

Figure 4.11: Comparison of Zn^{2+} Uptake at 500 °C at both 1 and 2 Hours

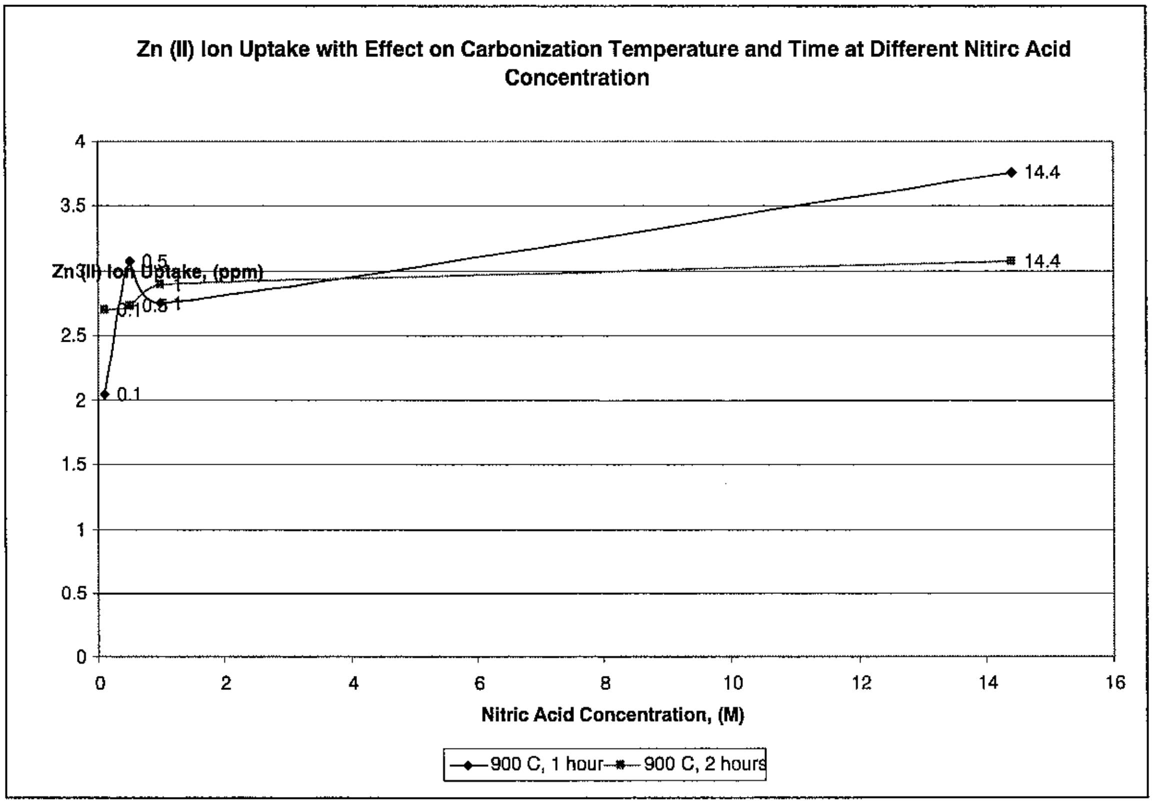

Figure 4.12: Comparison of Zn^{2+} Uptake at 900 °C at both 1 and 2 Hours

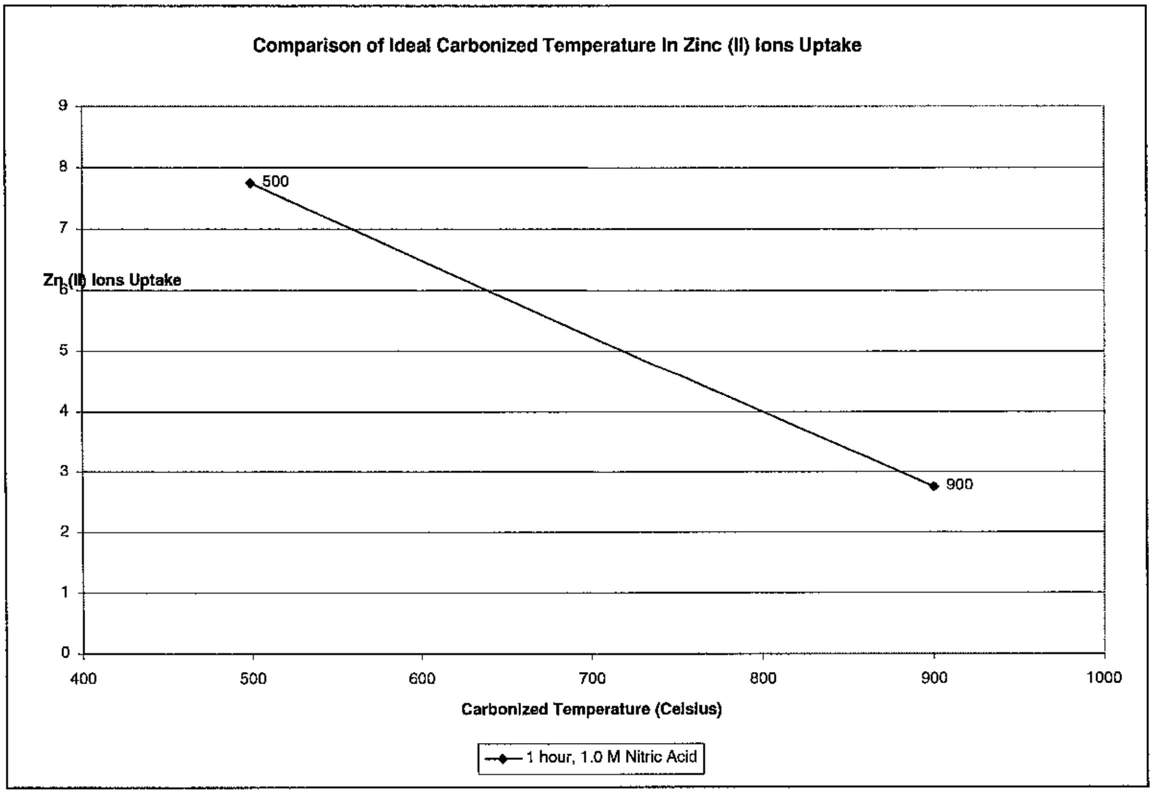

Figure 4.13: Choice of Adsorbent

4.3 EFFECT OF RICE HUSK PARTICLE SIZES

Rice husks with the sizes of 0.125 mm, 0.500 mm, 1.000 mm and 2.000 mm were used to investigate the effect of rice husk particle sizes and adsorption of Zn^{2+}. From Figure 4.14, and data in Table 4.3, 0.500 mm rice husk adsorbed higher Zn^{2+} than 0.125 mm and also 1.000 mm. According to theory, 0.125 mm should give better sorption than 0.500 mm rice husk but, the results obtained did not show much significance as compared to bigger particles sizes than 0.125 mm. The differences of Zn^{2+} uptake for 0.125 mm with 0.500 mm and 0.125 mm with 1.000 mm are 0.0392 ppm and 0.2155 ppm respectively. It is more significant in Zn^{2+} adsorption as compared with 0.125 mm sample with 1.000 mm sample. Meanwhile, the difference in Zn^{2+} uptake for 0.500 mm with 1.000 mm is 0.2547 ppm. This shows higher adsorption in comparison with 0.125 mm with 1.000 mm. Therefore, it is suitable to choose 0.500 mm rice husk for the sorption experiment in terms of adsorption capability and also in terms of grinding energy savings.

Theoretically, 2.000 mm particle size does not give the highest Zn^{2+} uptake because of small surface area. From the experiment conducted, 2.000 mm particle size shows the highest Zn^{2+} uptake compared to other sizes. In fact, this may regard as an error obtained. In future work, a detailed adsorption experiment should be analyzed with 0.500 mm and 2.000 mm rice husk size to confirm with the adsorption theory available. Research stated that it is important to stress that larger particles with spherical shapes, in general, present higher external mass transfer than smaller particles. In this case, higher metal adsorption from these particles is attracted to mass transport inside the sorbent particles. [15] This can be clearly seen that 2.000 mm rice husk has approximately spherical shape but though it considers more towards oval shape which is shown in Figure 4.15. On the other hand, when the main processes of metal adsorption into solid adsorbents are those based on adsorption on the particle surface, higher metal adsorption is verified on small particles.

Table 4.3: AAS Data on Effect of Rice Husk Particle Sizes

25 ml Zn(II) Uptake	150 rpm, 2 hours contact time	Rice husks = 0.1g, HNO$_3$ = 1M			
		Carbonization time: 500 °C, 1 hour			
		0.125 mm	0.500 mm	1.000 mm	2.000 mm
		5.8821	5.9214	5.6666	7.3397

