Removal of Amine Solutions from Artificial Wastewater Using Adsorbents Developed from Rice Husk

By

Siti Khadijah Binti Mohammed Yusof

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

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
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Approved by,

(AP Dr. Hilmi Bin Mukhtar)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 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.

SITI KHADIJAH BINTI MOHAMMED YUSOF

ABBREVIATIONS AND NOMENCLATURES

AC	Activated carbon
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DEA	Di-ethanolamine
FTIR	Fourier Transform Infrared
FYP	Final year project
GAC	Granular activated carbon
GPP	Gas processing plant
H_2SO_4	Sulphuric acid
HPLC	High-performance liquid chromatography
M	Molarity (mol/liter)
MDEA	Methyl di-ethanol amine
MEA	Methyl ethanol amine
NaOH	Sodium hydroxide
NOM	Natural Organic Matter
PAC	Powdered activated carbon
ppm	Parts per million
RH	Rice husk
RHA	Rice husk ash
RND	Research and Development
RND	Research and development
RRH	Raw rice husk
TDS	Total dissolved solids

TEA	Tri-ethanol amine
TOC	Total Organic Carbon
TSS	Total suspended solid
UV- Vis	Ultra Violet Visual
VPFESEM	Variable Pressure Field Emission Scanning Electron Microscope
$ZnCl_2$	Zinc chloride

ABSTRACT

The product after separating rice grains from the bran; rice husk, has high potential to be developed as adsorbent to remove amine wastewater from gas processing plant. Amine contributes to high chemical oxygen demand (COD) content. Raw rice husk needs to be treated in order to enhance the absorbance capacity. The rationale of the treatment process is to create and improve the active sites on the adsorbent. Three types of treatment are applied; by physical, chemical or activating agent. In the pretreatment phase, raw rice husk is washed using distilled water and dried at 100°C for 24 hours to remove moisture. Physicochemical treatment is selected for developing the adsorbent. First, rice husk are treated with different solution; sodium hydroxide (NaOH) at 0.5M, zinc chloride ($ZnCl_2$) at 0.01 M and sulphuric acid (H_2SO_4) at 1M. They are soaked and stirred for 3 hours. Then, they are rinsed through distilled water till clean. In the second step, they are burnt at temperature of 250 and 500°C for different hours. Characterization of adsorbent is made after the treatment phase using Fourier transform infrared (FTIR) and variable pressure field emission scanning electron microscope (VPFESEM). Lastly, performances of developed adsorbents are tested using artificial wastewater of monoethanolamine (MEA) using continuous and batch process. Amine concentration after adsorption process is analyzed by high-performance liquid chromatography (HPLC) with retention time at 5.2 minute. From findings, vary treatment processes could enhance the active sites on RH. Thus, the ability of RH adsorbent to remove amine from industrial effluent is more effective.

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Siti Khadijah

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CHAPTER 1: INTRODUCTION

1. INTRODUCTION

Environmental pollution has reached a stage in which it must be seriously looked at. Among the various classes of pollution, water pollution has attracted various attentions of researchers and scientists around the world. The crisis of removing pollutants from effluent has increased with rapid industrialization activity (Ahmaruzzaman M., Gupta V.K., 2011).

Contaminants found in industrial effluent vary since industrial effluent is generated by many sources and regarding their purposes. They consist of organic material, pathogens, heavy metals, salt, ammonia, pesticides, pharmaceuticals, and endocrine disruptors. Some, such as pathogens and heavy metals, are detrimental in all treatment plant effluents because they are harmful to humans and the environment. Others, such as nitrates and phosphorus, can be harmful if the effluent is being discharged to receiving waters but advantageous if the effluent is going to be reused for agricultural irrigation. Thus, it is vitally important to comprehend that different uses of wastewater effluent will require different levels of contaminant elimination.

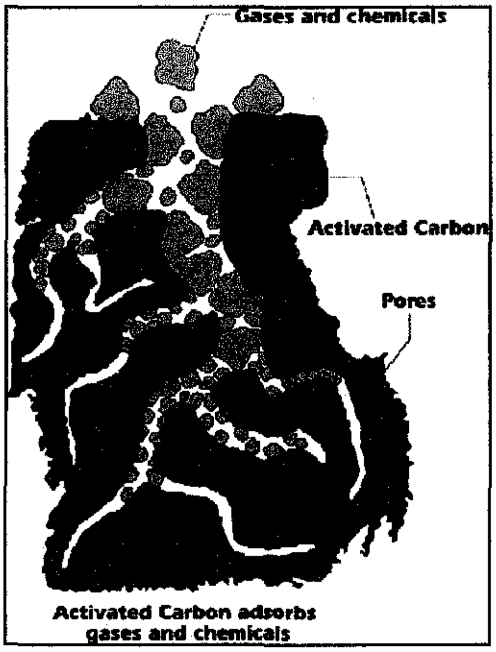
Activated carbon is a new alternative to remove contaminants from industrial effluent. As been mentioned by Pollard (1992), in previous decades, active carbons had been prepared from coconut shells, wood char, lignin, petroleum coke, bone-char, peat, sawdust, carbon black, rice hulls, sugar, peach pits, fish, fertilizer waste and waste rubber tire. There are two size classification for activated carbon; powdered activated carbon (PAC) and granular activated carbon (GAC). PAC has a diameter less than 0.074 mm while GAC has a diameter greater than 0.1mm. In this project, the developed activated carbon falls under GAC type.

1.1 Background of Study

There has been increasing concern in recent years over the discharge of contaminants into the aquatic environment (Hasar H., Cuci Y., 2000). Concentration of chemical oxygen demand (COD) in industrial effluent is generally contributed by the discharge of amine from industrial and domestic waste to sewer and drainage system. Regulation has enacted that concentration of COD in industrial effluent must be 50 and 100 ppm for standard A; discharged at upstream and B; discharged at downstream.

Amines are widely used in cleaning products as effective surfactants to kill microorganisms. On the other hand, in gas processing plant, amines are used in process of sweetening hydrogen sulphide and capturing carbon dioxide (Haugmo et al, 2009). Ethanolamines are used in wide areas. For instance, gas sweetening where they serve as lubricants and scouring agents. They also used in detergent and cleaner formulations which they are used to form various amine salts and pH controller. Part of that, ethanolamines are used in lot other industries as in concrete admixtures, flexible urethane foam catalyst, pharmaceuticals, personal care products, agricultural chemicals, photographic emulsions and more.

Adsorption is an alternative to remove contaminants from industrial effluent. Adsorption is known as the most promising option for treating all aromatic compounds from aqueous streams, due to extended surface area, high adsorption capacity and micro porous structure and special surface reactivity. Despite of the advantages, adsorption method is expensive as for the adsorbents and regeneration process. As to resolve the problem, cheaper and low cost alternative material is being used as adsorbents. The main objective of this project is to develop effective adsorbents from RH by modifying with thermal and chemical treatments for removal of amine from effluent.



According to Hamerlinck (1994)

> *Activated carbon is a crude form of graphite with a random or amorphous highly porous structure with a broad range of pore sizes, from visible cracks and crevices, to crevices of molecular dimensions.*

Figure 1.1: Granular activated carbon (GAC)

1.2 Problem statement

Industrial effluent as in from domestic effluent contains amine solutions. Amine existence contributes towards high COD content. As a result of high COD content, treating it using conventional activated sludge has aroused issue regarding slow time of treatment. This study will examine the performance new developed adsorbent from RH to separate various types of amine solutions from artificial effluent.

Oil and gas industry contains amine in its discharge system. This includes monoethanolamine (MEA), di-ethanolamine (DEA), methyl di-ethanolamine (MDEA) and tri-ethanolamine (TEA). It is used in the purification process of natural gas to remove impurities as in carbon dioxide and hydrogen sulphide.

Activated sludge is widely being used for effluent treatment at current. However, the issue of long time taken for treatment has been aroused. Researches prove this significantly due to high content of COD in effluent. By using an alternative way, a newly developed activated carbon from RH is being tested as adsorbent in effluent treatment. There are numbers of constituents contribute to high COD content. Amine is one of them. Thus, in this project, the newly developed adsorbent is targeted to remove amine contaminants from effluent. COD is the amount of oxygen required to stabilize organic matter determined by using a strong oxidant.

Ion exchange is an effective method in removing substances from water supplies. A range of anion exchangers have been explored for removal of natural organic matter (NOM), both as isolated from surface waters and after fractionation into four fractions based on hydrophobic and hydrophilic properties.

Amine is a toxic chemical and harmful to human health. Thus, the release of amine into wastewater must be controlled. Amine solutions commonly released from gas processing plants which included MEA, DEA, MDEA and TEA. As reported by Haugmo et al in 2009, DEA and MEA need 43 and 22% of COD for each of them. On the other hand, MDEA has very small of COD percentage. Activated carbon is agreed to be as the most consumable adsorbent in wastewater treatment by Bhatnagar. However, its application is restricted due to the high cost for adsorbents. Coherent to that, researchers have tried to develop new adsorbent using low cost material from agricultural waste. Fortunately, RH can be found easily. It can be treated in variety of ways to examine the best treatment will create RH a better adsorbent for adsorption of amines from wastewater.

1.3 Objectives and Scope of Study

1. To develop new adsorbent with low cost production with best efficiency in removing amine solutions from wastewater
2. To characterize each type of adsorbent after gone through various treatment

In this project, in order to develop adsorbents using RH, various treatments are applied onto raw rice husk. In all researches and investigations done, modified and treated rice husks were proven to be more efficient in absorbency compared to the raw rice husk (Ahmaruzzaman, 2011). Firstly, raw rice husk is cleaned by wash it thoroughly with distilled water and dried until the mass is at constant. This phase is called as pre-treatment phase. Secondly, RH will be modified using physical and chemical treatment. In physical treatment, RH is burnt at two different temperatures. This is to transform the surface of RH by increasing the surface area.

This research is to develop effective adsorbents from RH by modifying through thermal and chemical treatments for removal of amine from wastewater. As for the scope of study, raw rice husk first is cleaned by wash it with distilled water and dry it until the mass is constant. Three different treatments are applied to the prepared RH; first, by treating it thermally; second; by manipulating it with basic solution and lastly by treating it with organic solvent. RH is dried at 100°C for 24 hours. In thermal treatment, RH is burnt at two different temperatures. This is to transform the surface of RH by increasing the surface area. From chemical treatment by basic and organic solution, functional groups on RH is expected to be varied thus make the adsorption capacity is improved. In overall, all treatments are targeted to active the adsorption sites on RH. This project is to examine the condition which gives best for adsorption efficiency to separate amines by using a new developed adsorbent.

CHAPTER 2: LITERATURE REVIEW

2. LITERATURE REVIEW

Handling a research project which relates with industrial effluent or wastewater, it is a need to acknowledge about what is the definition of wastewater and terms relate to it. Wastewater properties and characterization is in need to be understood.

2.1 Effluent and Sewage

Effluent is basically the water supply of the public after being fouled by variety of uses (Metcalf, 1991). It may defined as a combination of liquid- or water-carried waste removed from residences, institutions, industrial and commercial establishments, together with groundwater, surface water and storm water. Effluent contains numerous pathogens, nutrients which can cause diseases and stimulate the growth of aquatic plants. As of these reasons, removal of contaminants and treatment of effluent are necessary to be conducted in industrialized society.

Sewage is a subset of effluent. From Environmental Quality Act 1974, Sewage and Industrial Effluents Regulations 1979, sewage is defined as any liquid waste or effluent discharge which contains animal or vegetable matter in suspension or solution, and may include liquids containing chemicals in solution.

Most conventional wastewater treatment plants discharge into streams, lakes, and rivers. These plants must possess a NPDES (National Pollutant Discharge Elimination System) permit that determines the type and amount of contaminants they can discharge into the receiving water. Most NPDES permits regulate BOD (biological oxygen demand), TSS (total suspended solid), pH, coliforms and nutrients although the acceptable levels will vary depending on the wastewater treatment process and the use and health of the receiving waters.

Contaminants, such as metals, TDS, pharmaceuticals, and endocrine disruptors, may or may not include in NPDES permits; however, they can be detrimental to water reuse. Some of these contaminants are just now being studied and their effects on the environment, humans, and reuse are unknown.

2.1.1 Biochemical Oxygen Demand (BOD)

BOD is a measure of how much organic material is in the wastewater plant effluent calculated by the amount of oxygen used by microorganisms in the oxidation of organic matter. If the amount released in the effluent is too high, microorganisms in the receiving waters will eat the organic material utilizing dissolved oxygen as they do so. This depletes the dissolved oxygen available to aquatic life and results in fish kills, invasions of weeds, and changes in the body of water.

2.1.2 Total Suspended Solids (TSS)

Total suspended solids are organic and inorganic solid materials that are suspended in water. High concentrations of suspended solids can lower water quality by absorbing light. Waters then become warmer which lessens the ability of the water to hold oxygen necessary for aquatic life. Because aquatic plants also receive less light, photosynthesis decreases and less oxygen is produced. Suspended solids can also clog fish gills, reduce growth rates, decrease resistance to disease, and prevent egg and larval development. The material that settles fills the spaces between rocks and makes these microhabitats unsuitable for various aquatic insects.

2.1.3 pH

pH is a measure of the acidity of the water. Most organisms thrive in a fairly neutral environment, pH of 6 - 9, and will die or have reproductive problems if the pH is too high or too low.

2.1.4 Coliform bacteria

Coliform bacteria are found in abundance in raw wastewater but their numbers are reduced through the disinfection step of the treatment process. These organisms do not normally cause disease but are used as indicator organisms for disease-causing organisms called pathogens. If a wastewater plant's effluent contains large numbers of coliform bacteria, it is likely that a large number of pathogens are also being released into the environment. These pathogens can present a major health hazard.

2.1.5 Nutrients

Nutrients, especially nitrates and phosphorus, can also cause problems in receiving waters. Large amounts of these nutrients will lead to extensive growth of aquatic plants, algae, and plankton. This process is called eutrophication. It disturbs the eco-system and damages the biodiversity and flora. As a result, the plants use up more oxygen when they decompose, and this leads to oxygen depletion in the water resulting in the death of fish and other aquatic creatures. Phosphorus in wastewater comes from food, pesticides, and industries. Nitrates in wastewater come from ammonia being converted to nitrates by bacteria in the treatment process.

2.1.6 Metals

Metals are present in wastewater mainly due to manufacturing processes, industries, and piping in household plumbing and collection systems. Heavy metals found in wastewater include lead, silver, mercury, copper, nickel, chromium, zinc, cadmium, and tin. These metals, when found in sufficient concentrations, can be detrimental to human health as well as the environment. If wastewater is used to irrigate fields without having the metals removed, they will accumulate in the soil and may infiltrate the groundwater or render the fields useless.

2.1.7 Total Dissolved Solids (TDS)

Total dissolved solids comprise inorganic salts as in calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulfates which can be found in industrial effluent. Effluents with high levels of TDS are not suitable for irrigation or landscaping because many plants are intolerant of the chlorides and the TDS may leach into the groundwater. TDS are also not desirable for industry reuse because they will cause corrosion and incrustation.

2.1.8 Pesticides/Endocrine Disruptors

An endocrine disruptor is a synthetic chemical that when absorbed into the body either mimics or blocks hormones and disrupts the body's normal functions. This disruption can happen through altering normal hormone levels, halting or stimulating the production of hormones, or changing the way hormones travel through the body, thus affecting the functions that these hormones control. Chemicals that are known human endocrine disruptors include di-ethylstilbesterol (the drug DES), dioxin, PCBs, DDT, and some other pesticides.

These chemicals are present in wastewater due to pesticide use and application, manufacturing, and industries. While human health effects of endocrine disruptors are still being investigated, numerous studies have shown that these chemicals have negative effects on the environment. Releasing them into the environment or to humans through wastewater discharge and/or reuse may cause unknown problems now and into the future.

2.2 Effluent characteristics

Effluent can be classified into domestic, municipal and industrial effluent. Industrial effluent means effluent not otherwise defined as domestic effluent, including the runoff and leachate from areas that receive pollutants associated with industrial or commercial storage, handling or processing facilities. Municipal effluent is referred as effluent collected in sewer systems, including domestic effluent which may be black and grey water from households as well as effluents from institutions, businesses and industries. While domestic effluent means effluent that is composite of liquid and water-carried wastes associated with the use of water for drinking, cooking, cleaning, washing, hygiene, sanitation or other domestic purposes, together with any infiltration and inflow effluent, that is released into a effluent collection system.

After effluent been treated, it can be reused or disposed of to the environment. Usually treated effluent is discharged into streams, rivers, lakes, estuaries or the ocean. Treated effluent can be reused as drinking water source, industrial purpose as in for cooling towers, in agriculture and rehabilitation of natural ecosystems.

Effluent characteristics can be classified into two; by physical and chemical characteristics. The physical characteristics are temperature, color, odor and solids. The temperature of effluent differs greatly, depend upon types of operation. Wide variation in the effluent temperature indicates heated or cooled discharges. Changes in effluent temperatures affect the settling rates, dissolved oxygen levels and biological action. The temperature of effluent becomes really important in certain effluent unit operations such as sedimentation tanks and recirculating filters.

2.3 Surface Chemistry and Effects

As mentioned by Yang (2003) in his writing, by treating the RH with chemical as in sodium hydroxide and activating agent, functional groups on the surface of the RH could be added and varied as in –OH, –OR, –COH and –COOH.

The heteroatoms on the surfaces of adsorbent consist of characters of functional groups which can be found in aromatic compounds. They react similar ways with many reagents; including amine solutions. The surface groups attached on the treated rice husk is the key role in surface chemistry of an activated carbon. Acidic surface on adsorbent will reasoned for cation exchange properties in amine solutions. Oxidation increases the preference for the more polar component of the solution (Yang, 2003).

2.4 Rice Husk as Activated Carbon

Rice husks are agricultural waste produced from the rice milling industry as by-product. The world wide annual production of rice husks is estimated to be about 100 million tonnes, 90% of which is generated in developing countries (Paul T.W. and Nittaya N., 2000). The utilization of this source of biomass through energy recovery processes would solve both a disposal problem and also generate useful energy.

It is estimated that over nine million tonnes of rice waste are generated annually from rice milling industry in Malaysia (Wahi R. *et. al.*, 2006). Normally rice waste is used as animal feed, composting, burned as thermal energy for during purposes and others are burned on the field. Utilization of this source of waste via energy recovery has the potential to solve waste management problem and also generate useful energy. Paul T. Williams and Nittaya Nugranad (2000) had stated in their study regarding the component analysis of RH as in the table below.

Table 2.1 : Component analysis of RH (Paul T.W. and Nittaya N., 2000)

Component Analysis	Weight Percentage, %
Cellulose	34.4
Hemicelluloses	29.3
Lignin	19.2
Ash	17.1

Adsorption process is proclaimed as the most promising and efficient option for treating all aromatic compounds from aqueous streams, due to its extended surface area, high adsorption capacity and micro porous structure and special surface reactivity by Abdelwahab et al. (1996), Imagawa et al. (2000), Mohan et al. (2001), Malik (2003) and Babiker (2009). The characteristics of activated carbon are listed as mentioned by Yang (2003) are:

1. Activated carbon is the most commercial adsorbent to remove contaminants without needs of stringent moisture removal. It also broadly applied in treating aqueous solutions.
2. Activated carbon has large, accessible internal surface; which provide more pore volume, ability to absorb non-polar and weak polar organic molecules.
3. Activated carbon has low heat of adsorption and bond strength

Sources are taken from journal by Ahmaruzzaman M. and Gupta K. (2011) from Industrial and Engineering Chemistry Research. Properties and composition of RH (reference from 9-13):

Table 2.2: Physicochemical properties of RH

Proximate Analysis (wt %)					Ultimate Analysis (wt %)					
Combustibles	Moisture	Ash	Volatile matter	Fixed carbon	C	H	O	N	S	Cl
72.87	10	17.13			38.92	5.55	37.94	0.35	0.02	0.09
		19.8	64.3	15.9	37	5.1	36	0.4		
	7.9	17.1	59.9		44.6	5.6	49.3			
		20	66.4	13.6	37.8	5.2	39	0.39	0.05	
		17.9	72.8	9.3	48.9	6.2	44.1	0.4		

Table 2.3: Chemical composition of rice husk ash

		Composition	**(%)**		
Cellulose	32.24	34.4	29.20	32.24	33.47
Hemicelluloses	21.34	29.3	20.10	21.34	21.03
Lignin	1.82	19.2	30.70	1.82	26.70
Extractives	8.11			8.11	
Water	15.05			15.05	
Mineral ash	15.05	17.1		15.05	

Typical properties of GAC and PAC are given as follow:

Table 2.4: Properties of GAC and PAC

Parameter	Unit	Type of activated carbon	
		GAC	PAC
Total surface area	m^2/g	700-1300	800-1800
Bulk density	kg/m^3	400-500	360-740
Particle density, wetted in water	kg/L	1.0-1.5	1.3-1.4
Particle size range	mm (μm)	0.1-2.36	(5-50)
Effective size	mm	0.6-0.9	na
Uniformity coefficient	UC	≤1.9	na
Mean pore radius	Å	16-30	20-40
Iodine number		600-1100	800-1200
Abrasian number	minimum	75-85	70-80
Ash	%	≤8	≤6
Moisture as packed	%	2-8	3-10

**Source taken from Metcalf & Eddy (2003), pg. 1139*

2.5 Equilibrium Isotherms

Equilibrium isotherm is the most important basis for selecting the sorbent. Based on isotherm, these factors must be considered in designing the separation process or removal process:

1. Capacity of the adsorbent at operating temperature and pressure
2. Regeneration process of adsorbent
3. Length of unused bed (LUB)

4. Product purities

2.5.1 The Langmuir Isotherms

This isotherm is widely used in practical applications. It is related for single layer adsorption.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad \text{(Equation 2.1)}$$

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \qquad \text{(Equation 2.2)}$$

q_e = equilibrium adsorbent capacity (mg/g)
q_m = mass of adsorbent (g)
K_L = Langmuir constant
C_e = partial equilibrium concentration (mg/L or ppm)

It is a semi-empirical isotherm derived from a proposed kinetic mechanism. It is based on four assumptions:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

2.5.2 The Brunauer – Emmett – Teller Isotherm

From S. Brunauer, P.H. Emmett na dE. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938), this type of isotherm is for one component, non-dissociation and multilayer at around boiling of adsorbate.

$$v = \frac{v_m c\left(\frac{p}{p_0}\right)}{\left[1-\left(\frac{p}{p_0}\right)\right]\left[1-\left(\frac{p}{p_0}\right)+c\left(\frac{p}{p_0}\right)\right]}$$ (Equation 2.3)

$$\boxed{0.05 < p/p_0 < 0.35}$$

Where,

	v	= amount of adsorbate on adsorbent at equilibrium (mol/kg)
	v_m	= amount adsorbate required to form one monolayer over the entire adsorbent surface
	c	= system constant (100)
	p	= partial pressure of adsorbate (subscript 0 denotes saturation)

2.5.3 Breakthrough

Breakthrough is the phenomenon where appearance of small but detectable concentration in the effluent from the bed occurs, as mentioned by Dutta B.K.

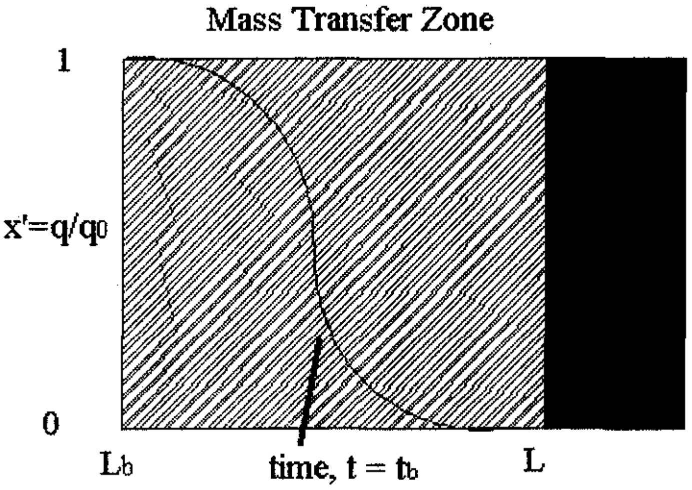


Figure 2.1: Breakthrough study

In continuous mode study, experiment of adsorption is done using ion exchange apparatus. Before conducting experiment, system is lined up as required. Tank is filled with artificial MEA at different concentration. A pump is used to suck up MEA wastewater into column filled with adsorbent. A filter paper is set up below of the column to prevent "adsorbent-carry over" phenomenon. The outlet of system should be fixed to one outlet in order to ease the process to collect the product. Product is taken at certain time intervals. Setting up the equipment is a vital procedure. Thus, Armfield ion exchange apparatus is used.

Details in setting up experiment:

Flowrate : 10 cc/ min
Mass of Adsorbent : 5 ± 0.001 g
Diameter of column : 0.016 m
**Mass of adsorbent used is made constant while adsorbents used are different.*

By using an ion exchange unit, adsorbents performances are being tested. Packed bed length is made at constant. But, the more the volume of adsorbent used, the slower for the adsorbent to breakthrough. Flow rate of industrial effluent can be varied. The higher the flowrate of artificial industrial effluent, thus, breakthrough of the adsorbent will be faster. Performance of adsorbent is measured by the rejection of amine concentration from the initial source of wastewater. Rejection formula as shown below:

$$Rejection, R = 1 - \frac{C_t}{C_0}$$

Notes: C also can be notified as q; flux. At time = 0, usually noted as t_0 , mostly the rejected concentration will be 0 since the absorbency of adsorbent is at highest efficiency level. For all cases, C_0 is at 100 ppm.

2.6 Existing Studies

Rice husk has been treated with many methods in order to activate the site for adsorption. Many components can be removed using the treated rice husk. Nasir et al.

has reported that arsenic can be removed from water using rice husk. Maximum adsorption after treatment was reported by using 0.01M of HNO3, HCl and H2SO4. In Wang and Lin experiment, they found that by increasing the initial constituent concentration, pH or adsorption temperature, the kinetics and equilibrium adsorption can be increased. Zafar et al. stated in his report that maximum adsorption capacity of nickel (Ni) is at pH 6. In Mahvi et al findings, he stated that rice husk ash was more effective.

By treating with acid or base, the porosity of adsorbent is improved since the acid and base cleaned the rice husk from unwanted inorganic compounds. By activating the rice husk with either zinc chloride or phosphoric acid, the functional groups of –OH, C-H, C≡C, C=O, C=C, C-C and C-O, contribute in ability to absorb the contaminants (Daffalla S.B., Mukhtar H., Shaharun M.S., 2009).