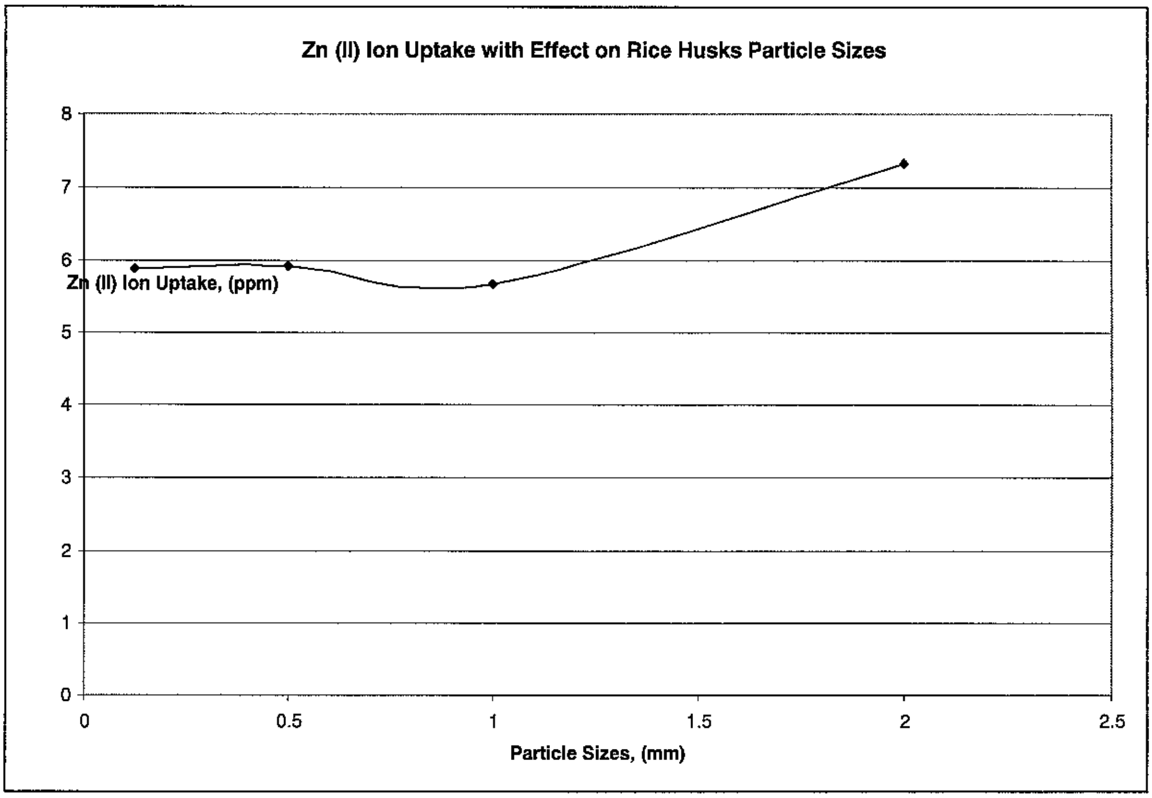

Figure 4.14: Graph of Zn^{2+} Uptake with Effect of Rice Husk Particle Sizes

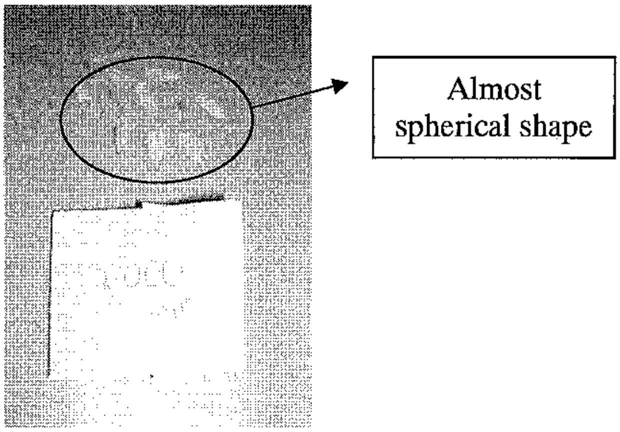

Figure 4.15: Structure of 2.000 mm Rice Husks

4.4 EFFECT OF RICE HUSK LOADING AT DIFFERENT PARTICLE SIZES OF RICE HUSK

According to Figure 4.16, and Table 4.4, at 0.1 g of rice husks that contained in the conical flasks during adsorption, Zn^{2+} uptake for 0.125 mm rice husk size is lower than 2.000 mm rice husk size. From the results obtained, 2.000 mm rice husk size at 0.1 g rice husk loading adsorbed more Zn^{2+} than that of 0.125 mm rice husk.

This is not the case when loading was 1.0 g of rice husk. 0.125 mm rice husk size shows more Zn^{2+} uptake than 2.000 mm rice husk size. The Zn^{2+} uptake of 0.125 mm and 2.000 mm at 0.1 g rice husk loading are 5.3369 ppm and 8.6887 ppm respectively. At 1.0 g rice husk loading, Zn^{2+} uptake of 0.125 mm rice husk is greater than 2.000 mm rice husk by 4.1818 ppm. Based on theory [16], results matched at 1.0 g loading for particle size comparison of 0.125 mm and 2.000 mm.