In conclusion, since there is none of research being done using RH to remove amine from industrial effluent or artificial wastewater, thus the pattern of isotherm is still in the process of study.

CHAPTER 3: RESEARCH METHODOLOGY

3. RESEARCH METHODOLOGY

This project requires experimental works which consists of three phases; adsorbent preparation, treatment phase and test performance. All procedures are conceived from existing projects and investigations by researchers in literature review process.

3.1 Adsorbent preparation

Raw material was obtained from paddy field in Bukit Lada, Kedah. The raw rice husk first is washed thoroughly using distilled water. This is to make sure the contaminant as in soil on RH is totally removed. After that, rice husk is dried in electrical oven at 100°C for the whole day to remove moisture. Until the mass is constant, the prepared rice husk is taken out and set aside to a fine container, ready to be grinded. The grinded rice husk is then sieved by the size of 250 to 500 micrometer (μm). It is important in setting the size of the adsorbent since it affects the performance of the adsorbent. Last step for the first phase is labeled and stored the rice husk inside a container.

3.2 Calibration curve and standard solution

Using instrument as of UV-Vis, a standard calibration curve of MEA is analyzed. The standard must be possessed in order to determine concentration the calibration curve for further reference. A calibration for amine solutions is prepared using different concentration of methyl ethanol amine (MEA). MEA is set at 280nm wavelength. By using 25, 50, 100, 200 and 400 ppm of MEA solution, a straight inclining line proportional to the concentration is obtained. By referring other studies related to this research, physical and chemical treatment were applied for treatment process of the artificial activated carbon. However this time, modification is made in treatment process where physical and chemical are to be clustered and called as physicochemical treatment. With the intention of this study will give another contribution to the studies related with area focusing on agricultural waste modification into useful products.

3.2.1 Preparation of MEA solutions and standard calibration curve

Procedure:

1. Purity of monoethanolamine (MEA) is identified from the stock bottle (98%).
2. Prepare 100, 250, 500, 750 and 1000 ppm of MEA solutions by adding the stock solution with distilled water.
3. Apply formula of $M_1V_1 = M_2V_2$ to find out the amount of distilled water to be added.
4. Store the standard solution inside Erlenmeyer flask.
5. Fill a portion of each solution into test tube.
6. Analyzed the absorbency unit (AU) of solutions by using UV Vis.

Calculation:

Purity of MEA (stock solution) is 98%

Molecular weight of MEA (C_2H_7O) is 61.08 g/mol

$$C_1V_1 = C_2V_2$$

$$\left(1018\frac{mg}{L}\right)(V_1) = \left(100\frac{mg}{L}\right)(1L)$$

$$V_1 = 98.23\,mL$$

Table 3.1: Concentration and volume of MEA

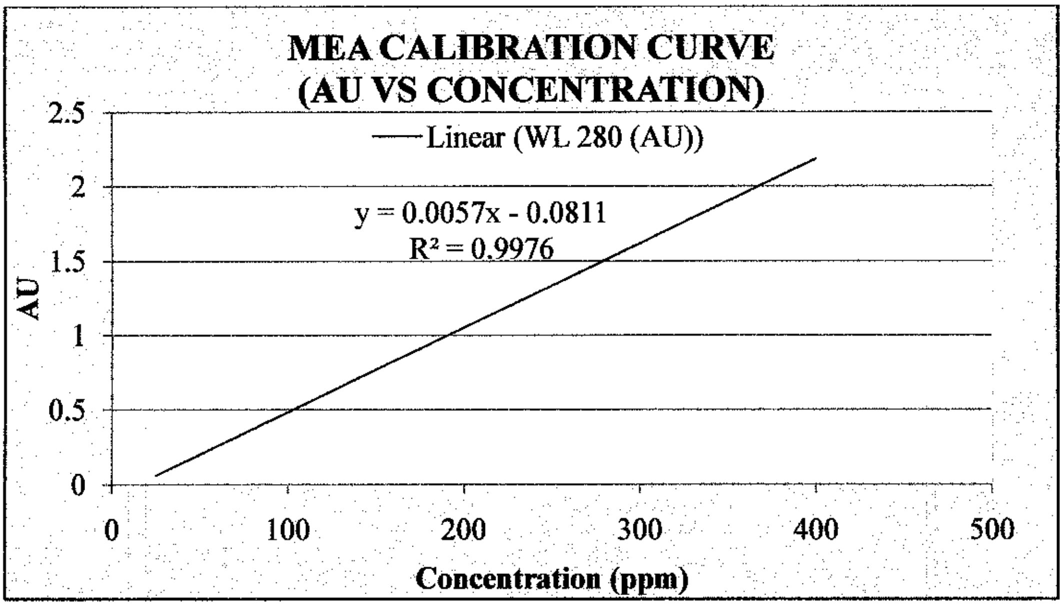
Concentration mg/L(ppm) of MEA required	**Volume stock needed to make 1L solution (mL)**
25	24.56
50	49.12
100	98.23
200	196.46
400	392.92

Table 3.2: Concentration of amine and its absorbency

Concentration, mg/L (ppm)	**AU**
25	0.068
50	0.226
100	0.497
200	0.977
400	2.214

**The above analysis is taken at wavelength of 280 nm.*

Dilution method also could be applied to prepare different concentration for standard solution. After studying the proper wavelength of monoethanolamine from UV Vis, UV Probe, Spectrum, it is found that best wavelength for amine group is 280 nm. Considering at this wavelength, the absorbency of MEA at concentration between 0 to 100 ppm are shown as below:



Graph 3.1: Calibration curve of MEA solution

The table 4 shown below is the properties of amines. The source is referred from flux and rejection characteristics of amine wastewater using membrane separation process by Binyam Seyoum Woldehawariat (July 2010).

Table 3.3 : Characteristics of artificial effluent amines in terms of COD and pH

CONC. (ppm)	MEA (monoethanolamine)		DEA (di-ethanolamine)		MDEA (methyl di-ethanolamine)	
	COD	pH	COD	pH	COD	pH
1500	1982	11	2355	10.62	2580	10.46
3500	4625	11.17	5425	10.80	6020	10.63
6000	7930	11.29	9215	10.91	10325	10.75
9000	11890	11.38	13825	10.99	15480	10.83
12000	15855	11.44	18430	11.05	20650	10.89
15000	19820	11.49	23440	11.09	25810	10.94

Other than UV-Vis, HPLC is also used in this research study. Concentration of amine after passing through the adsorption process is analyzed using this equipment. HPLC working principle is same as other chromatograph instrument. However, the conducted phase is in liquid form, not in gas phase. Standard calibration of amine solutions (MEA) too is carried out using low standard and normal standard of concentration MEA. MEA solutions ranging between 1 ppm to 100 ppm are prepared for analyzing process.

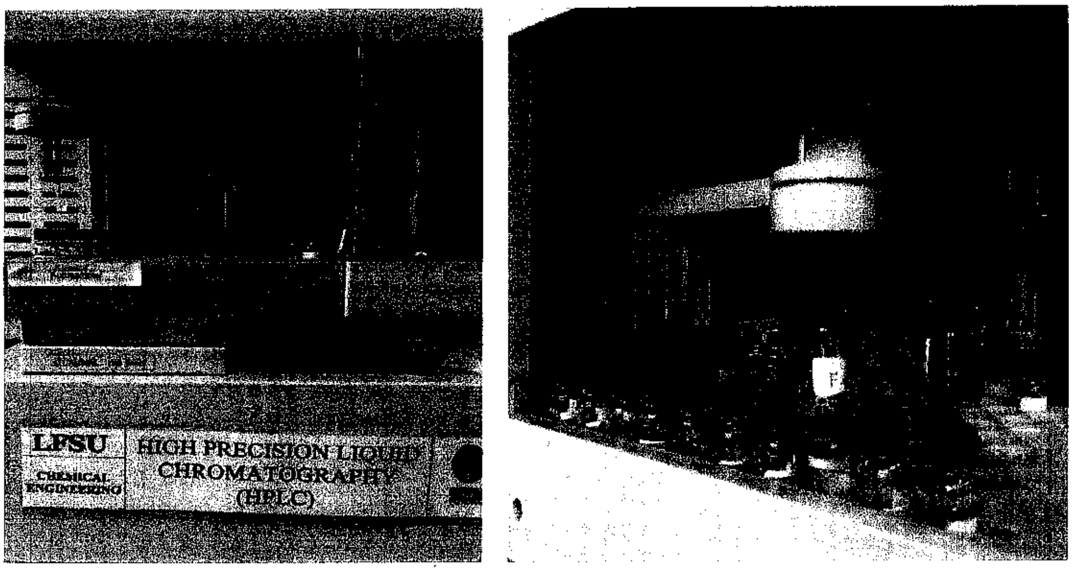


Figure 3.1: High Performance Liquid Chromatography

3.3 Treatment Phase

First stage of RH treatment is by treating rice with solution of sodium hydroxide (NaOH) at concentration of 0.5 M, zinc chloride ($ZnCl_2$) at concentration of 0.1 M and sulphuric acid (H_2SO_4) at concentration of 1M. This is to create the appearance of polar groups on the adsorbent surface in order to provide more cation exchange capacity to the presence of polar groups on the surface which likely give considerable cation exchange capacity to the adsorbent (Daffalla S.B., 2009). The pH of solution gives significant effects to the characteristics developed by the adsorbent (Chowdhury et al). Each needs to be discovered to identify which give best performance in removing the contaminants from industrial effluent. Next, the chemically treated rice husk is washed using distilled water and dried in oven until the mass is at constant.

3.3.1 Preparation of solution NaOH and $ZnCl_2$ for chemical activation

Preparing 0.5 M NaOH

NaOH molecular weight is 40 g/mol.

$$0.5\,M = 0.5\frac{mol}{L}$$

$$0.5\frac{mol}{L} = \frac{mass}{MW}$$

$$Mass\ of\ NaOH = 20\,g$$

$$MW\ of\ NaOH = 40\,g/mol$$

For 0.5M NaOH solution, 20 g of NaOH and a liter of distilled water are needed.

Preparing 0.01 M $ZnCl_2$

$$0.01\,M = 0.01\frac{mol}{L}$$

$$0.01\frac{mol}{L} = \frac{mass}{MW}$$

$$MW\ of\ ZnCl_2 = 136.3\,g/mol$$

$$Mass\ of\ ZnCl_2 = 1.363g$$

For 0.01M $ZnCl_2$ solution, 1.363 g of $ZnCl_2$ and a liter of distilled water are needed.

In the second stage of treatment, RH is burnt at two different temperatures; 500°C and 250°C each at different hours; 2.5, 3, 14 and 20 hours. The objective from this process is to vary and discover the carbon composition on the adsorbent. Carbon is useful in capturing contaminants inside of wastewater. In existing similar area of studies, the burning temperature was varied to study the effect of temperature towards the structure and absorbency of the RH. It was found by Daffalla S. B. that by increasing the temperature would increase the total surface area of the RH. This is due to the removal of hemicelluloses, lignin and reduction of cellulose crystallinity. However, the content of silica is increasing by the raise of temperature. The same procedures are applied to RH by using different time of burning and lower temperature. After both types of treatment done, adsorbents are washed until clean using distilled water.

As stated by Mohan in his journal, surface chemistry depends on the activation and temperatures employed. Pore structures are refined by activation made. A lot of reviews on surface chemistry has been done and reviewed by Pollard et al, Bansal et al and Radovic. The previous studies and researches have not yet mention about the double treatment method. Thus, from this project, it is hoped that the new method of treatment applied will make another contribution to the related area on the research and development (RND) of agricultural waste into useful product.