In contrast, by comparing rice husk loading of 0.1 g and 1.0 g at 0.125 mm rice husk, Zn^{2+} uptake is higher for 1.0 g rice husk loading than 0.1 g rice husk loading. These results do not agree with the theory available. This is due to as at higher loading, 'screen' effect can be produced from the dense outer layer of the cell, thereby, protecting the binding sites from metal. [16]

The results might be correct if assumption is made that all rice husk surface area adsorbed Zn^{2+} totally and also all rice husk were completely treated with HNO_3. If based on the assumption, it is true that more load of rice husk is required to adsorbed more

Zn^{2+} in $Zn(NO_3)_2$ solutions. In contrast, less loading will only be able to adsorbed little Zn^{2+}. In addition, the conical flasks used had big area for adsorption to occur. The conical flask used was 500 ml and the bottom size area is very large.

From Figure 4.16, there is an intersection point for both particles sizes tested. It can be seen that approximately 0.5 g of rice husk loading for both sizes is suitable for Zn^{2+} adsorption because the Zn^{2+} uptake was approximately 12 ppm and the region is higher compared to 0.1 g loading which ranges from 5 to 9 ppm. It is proposed that approximately 0.5 g of rice husk amount to be repeated in the future work.

Table 4.4: AAS Data on Effect of Rice Husk Loading

25 ml Zn(II) Uptake	150 rpm, 2 hours contact time	Carbonization: 500 °C, 1 hour, HNO_3: 1M; Finest = 0.125 mm; Coarse = 2.000 mm			
		0.1g rice husks		1.0g rice husks	
		0.125 mm	2.000 mm	0.125 mm	2.000 mm
		5.3369	8.6887	20.1250	15.9432