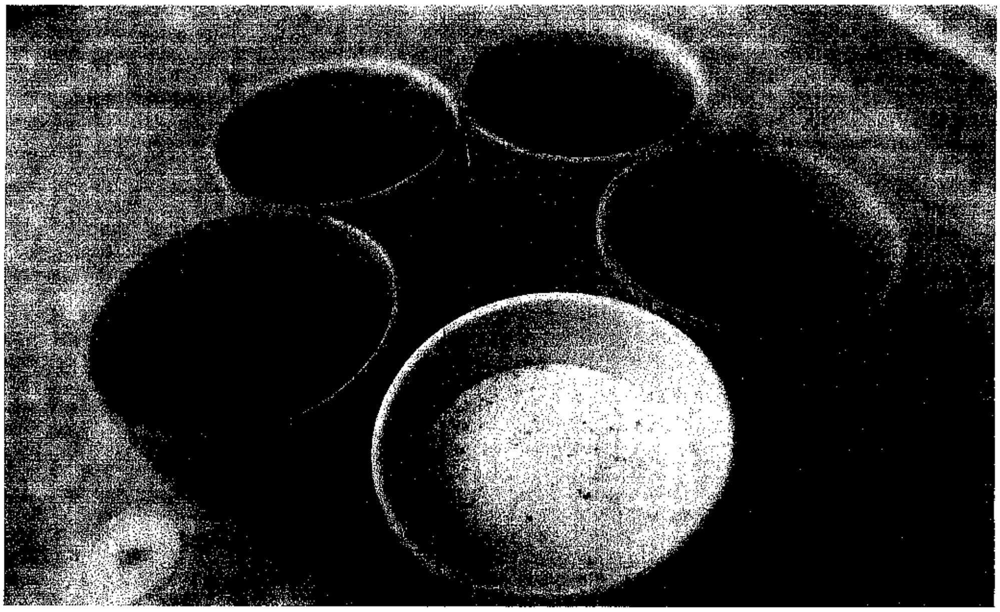


Figure 3.2: Developed adsorbents

3.4 Test performance

Mode of operation or performance test for this project is in continuous and batch mode. Through studies which had been conducted before, it is more successful for the experiment to be carried out in continuous mode of operation. Moreover, there is equipment availability related which support for this kind of operation. An ion exchanger unit is used in performing test of adsorbents. For continuous mode, experiment is done by adding 4 to 5 gram of treated adsorbent into the column. Artificial amine wastewater (MEA) is flowed through the column by using a pump to surge in the artificial effluent at 10 cc/min of flowrate. The ion exchange unit and its components labeling is shown as below:

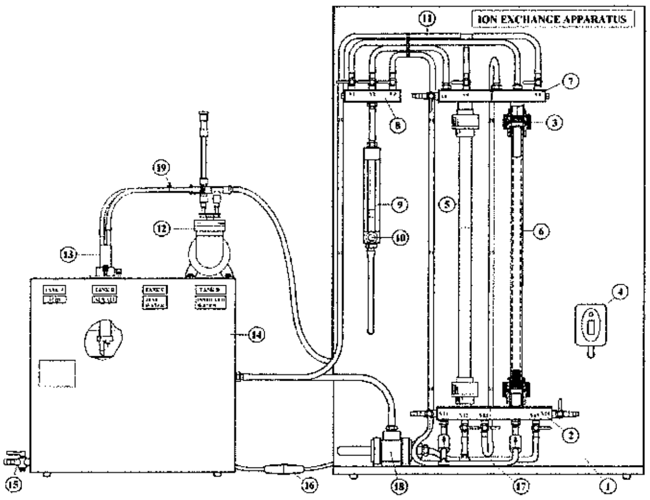


Figure 3.3 : Armfield Ion Exchange Apparatus used in the laboratory

Since this project is about testing the adsorptivity of adsorbent, it only requires certain part of section that is used from the ion exchange apparatus. Only a column is needed to run the test performance. Same goes to lines used from the apparatus. Adsorption only needs certain lines to be used in the experiment. Further procedure of studies is explained in the next chapter.

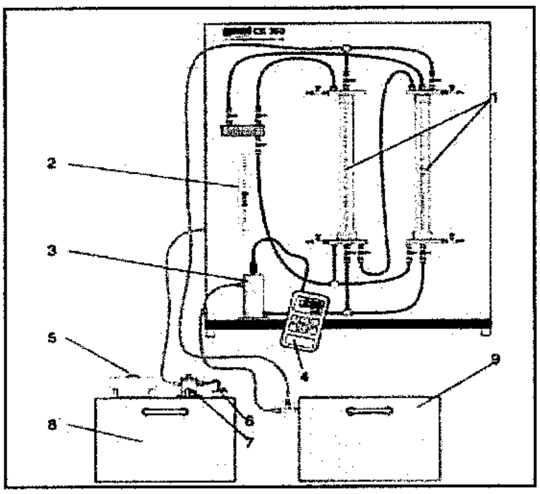


Figure 3.4: Typical ion exchange unit and its components

1. Column or container pipes for ion exchange material
2. Flow meter
3. Measuring tank with conductivity meter sensor
4. Conductivity meter
5. Pump switch
6. Intake pipe
7. Pump
8. Supply tank
9. Collecting tank

Besides that, for batch mode operation, experiment is done in a 150 mL conical flask. An amount of adsorbent is tested with constant volume of MEA solution at 100 ppm. Concentration of amine is taken at times to observe removal efficiency of each adsorbent type. Out of five Adsorbents of developed adsorbents, three of them are being tested using batch mode operation.

3.5 Gantt Chart and Key Milestones

Refer to Appendices.

CHAPTER 4: RESULT AND DISCUSSION

4.RESULT AND DISCUSSION

Test performances for developed adsorbents are done using amine (MEA) artificial wastewater with concentration of 100 ppm. This concentration is selected due to the upper limit of concentration for COD in standard B in Malaysia's Law and Regulation (see Appendix).

4.1 Characterization of adsorbent for each development

4.1.1 Characterization of adsorbent using SEM and FTIR

Raw rice husk (RRH)

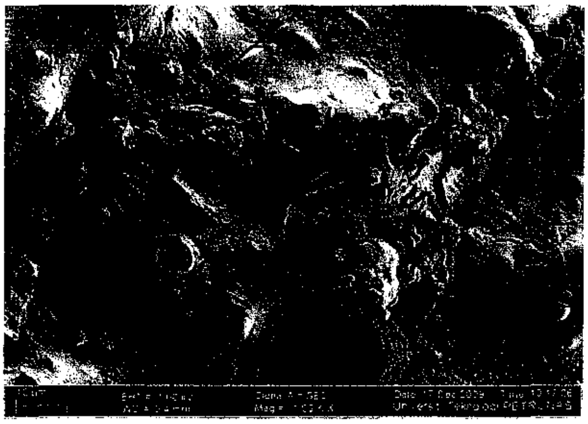
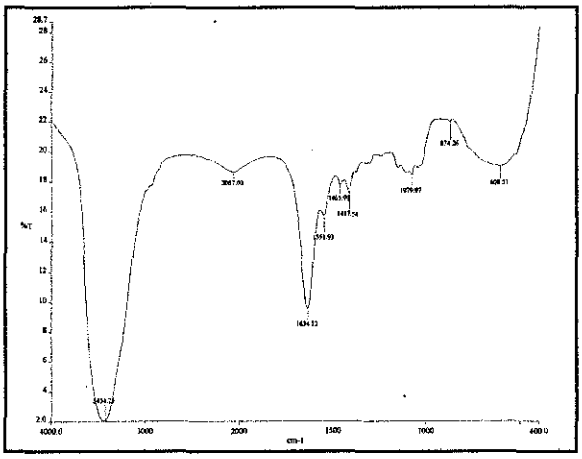


Figure 4.1: FESEM result for raw rice husk

Morphological study of raw rice husk could be done using Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM). By magnifying it with 1000 magnification, clearer pattern of surface adsorbent is observed. Raw rice husk looks more compact when it is in the form of not treated. The powdery look thus does not provide much pore structure on the adsorbent. A good adsorbent provide porous structure in order to enhance contaminants to be captured on it.



Graph 4.1: FTIR result for raw rice husk

Surface chemistry on RRH is as shown in graph 2. The typical functional groups on RRH are alcohol O-H stretch at 3434.23 cm^{-1}, amide C-O stretch at 1634.12 cm^{-1}, aromatic C=C bending at 1551.93 cm^{-1}, C-C stretch at 1465.99 and 1417.54 cm^{-1}, C-O or C-O-C stretch at 1079.97 cm^{-1}, C-H bend at 874.26 cm^{-1} and acetylenic C-H bend at 608.51 cm^{-1}. It is observed that most of bonds exist before treated are in carbon chain groups.

Rice husk treated with NaOH

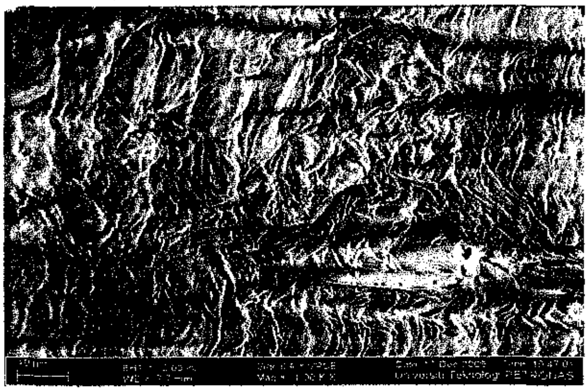
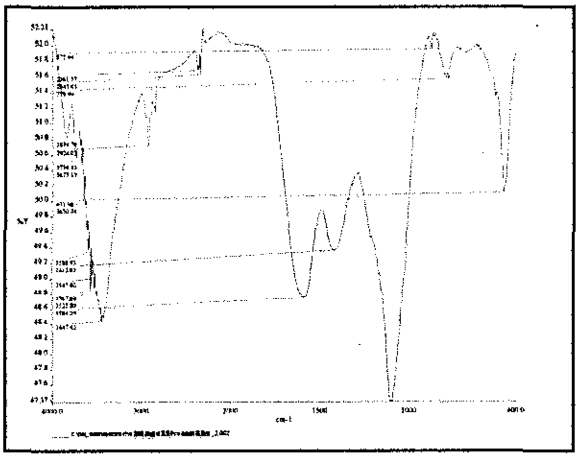


Figure 4.2: FESEM result for RH treated with NaOH

From the figure shown by VPFESEM, the pattern of adsorbent looks in shaped of threads. This might be caused of functional groups from chemical treatment process attached onto it. Sodium hydroxide and zinc chloride provide more functional groups on the activated carbon. As can be seen, surface area gets larger after treatment. Thus, from chemical treatment, morphological of adsorbents could be improved by increasing the total surface area and surface chemistry of the adsorbents.



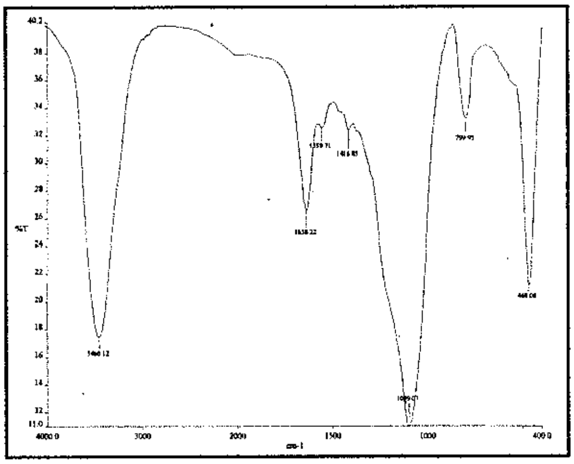
Graph 4.2: FTIR result for RH treated with NaOH

As shown in FTIR result, more functional groups are present compared to RRH. New functional groups as in amine and amide N-H stretch, alkyl C-H stretch and isocyanates N=C=O are introduced from the chemical treatment. Each appears at wavelength of 3447, 2924 and 2350 cm^{-1}.

Rice husk ash at 300 °C for 3 hours

Figure 4.3: FESEM result for RH burnt at 300° C

From SEM figures, rice husk ash after being treated with chemical and physical treatment, the activation sites are wider with functional groups that enhance the attraction with contaminants from artificial industrial effluent. The size of pores increased together with the surface area.



Graph 2.3: FTIR result for RH treated at 300° C

FTIR analysis shows less total functional groups attached on the adsorbent. The main cause could be because more carbon has been destroyed or consumed from oxidation process during burning activity inside furnace. However, when adsorbent is burnt, structure of raw rice husk is destroyed thus creating vary porous structure on the rice husk ash. This structure is important in order to develop a good adsorbent which is having larger surface area and porous structure to capture contaminants.

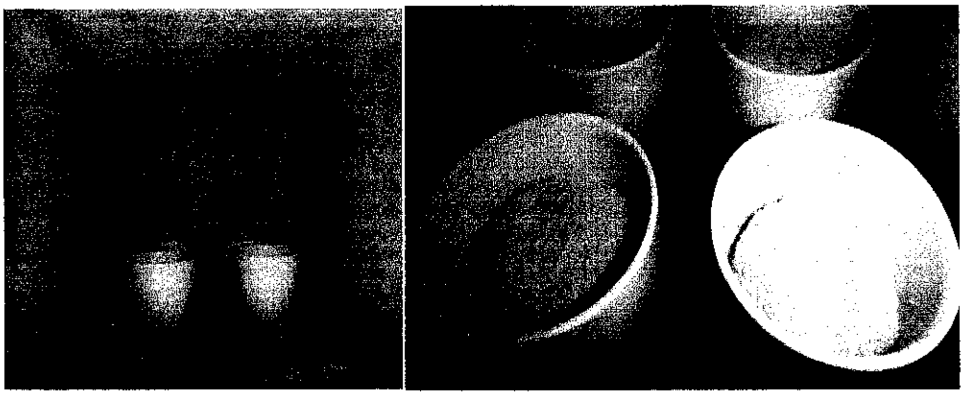


Figure 4.4: RHA treat with physical treatment in muffle furnace at different temperature for different hours

4.1.2 Analysis of adsorbent

Adsorption is an accumulation process of contaminants (MEA) substances on the GAC. MEA is named as adsorbate while developed GAC as adsorbent. The adsorption process occurs in three main steps: macrotransport, microtransport and sorption. According to Metcalf (1991), macrotransport involves movement of MEA through water to AC by advection and diffusion. Next, microtransport involves diffusion of MEA through macropores structure of AC, to adsorption sites in micropores and body of AC. Significances of developing the AC are due to it has:

1. **Extremely large surface area to volume ratio (A/V)**
2. **Preference of affinity for certain constituents in liquid phase**

By treating with NaOH and $ZnCl_2$, chemical structure on adsorbent will be differed. It changes the functional groups on the adsorbent. At the same time, it may also causes the removal of components on the rice husk as in lignin, cellulose crystal and hemicelluloses. This is where the pores could be generated and widely developed.