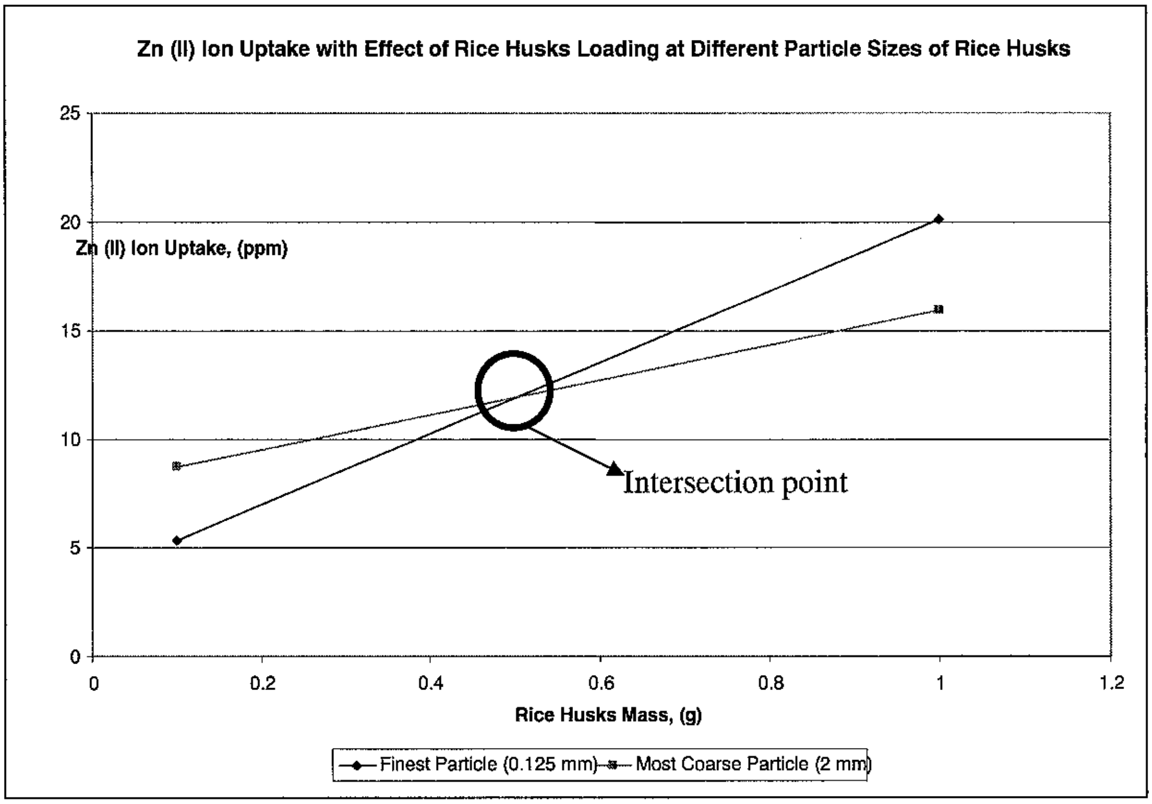

Figure 4.16: Graph of Zn^{2+} Uptake with Effect of Rice Husk Loading

4.5 EFFECT OF ADSORPTION CONTACT TIME AND SHAKER SPEED

All sorption batches were conducted in 2 hours contact time and 150 rpm shaker speed. Shaker speeds at 100, 150 and 200 rpm at 30, 60 and 120 minutes respectively were investigate on Zn^{2+} uptake. From Figure 4.17 and Table 4.5, it can be seen that higher shaker speed gives more Zn^{2+} uptake than lower shaker speed. At 200 rpm, Zn^{2+} uptake reached 10.8329 ppm. At 150 rpm, it is recorded 7.7575 ppm Zn^{2+} and at 100 rpm recorded 5.2671 ppm Zn^{2+} respectively.

The results agree with the theory [17]. In fact, adsorption reached equilibrium at 30th minute and stabilized thereafter. This batch tested is best applied if we have two or more types of different metal ions to be adsorbed. The results obtained will show which metal ion will adsorb faster to the adsorbent available. Other metal ions that can be tested are Pb^{2+}, Cu^{2+} and others. [17]

Table 4.5: AAS Data on Effect of Adsorption Contact Time and Shaker Speed

	Speed	Rice husks: 0.5g, HNO_3: 1M (500 °C, 1hr), Size = 0.500 mm		
25 ml Zn(II) Uptake		30 minutes	60 minutes	120 minutes
	100 rpm	5.2671	5.2671	5.2671
	150 rpm	7.7575	7.7575	7.7575
	200 rpm	10.8329	10.8329	10.8329

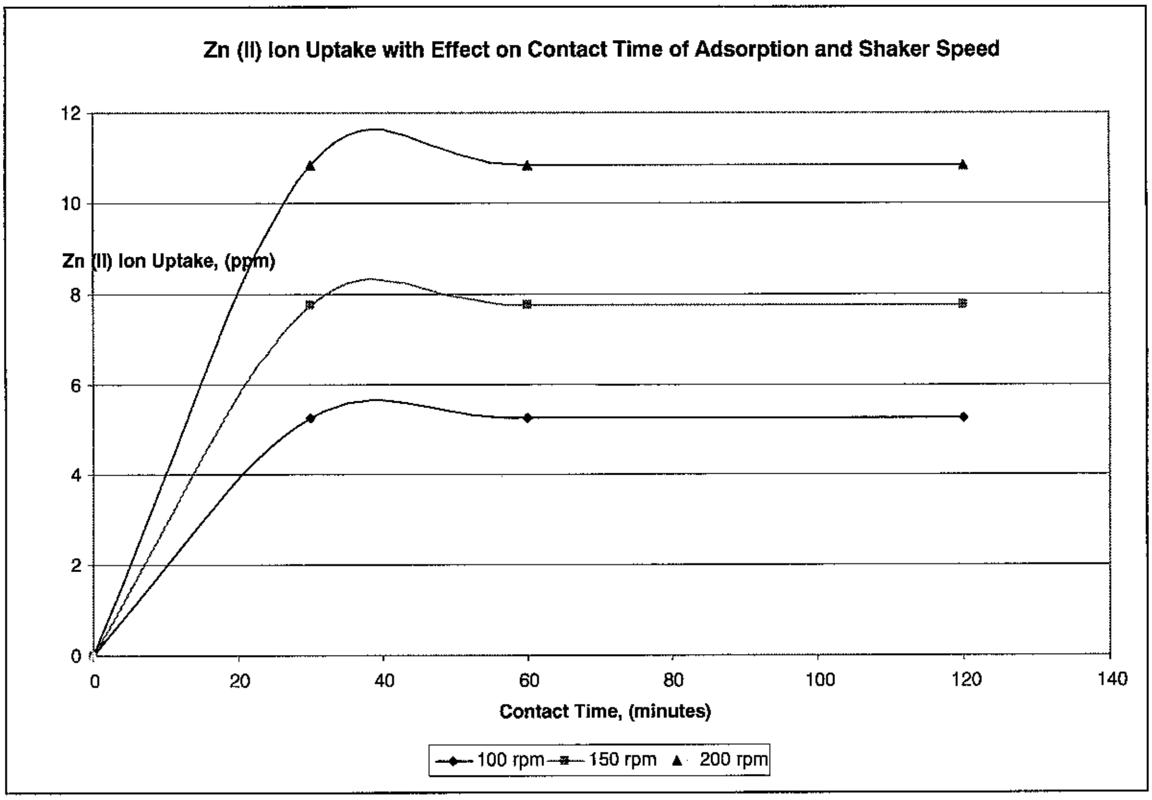

Figure 4.17: Graph of Zn^{2+} Uptake with Effect of Adsorption Contact Time and Shaker Speed