Using scanning electron microscope (SEM) or field emission electron microscope (FESEM), morphology of rice husks can be observed clearly before and after treatment process. It is found that total surface area after burning is larger compared to raw rice husk. By burning, structure of raw RH is destroyed. Thus, surface of adsorbent is more porous and resulting for larger specific particle surface area.

Chemical surface study is important since it affects the result of adsorption process. Functional groups attached on the rice husk are analyzed using Fourier Transform Infra Red (FTIR) equipment. The FTIR result for Adsorbents of adsorbent is shown in the table below:

Table 4.1: FTIR Analysis Adsorbent RHA at 250° C, 2.5 hours, NaOH 0.5M

Wavelength (cm^{-1})	**Bond/ Functional Groups**
3840, ~3700	Probably O-H stretch and Si-OH stretch
3650	Amide N-H stretch
3447	Amine N-H stretch
2924	Alkyl C-H stretch Carboxylic acid O-H stretch
2350	-N=C=O, isocyanates
1584	C-C stretch (in-ring) aromatics
1413	C-H bend
875	C-H , aromatics
780	C-H

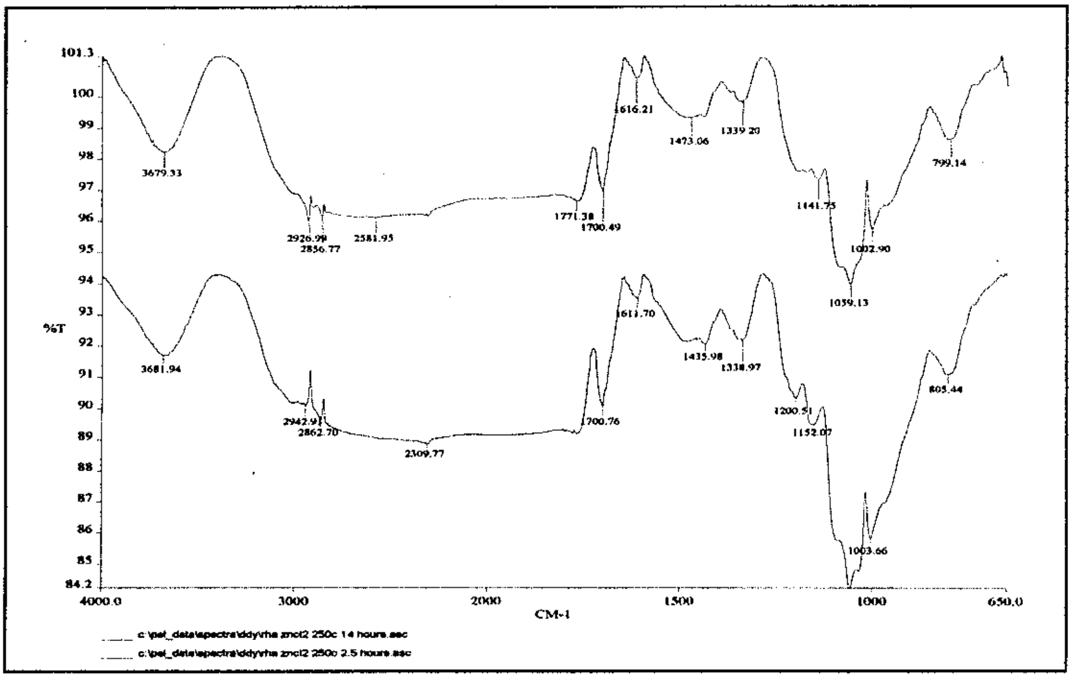
Table 4.2: RHA at 250° C for 20 hours NaoH 0.5M

Wavelength (cm^{-1})	**Bond/ Functional Groups**
3839	O-H and Si-OH
3446	Amine N-H sretch or alchol / phenol O-H stretch
1621	Aromatic C=C Bending
1096	C-O stretch (strong)
798	-C=H Bending
557	C-Cl stretch Halogen may came from tap water **Source :* *Ministry of Health Malaysia has standardize criteria of raw water in the National Standard for Drinking Water Quality, refer to Appendix*
468	$-OCH_3$

From the FTIR table result, O-H and Si-OH groups are detected at peak of 3840 to 3700 cm^{-1}. Amide N-H stretch is detected at 3650 cm$^{-1\cdot}$ Around 3446 and 3447 cm^{-1}, the presence of N-H can be found. By increasing the time of burning more than 2.5 hours, less functional carbon group is detected. At 250°C burning for 2.5 hours, at adsorption peak of 2924 and 2350 cm^{-1}, C-H, O-H and –N=C=O are detected. However, these functional groups are removed by the longer time of burning in the furnace. The peaks around 1584, 1413, 875 and 780cm^{-1} from the 2.5 hours burning correspond to C-

H group. The $-OCH_3$ can be detected at 468 cm^{-1}. Thus, by increasing the time of burning, more carbon chain is removed since carbon is oxidized during the process takes place. Good activated carbon is to be burnt at shorter time of burning.

On the other hand, this is the FTIR analysis between rice husk ashes burnt at same temperature at different time of burning.



Graph 4.4: RHA burnt at 250 °C for 3 and 14 hours treated with $ZnCl_2$

The table below shows the distribution of functional groups present on the surface of the developed adsorbent, ZnCl2 treated rice husk burnt at 250 °C.

Table 4.3: Difference distribution of functional groups on 3 and14 hours burning (treated with ZnCl2)

Wavelength (cm^{-1})	**Functional Group**
3679, 3681	-OH
2927, 2943, 2857, 2863	C-H stretch
2582	O-H stretch
2310	P-H stretch
1771, 1700	Carboxylic acid –OH stretch
1616, 1611	C=C stretch
1473	C=C
1436	O-H bend
1339	C-H
1141, 1200, 1152 (2.5 HR)	C-C stretch
1003	C-O or C-O-C stretch
799, 805	C-H bend (meta and para)

4.2 Test Performance

4.2.1 Adsorbents done for test performance

Certain Adsorbents are tested by batch and certain by continuous mode. Using constant amount of adsorbent per experiment, 150 mL of artificial MEA solutions is added inside conical flask. At each 3 minutes interval time, 5 mL volume of wastewater is taken from the flask. Concentration of artificial MEA wastewater will be measured later using chemical analytical equipment. In this case, MEA concentration after adsorption process is analyzed using HPLC. Below is the list of adsorbents done with adsorption process using MEA 100 ppm artificial wastewater solution.

Table 4.4: Adsorbents done with test performance

CONTINUOUS	BATCH
Adsorbent A - 0.5M NaOH, 250 °C	**Adsorbent C** - 0.01M $ZnCl_2$ 250 °C
Adsorbent B - 0.5M NaOH, 500 °C	**Adsorbent E** - 1M H_2SO_4 300 °C
	Adsorbent F - 1M H_2SO_4 250 °C

Figure 4.5: Conical flask used for test performance done in batch mode

4.2.2 HPLC Result Analysis

Calibration curve for low standard concentration and normal concentration of MEA solution from HPLC:

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==================================================================
                        Calibration Curves
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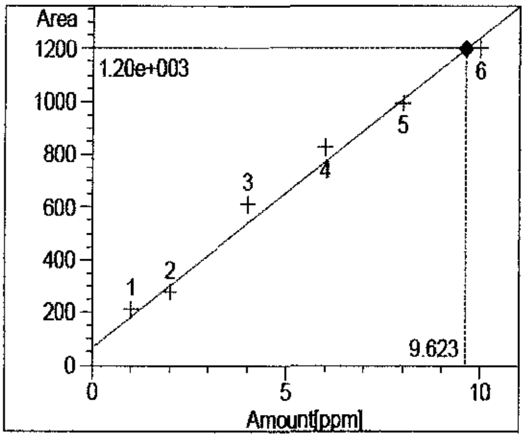
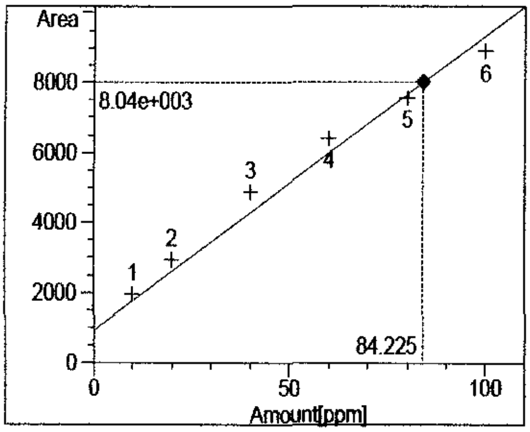


```
MEA at exp. RT: 5.232
DAD1 A, Sig=215,4 Ref=360,100
Correlation:             0.99325
Residual Std. Dev.:   56.36051
Formula: y = mx + b
     m:     117.96957
     b:      66.41428
     x: Amount
     y: Height
```

```
==================================================================
                        Calibration Curves
==================================================================
```



```
MEA at exp. RT: 5.199
DAD1 A, Sig=215,4 Ref=360,100
Correlation:             0.98605
Residual Std. Dev.:  583.77417
Formula: y = mx + b
     m:      84.50752
     b:     918.68056
     x: Amount
     y: Height
```

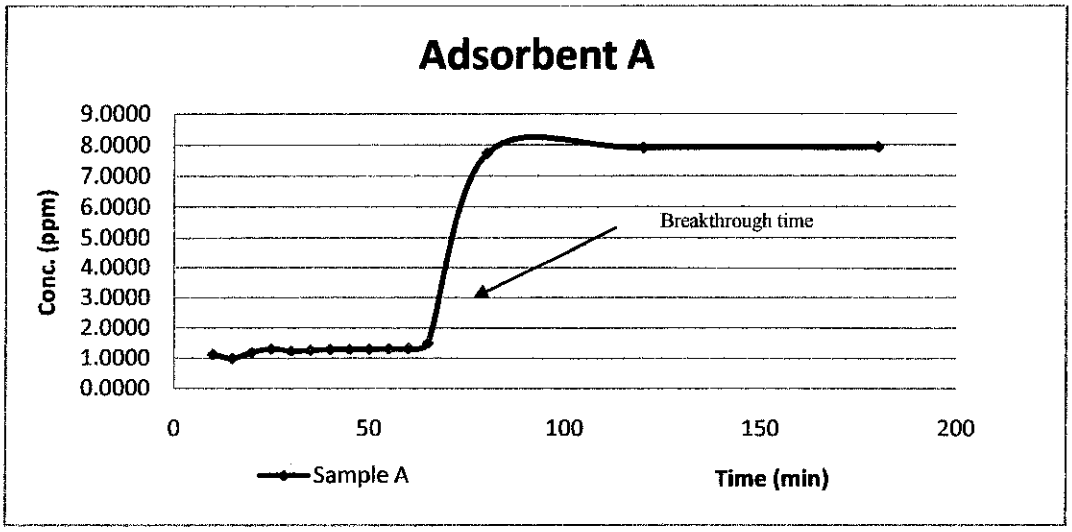
MEA solutions are prepared at 1, 2, 4, 6, 8 and 10 ppm for low standards calibration. As for standard concentration, 10, 20, 40, 60, 80 and 100 ppm are prepared. Slope and intercept could be obtained from HPLC calibration curve result analysis.

These are the results for five types of adsorbents which had been tested. Adsorbent A and B are conducted by continuous mode of operation. As for three other Adsorbents; C, E and F are conducted by batch mode operation.

4.2.2.1 Adsorption results by continuous operation

Table 4.5: Adsorbent A- HPLC result analysis

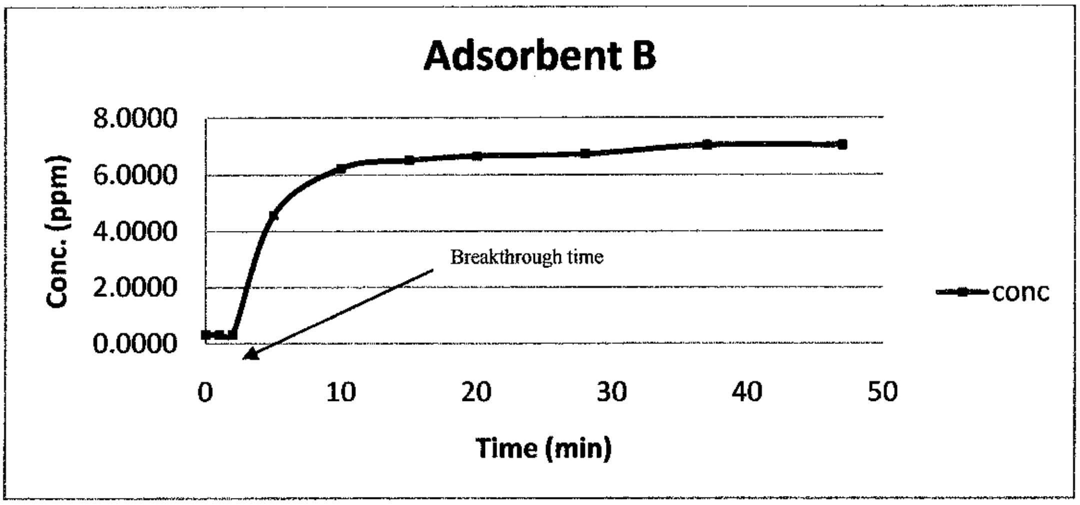
Time (min)	**Area (mAU.s)**	**Conc. (ppm)**
10	199.351	1.1269
15	183.933	0.9962
20	207.614	1.1969
25	220.345	1.3048
30	212.393	1.2374
35	215.450	1.2633
40	219.266	1.2957
45	219.800	1.3002
50	220.234	1.3039
55	221.561	1.3151
60	223.289	1.3298
65	245.000	1.5138
80	980.000	7.7442
120	1000.000	7.9138
180	1002.000	7.9307