4.6 BET METHOD

The texture characteristics could be determined by the standard N_2 adsorption isotherms, followed by their analysis to evaluate the porous parameters. The BET method results were not achieved due to unavailability of the machine but, expected results are discussed. Plots were done from the BET procedures, results obtained would be the "monolayer equivalent surface area" which is the total pore volumes estimated from the volume of nitrogen adsorbed at P / P_0 and an average pore radius by assuming cylindrical pore dimensions with circular cross-section. [18]

In addition, the surface area of rice husk can be determined and calculated if experiment can be conducted. Classification of rice husk as adsorbent can be classified to micropore, mesopore and macropore. Each classification is tabulated in Table 4.6. [18]

Table 4.6: Classification of Rice Husk Porous Volume

Porous Volume	Surface Area (cm^3/g)
Micropore	0.20 – 1.10
Mesopore	0.04 – 0.90
Macropore	0.90 – 1.10

4.7 SCANNING ELECTRON MICROSCOPY (SEM)

SEM had been conducted to investigate the structures of rice husk after carbonization at 500 ^{0}C for 1 hour and adsorbed rice husk. As a reference, a SEM image is attached showing a raw rice husk was obtained from a literature review. [19]

By referring to Figure 4.18, which obtained from literature review, shows a raw rice husk before any chemical activation and carbonization were done. It is also seen that the raw rice husk has smooth surface. Interestingly, from result of experiment done, in Figure 4.19, it shows that the rice husk fibrous structure has opened up to its pore sizes and the pores are ready for adsorption to occur. Porous structure as shown has proven that rice husk is capable to adsorb metal ions at anytime after carbonization.

Besides that, another SEM image had been attached to show the structure of adsorbed rice husk. This image is shown clearly in Figure 4.20.

Energy Dispersive X-ray (EDX) analysis was done on both carbonized and adsorbed rice husks. It has been proven that after adsorption occurred, zinc element was found in the sample. There is no zinc element found on carbonized rice husk as it had not gone through adsorption process yet. EDX analysis is able to detect the zinc element as it detects from the element's electronegativity. The EDX analysis images are shown in Figure 4.21 and Figure 4.22. Zinc's electronegativity is approximately 1.60. [20]