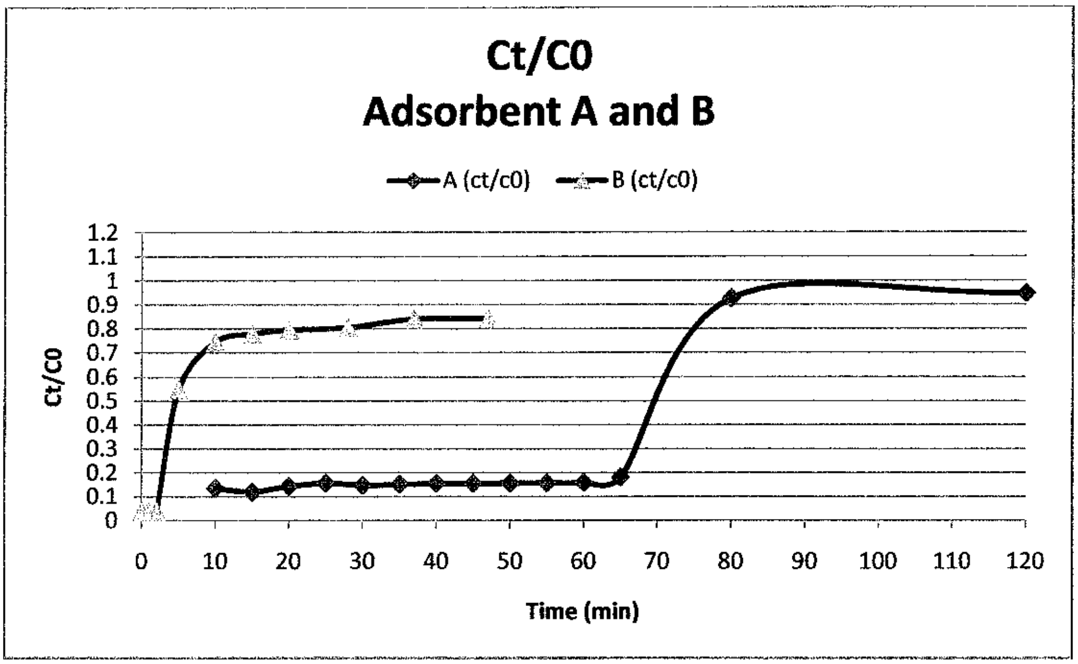
Graph 4.5: Adsorbent A- Concentration MEA vs time (min)

Table 4.6: Adsorbent B- HPLC result analysis

Time (min)	Area (mAU.s)	Conc. (ppm)
0	104.402	0.3220
1	104.800	0.3254
2	105.230	0.3290
5	605.895	4.5731
10	801.587	6.2319
15	834.379	6.5099
20	851.730	6.6569
28	860.625	6.7323
37	896.456	7.0361
47	897.000	7.0407



Graph 4.6: Adsorbent B- Concentration MEA vs time (min)



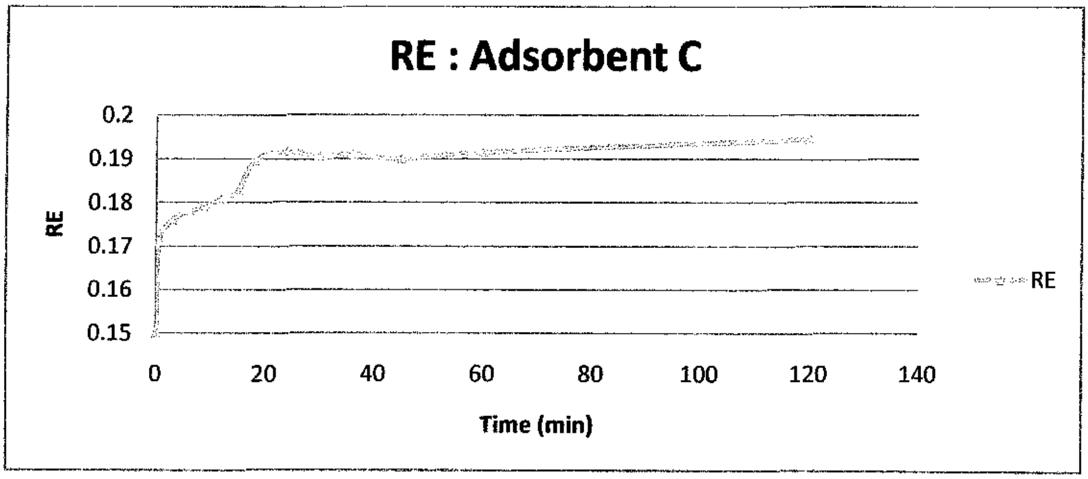
Graph 4.7: Ct/C0 – Comparison of adsorbent in continuous mode operation

Adsorbent A which is treated with NaOH at 250 °C shows slower breakthrough point than Adsorbent B which treated at 500 °C. Both show lowest concentration achieved before inclining at high slope at the breakthrough points. After some time, a plateau pattern could be seen. Breakthrough point for adsorbent B is faster where pointed at 2 minutes and increased sharply to 10 minute. On the other side, Adsorbent A's breakthrough time is between 65th to 80th minute. This shows that adsorbent A became saturated at longer time compared to adsorbent B. It could adsorb amine longer compared to adsorbent B. From the result, it is concluded that RHA treated at 250 °C prepare a better adsorbent compared to treated adsorbent at higher temperature. This could be related with total carbon chains presence on adsorbents. The higher numbers of carbon chains promising for more active sites compare to lower number of carbon chains. Carbon chains are destroyed during burning process where much carbon loss due to high temperature of burning during treatment.

4.2.2.2 Adsorption results by batch mode

Table 4.7: Adsorbent C- HPLC result analysis

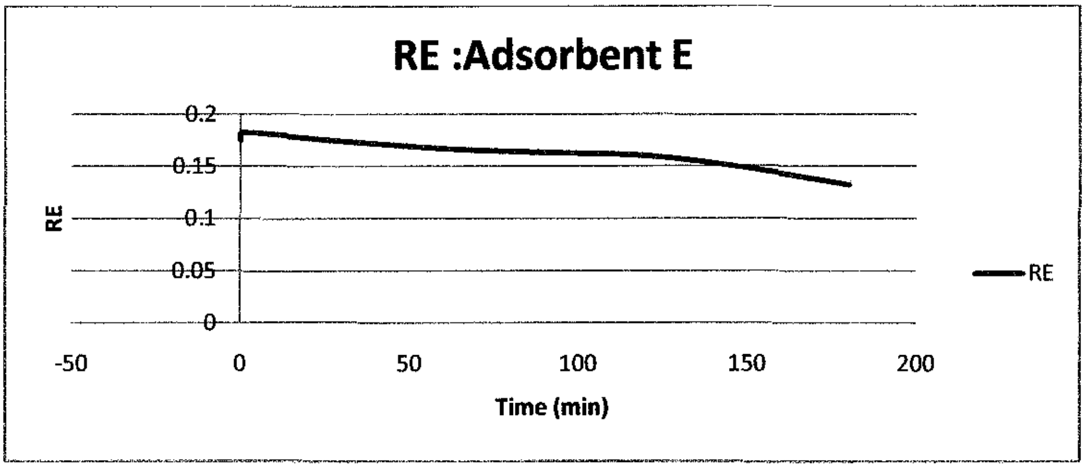
Time (min)	**Area (mAU.s)**	**Conc. (ppm)**	**RE (1-Ct/C0)**
0	8101	84.9903	0.150097
0.5	7921.5	82.8662	0.171338
3	7881.6	82.3941	0.176059
6	7864.2	82.1882	0.178118
9	7855.5	82.0852	0.179148
12	7840	81.9018	0.180982
15	7825.5	81.7302	0.182698
18	7766.8	81.0356	0.189644
24	7748.6	80.8203	0.191797
30	7759.7	80.9516	0.190484
36	7754.6	80.8913	0.191087
45	7763.8	81.0001	0.189999
60	7750.2	80.8392	0.191608
120	7725.88	80.5514	0.194486



Graph 4.8: Adsorbent C- Rejection efficiency vs time (min)

Table 4.8: Adsorbent E- HPLC result analysis

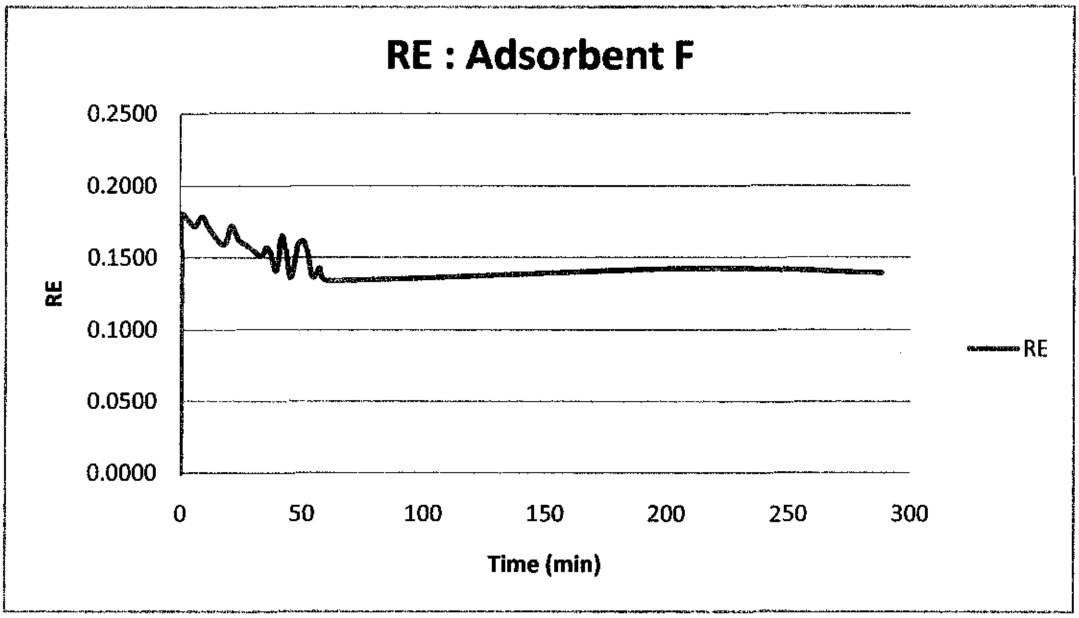
Time (min)	**Area (mAU.s)**	**Conc. (ppm)**	**RE (1-Ct/C0)**
0	7890.000	82.49348034	0.175065
0.5	7926.738	82.9282084	0.170718
30	7896.461	82.56993437	0.174301
60	7956.698	83.28274419	0.167173
90	7990.000	83.67680699	0.163232
120	8015.000	83.97263865	0.160274
150	8116.893	85.17836649	0.148216
180	8250.749	86.76231961	0.132377



Graph 4.9: Adsorbent E- Rejection efficiency vs time (min)

Table 4.9: Adsorbent F- HPLC result analysis

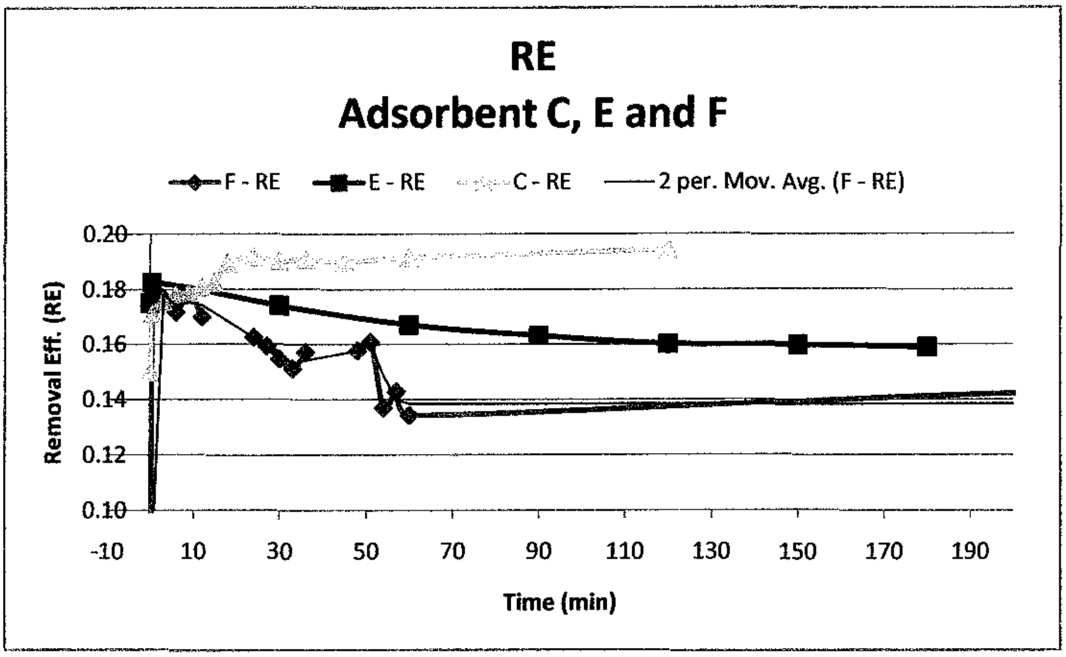
Time (min)	**Area (mAU.s)**	**Conc. (ppm)**	**RE (1-Ct/C0)**
0	9369.43	100.00	0.0000
0.5	7848.30	82.00	0.1800
3	7877.30	82.34	0.1766
6	7916.87	82.81	0.1719
9	7858.21	82.12	0.1788
12	7932.80	83.00	0.1700
18	8024.86	84.09	0.1591
21	7913.04	82.77	0.1723
24	7995.50	83.74	0.1626
27	8023.10	84.07	0.1593
30	8062.69	84.54	0.1546
33	8091.22	84.87	0.1513
36	8040.91	84.28	0.1572
39	8177.48	85.90	0.1410
42	7969.04	83.43	0.1657
45	8215.68	86.35	0.1365
48	8036.31	84.22	0.1578
51	8009.31	83.91	0.1609
54	8211.57	86.30	0.1370
57	8162.67	85.72	0.1428
60	8234.86	86.57	0.1343
210	8164.66	85.74	0.1426
288	8191.61	86.06	0.1394



Graph 4.10: Adsorbent F- Rejection efficiency vs time (min)

Adsorbent C is treated by 0.01M ZnCl2 and burnt at 250 °C for 2.5 hours. Adsorbent E is treated by 1M H2SO4 and burnt at 250 °C for 3 hours. Adsorbent F is treated by 1M H2SO4 and burnt at 300 °C for 3 hours. The graph shows the removal efficiency of amine at specific time; which corresponds at precise time, how many concentration of MEA left in the system.

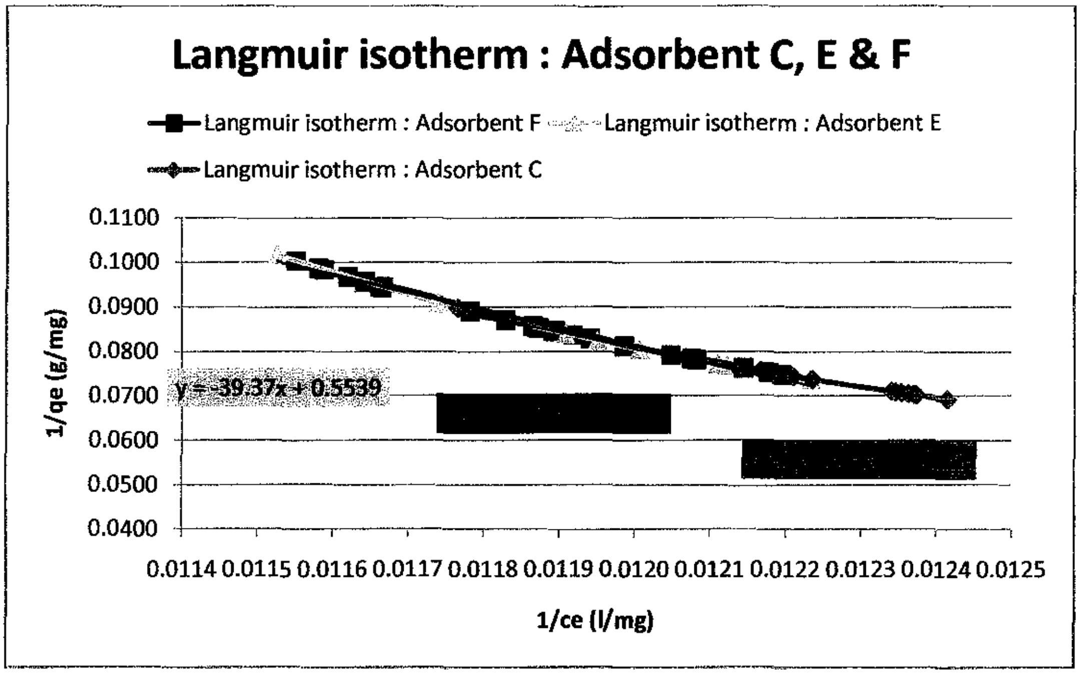
This result analysis is done via high performance liquid chromatography (HPLC). Previously, other chemical analysis equipments had been used however the result is not reliable due to some causes. By using UV-Vis, concentrations detected are increasing by time. This is opposing the nature of adsorption. The main cause of this situation is due to colour or dye occurrence by the degradation of adsorbent after certain time. Thus, turbidity of artificial wastewater increases next affecting the light diffraction inside UV-Vis. Column used for HPLC is YMC Polymer C18 S-6UM which suitable to be used for amine Adsorbent type. The solvent used are mixture of sodium hydroxide and sodium hydrogen phosphate at concentration of 100mM with ratio of 4 to 6. This mixture of solution acted as mobile phase inside the column.



Graph 4.11: RE – Comparison of adsorbents in batch mode operation

From the graph above, all adsorbents which went through for batch mode has same pattern of removal efficiency. At first, removal shooting at highest until they reach points where the removal get declining at lastly reach plateau pattern. From the three adsorbents, adsorbent C shows the best RE followed by adsorbent E and F. The removal of amine is at range of 20 to 10 percent. This amount might be increased by increasing the amount of adsorbent in the system. In this mode of operation, only 0.2020 g of adsorbent is poured into a 150 mL system. Theoretically, by increasing it 5 times, the removal of amine could reach 100 to 90 percent. The graph shows plateau pattern because adsorbent has reached the saturation limit. In the earlier stage, RE is shooting at highest due to the availability of active sites on the adsorbent. Solute (MEA molecules) were competing each other to be absorbed by the adsorbent. However, the competition gets harder when there is limitation of active sites left on the adsorbent. Therefore, adsorbent treated with $ZnCl_2$ shows better removal efficiency followed by adsorbent treated with H_2SO_4.

4.4 Modeling into Langmuir isotherm



Graph 4.12: Langmuir isotherm modeling

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

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

$$y = mx + c$$

$$c = \frac{1}{q_m},\ m = \frac{1}{q_m K_L}$$

ADSORBENT	**Slope, $m = 1/q_m K_L$**	**$K_L = 1/mq_m$**	**$1/q_m$**	**q_m**
C	30.749	0.01464	0.45	2.2207
E	39.37	0.01356	0.534	1.873
F	39.556	0.01405	0.556	1.7989

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5. CONCLUSION AND RECOMMENDATION

Treated rice husk ash (RHA) is a potential alternative of activated carbon and as adsorbent for removal of amine contaminants (monoethanolamine, MEA) from industrial effluent. By modifying it physically, chemically or both, different results of efficiency in removing contaminants in industrial effluent could be achieved. Carbon content on the rice husk ash varies as temperature and time exposure of burning is varied. On the other hand, functional groups on the adsorbent; rice husk ash will decide on exchanging of cation with the contaminants cation groups. In short says, chemical activation on rice husk has created and improved the surface chemistry of the adsorbent.

Comparing the two adsorbents tested in continuous mode, breakthrough time for adsorbent A is slower compared to B. Both adsorbents are treated by NaOH at 0.5M. Adsorbent A is burnt at 250 °C while B at 500°C. This shows that RH burnt at 250°C is better to develop the adsorbent than at 500 °C. From FTIR analysis, carbon content on RH burnt at higher temperature is lesser. This is due to carbon is loss during the oxidation process in furnace. Thus, 250 °C is an ideal condition to prepare activated carbon from RH. As for Adsorbents tested by batch mode, rice husk treated by $ZnCl_2$ gives better amine removal than H_2SO_4 treated adsorbent.

In order to improve this research studies, ample time is needed in order to properly plan and implement this project. The adsorbent development phase takes long time from the whole schedule. Since time given is quite constraint, less section of parameter could be studied. Other than mode of operation, effects of concentration of amine, flow rate of injection, amount of adsorbents and type of amine too can be investigate. Thus, rejection efficiency of developed adsorbents can be analyzed thoroughly.

Next, particular ways of washing rice husk during chemical treatment phase is crucially need to be taken into account. Agricultural wastes; rice husk, rice bran, bagasse, or nuts consist of organic components. Thus, without proper cleaning process, they may produce dirt after transformed into activated carbon and passing through adsorption process.

In this research studies, percentage of removal is quite low due to the limiting factor of amount of adsorbent. In order to improve the removal performance, amount of adsorbent must be increased to 1g or more correspond to the method used in this project. Thus, removal of MEA would be convincing to public.