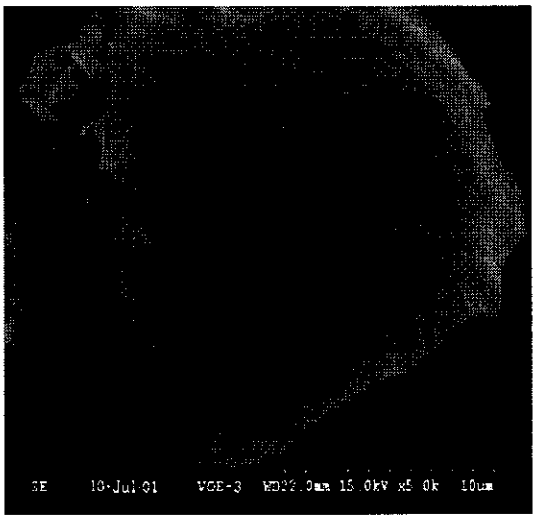

Figure 4.18: SEM Image of Raw Rice Husk

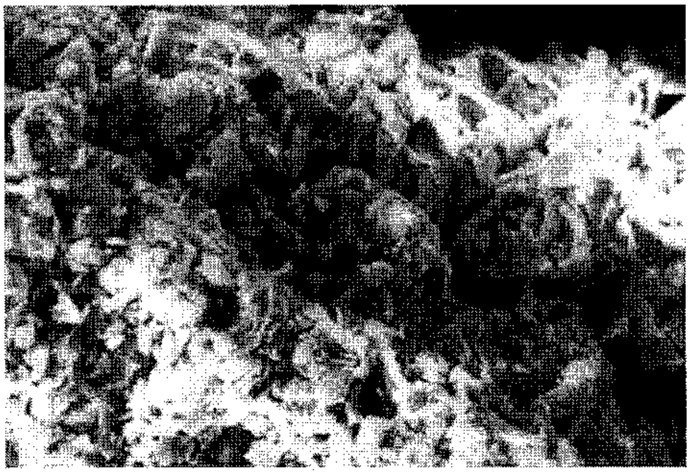

Figure 4.19: SEM Image of Carbonized Rice Husk

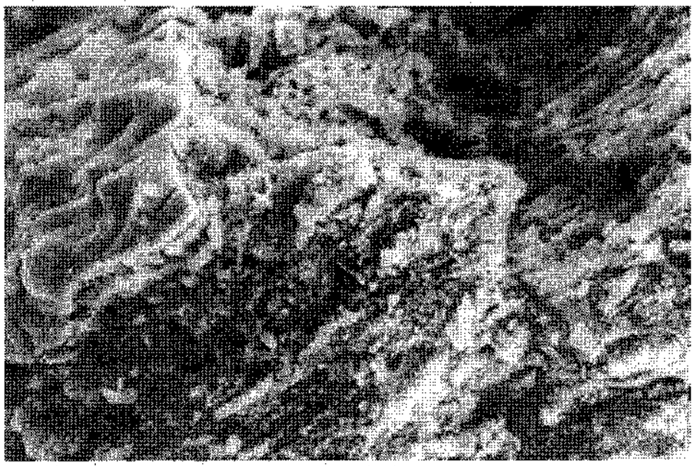

Figure 4.20: SEM Image of Adsorbed Rice Husk

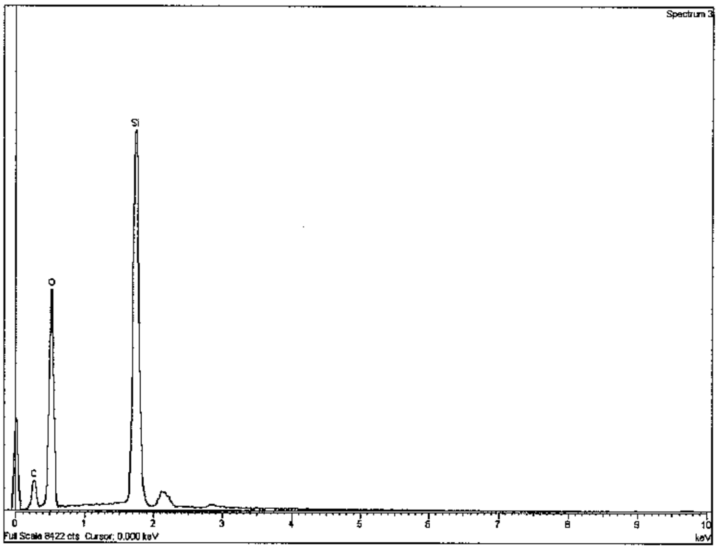

Figure 4.21: EDX Analysis on Carbonized Rice Husk

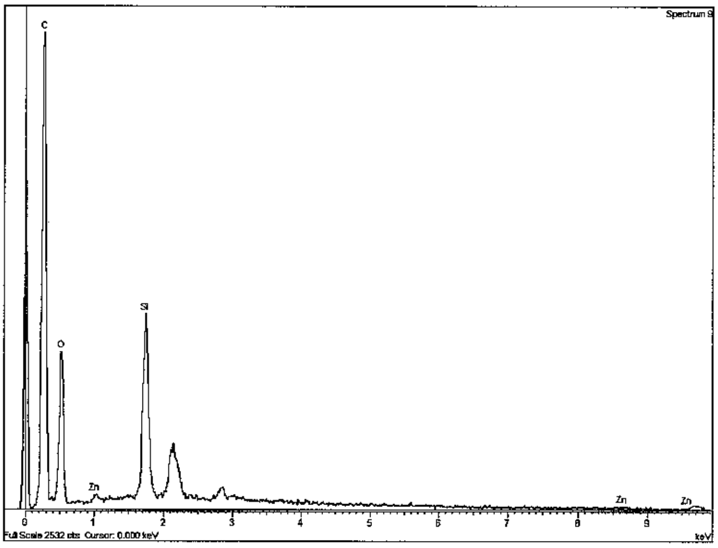

Figure 4.22: EDX Analysis on Adsorbed Rice Husk

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The potential use of activated carbon, prepared from rice husk digested with nitric acid HNO_3, was demonstrated in the removal of Zn^{2+} in zinc (II) nitrate $Zn(NO_3)_2$. Batch sorption experiments were performed to investigate the feasibility of a sorptive material system. Overall, rice husks can be used as adsorbent to eliminate metal ions that present in waste stream but, certain criteria are required to meet and for the betterment of the adsorption capability, recommendations and future work are required to be studied. However, the process of adsorption of Zn^{2+} onto rice husk is endothermic in nature. [21]

5.1.1 Effect of HNO_3 Concentration and Carbonized Temperature and Time

The amount uptaken was found to be a direct function of the concentration of HNO_3 acid at 1.0 M with carbonization temperature and time at 500 °C and 1 hour respectively as these characteristics of rice husk performed adsorption at best. At these characteristics of rice husk, Zn^{2+} uptake recorded 7.7575 ppm.

Optimum nitric acid concentration must be used for rice husks digestion in order to create some hydrophilic character in adsorbent which can be used to advantage in the adsorption.

5.1.2 Effect of Rice Husks Particle Sizes

The digested rice husks has high sorption capacity at particle size of 0.500 mm. Besides being able to adsorb 5.9214 ppm at larger number of surface area, this particle size saves more grinding energy costs in engineering economic analysis as compared to 0.125 mm size.

5.1.3 Effect of Rice Husks Loading

The higher the mass loading of rice husk, the greater adsorption capability in Zn^{2+} uptake. Results had shown that larger adsorption at 1.0 g than 0.1 g loading rice husks.

5.1.4 Effect of Adsorption Contact Time and Shaker Speed

The adsorption of Zn^{2+} on digested rice husk reached equilibrium at 30-minute. It is clearly seen that 200 rpm shows higher adsorption capability than at 100 and 150 rpm shaker speed.

5.1.5 Isotherms

Freundlich isotherm has the best fit in this experiment as it has the highest correlation coefficient.

5.1.6 BET Method

BET analysis can be done to determine surface area and pore volume with respect to classification of micropore, mesopore and macropore volumes on the rice husks.

5.1.7 SEM and EDX Analysis

Raw rice husk which has smooth surface area has been digested with nitric acid and carbonization at high temperature to 'open' up the porous structure and ready for adsorption to occur. The 'opened' structure has 'closed' after adsorption has occurred. EDX analysis showed that zinc element present at rice husk after adsorption occurred.

5.2 RECOMMENDATIONS

Listed below are discussions on recommendations suggested for the betterment of the sample preparation activity.

1. Wash rice husks in siever for easier water removal from rice husks.
2. Frequently overturn the rice husks for cleaning when heating in the oven at 35 °C to obtain complete drying.
3. Rice husks are required to grind and sieve at a large sum to avoid major loss due to pH level constant and carbonization activities.
4. Use pump filter to separate rice husks from any solutions especially on section to maintain pH level.
5. Reflux with 0.1 M of NaOH standard solution to remove humic products formed during acid treatment.
6. Use thermal gloves when handling furnace. Wait until the furnace temperature reaches at desired temperature and stabilize to count for the first period of required heating period. Only remove out samples from furnace after the furnace temperature has reached to room temperature. Careless handling of furnace will cause fire flame to gush out from the furnace.

Listed below are discussions on recommendations suggested for the betterment of the adsorption calibration activity.

1. Prepare standard solutions accurately for Atomic Absorption Spectrophotometer (AAS) calibration and preferably avoid dilution.
2. Conduct more trials on AAS calibration to get optimum results on Zn^{2+} uptake.

5.2.1 Future Work

Listed below are discussions on recommendations suggested for the betterment of the adsorption calibration activity.

1. Prepare standard solutions accurately for Atomic Absorption Spectrophotometer (AAS) calibration and preferably avoid dilution.
2. Conduct more trials on AAS calibration to get optimum results on Zn^{2+} uptake.
3. Do acid treatment on rice husk at concentration of 6.4 ppm and carbonization of 500 °C, 1 hour.
4. Study of effect of oxidation time (Acid treatment)
5. Focus on 0.125 mm and 2.000 mm rice husk particle sizes in adsorption performance.
6. Repeat the experiment with 0.5 g rice husk loading for adsorption process.
7. Send rice husk for FTIR or UV Visible for functional group detection.
8. Consider in doing mixed agriculture wastes as adsorbent.
9. Compare the usage of acid treatment between nitric acid and sulfuric acid.
10. In order to plot a better isotherm, it is required to create an experiment involving effect of metal ion concentration in adsorption performance as isotherm is important in designing sorption systems. Repetitions of experiments will give better results.
11. Although the presence of surface functional groups on carbonaceous materials have been long investigated, but the debate is ongoing to determine which activation process or surface treatments will produce the best functional groups suitable for specific applications. Manufacturers of activated carbon fibres could provide researchers with information concerning the nature and properties of functional groups, which would enable their products to be more extensively used if the details given are helpful.
12. Chemical oxidation of activated carbon fibre can be performed using a number of oxidising agents including sulphuric acid, phosphoric acid, hydrogen peroxide, sodium hypochlorite, potassium permanganate, air and ozone.

13. Use of wastewater instead of ionic solution. Metal sorption experiments were performed using distilled water containing only ionic species. However these experiments are not completely realistic since water in the real environment may also contain organic impurities.
14. Engineering economic analysis is done to calculate the feasibility of the experiment.

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