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APPENNDIX I: FTIR ANALYSIS

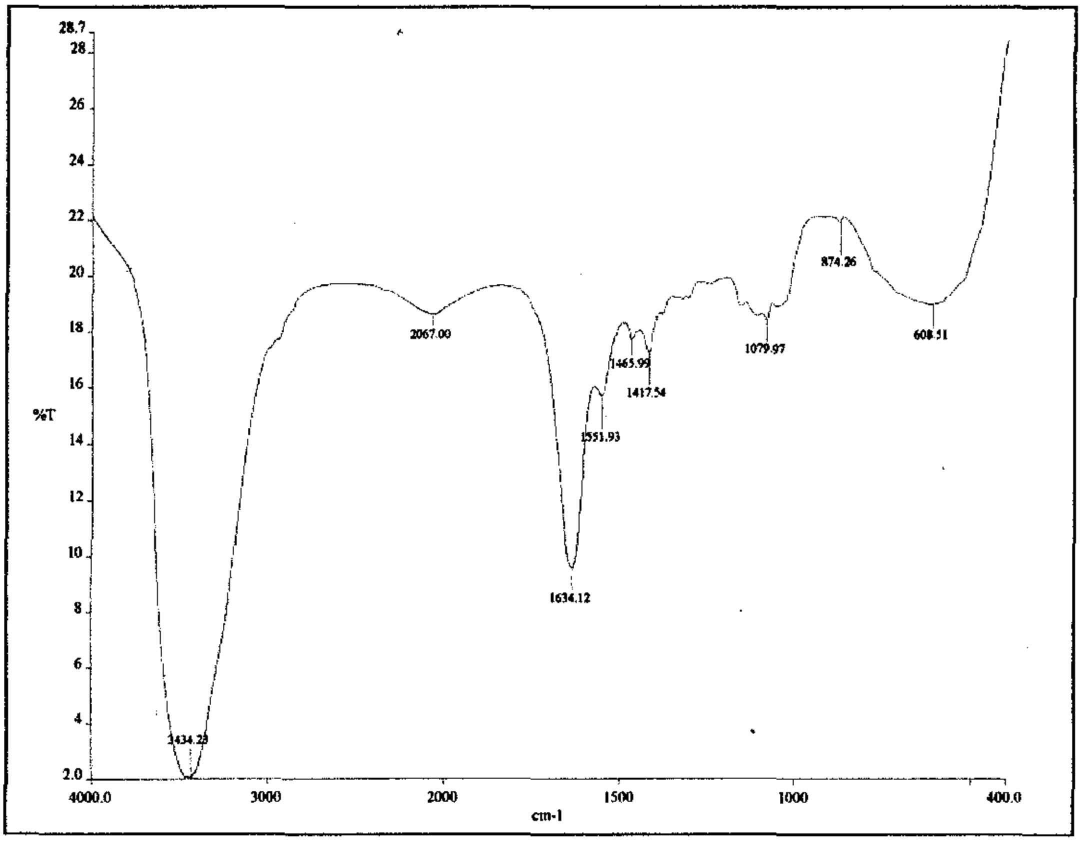

Figure A: Raw rice husk

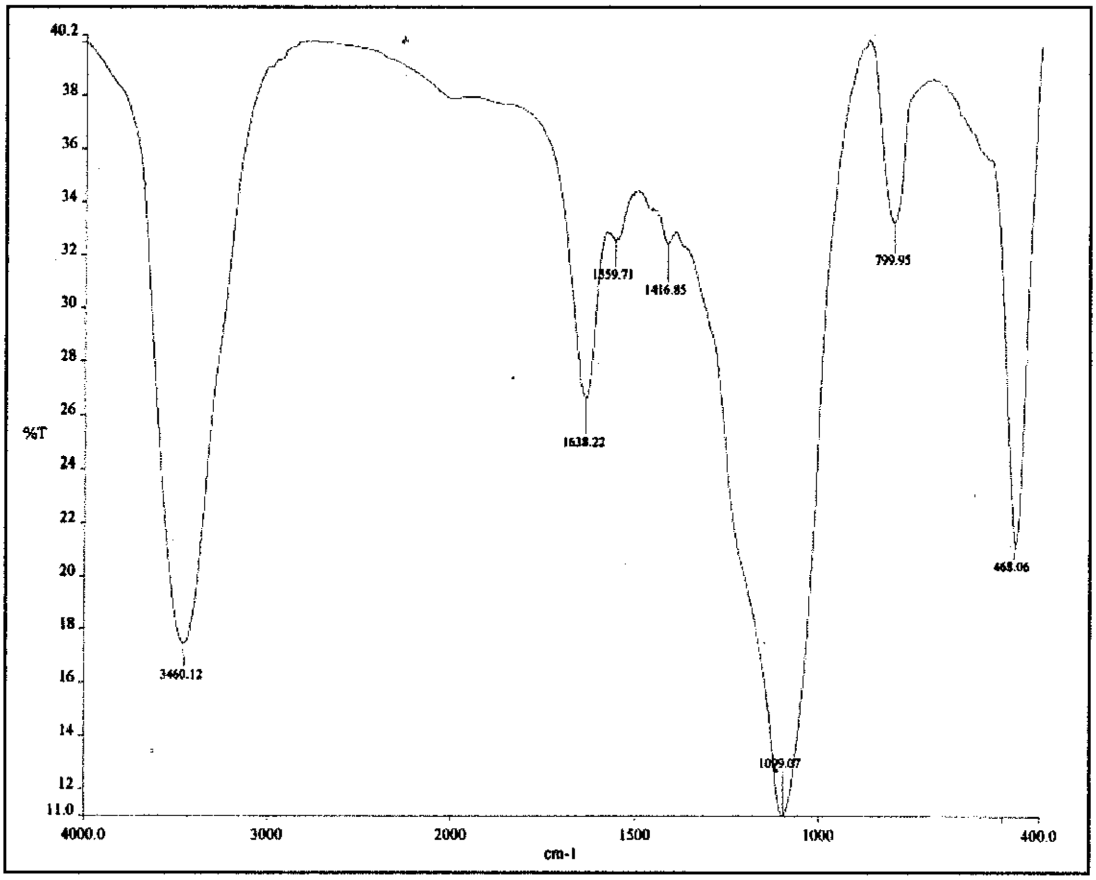

Figure B: RH 500°C, 3 HR

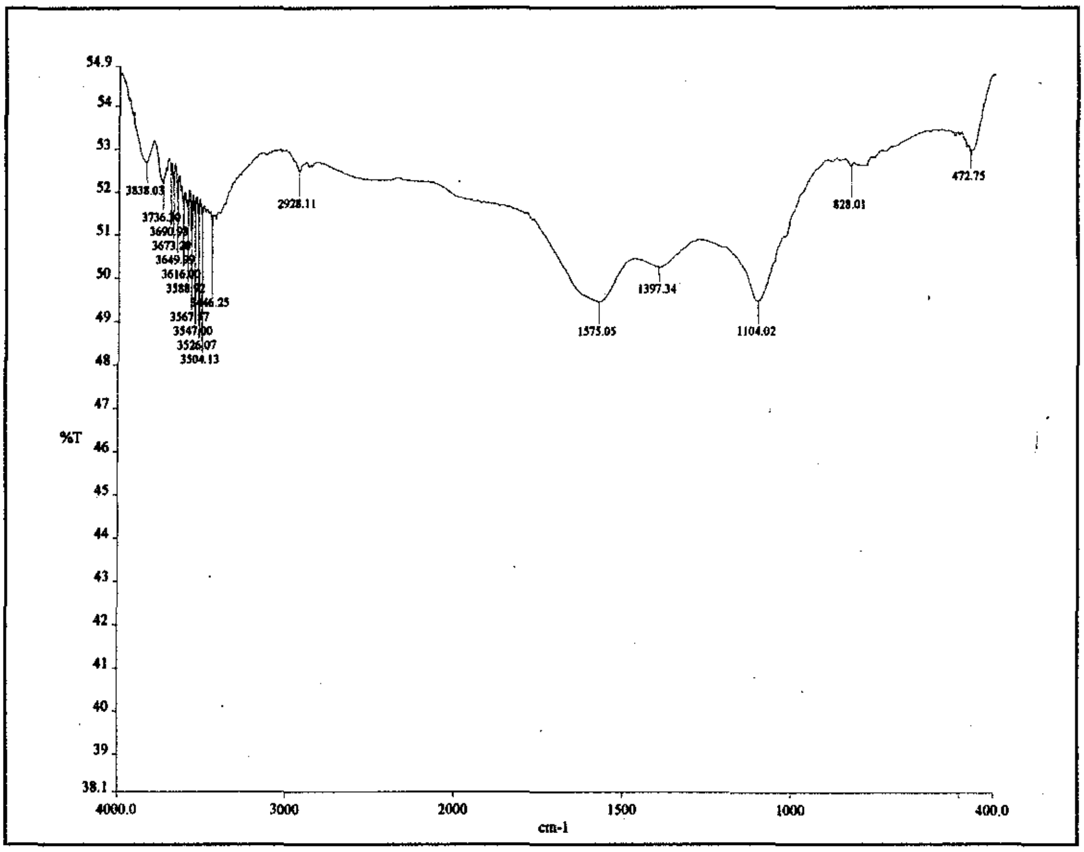

Figure C: RHA at 250°C for 2.5 hours treated with NaOH 0.5M

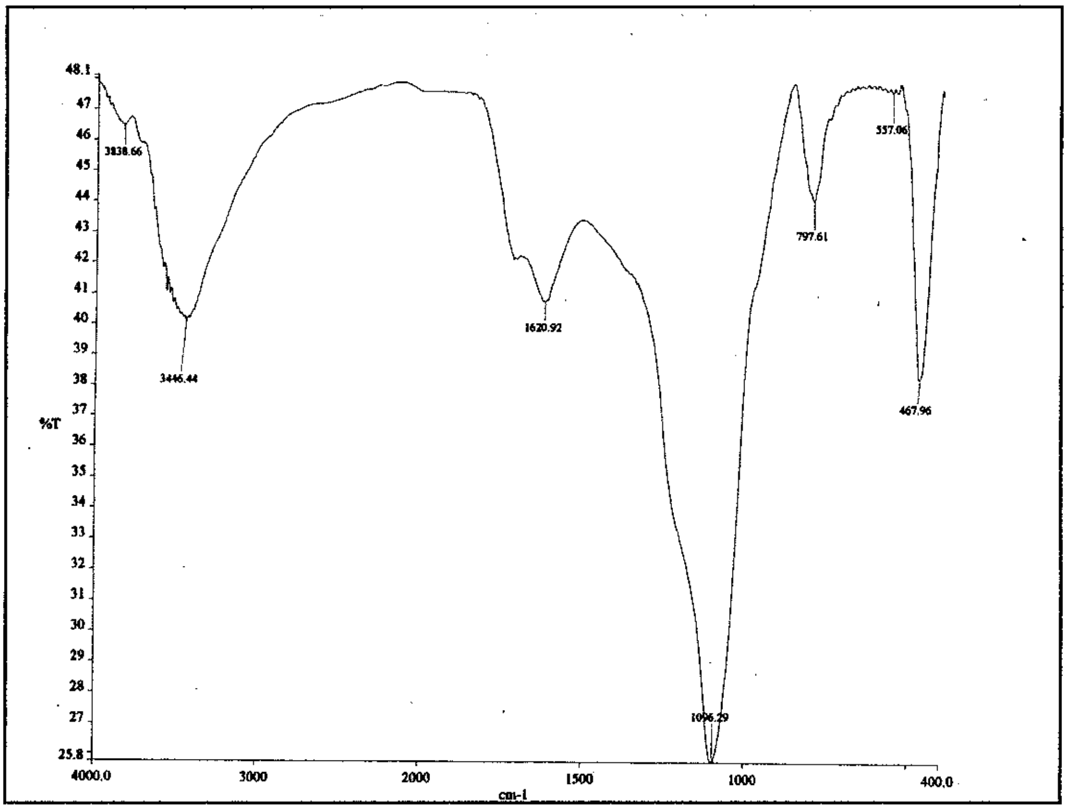

Figure D: RHA at 250 °C for 20 hours treated with NaOH 0.5M

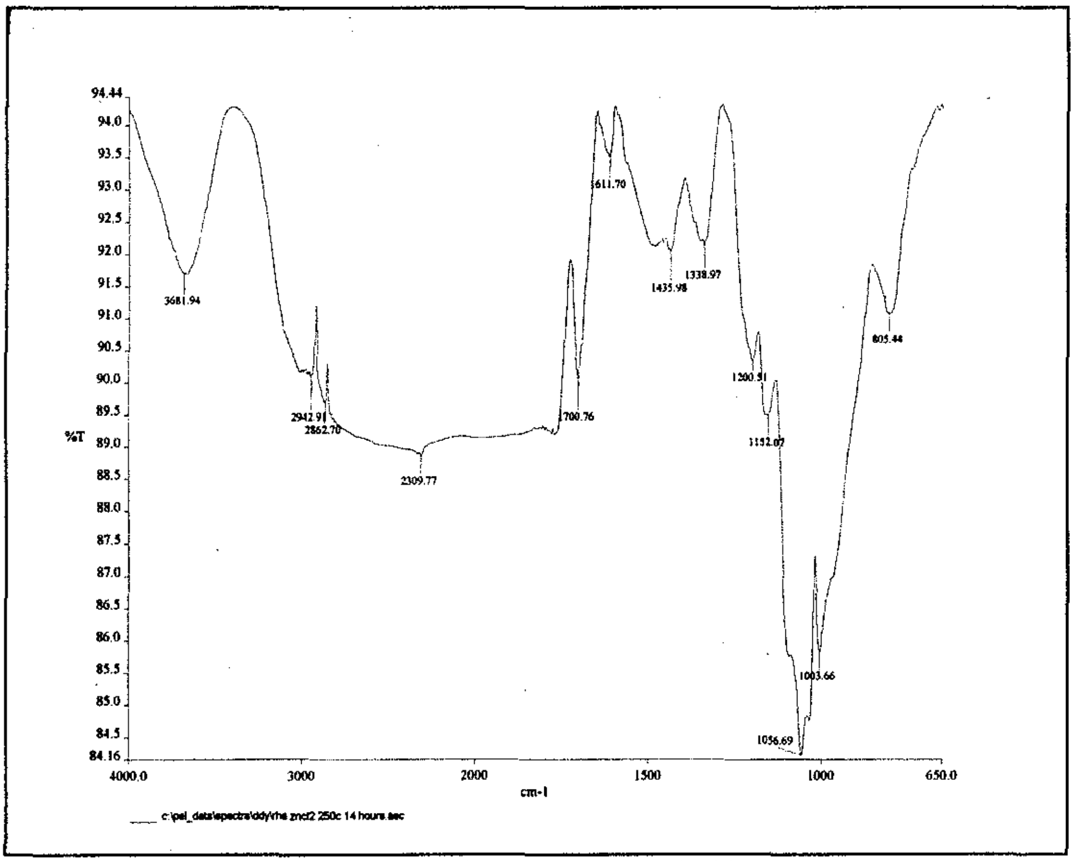

Figure E: RHA at 250 °C for 2.5 hours treated with ZnCl2 0.01M

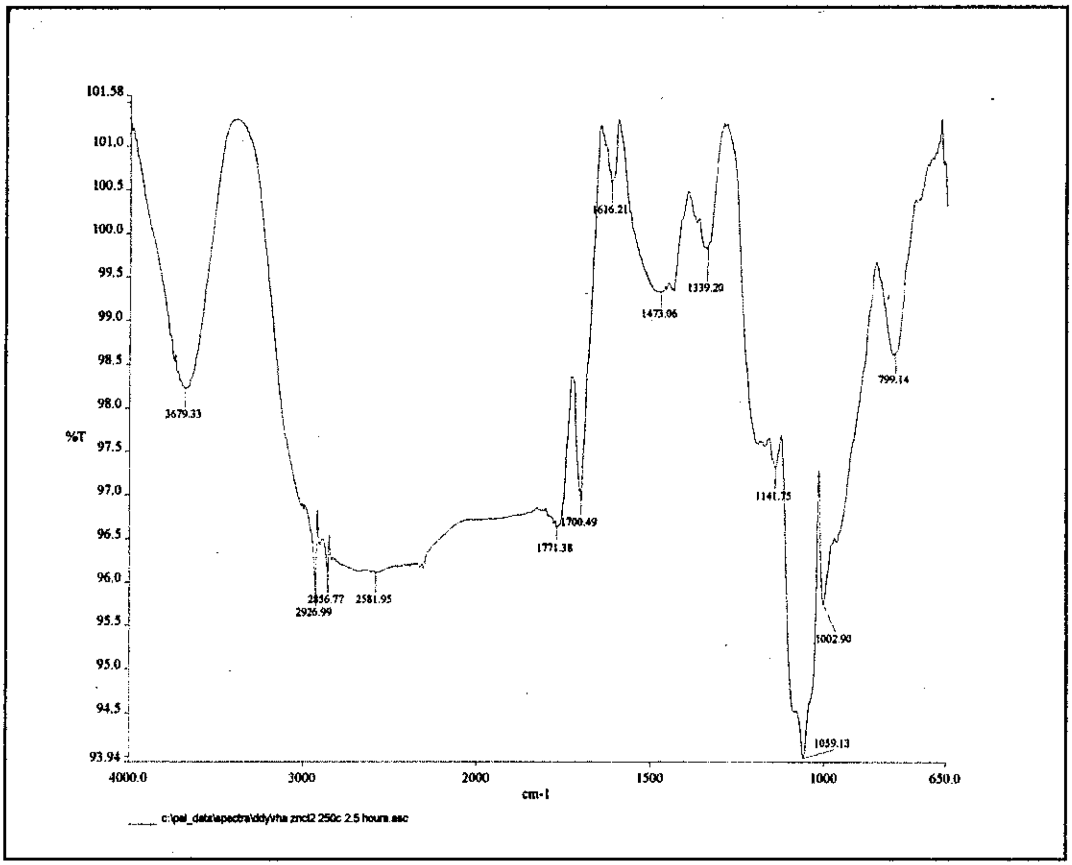

Figure F: RHA at 250 °C for 14 hours treated with ZnCl2 0.01M

APPENDIX II: SEM FIGURES

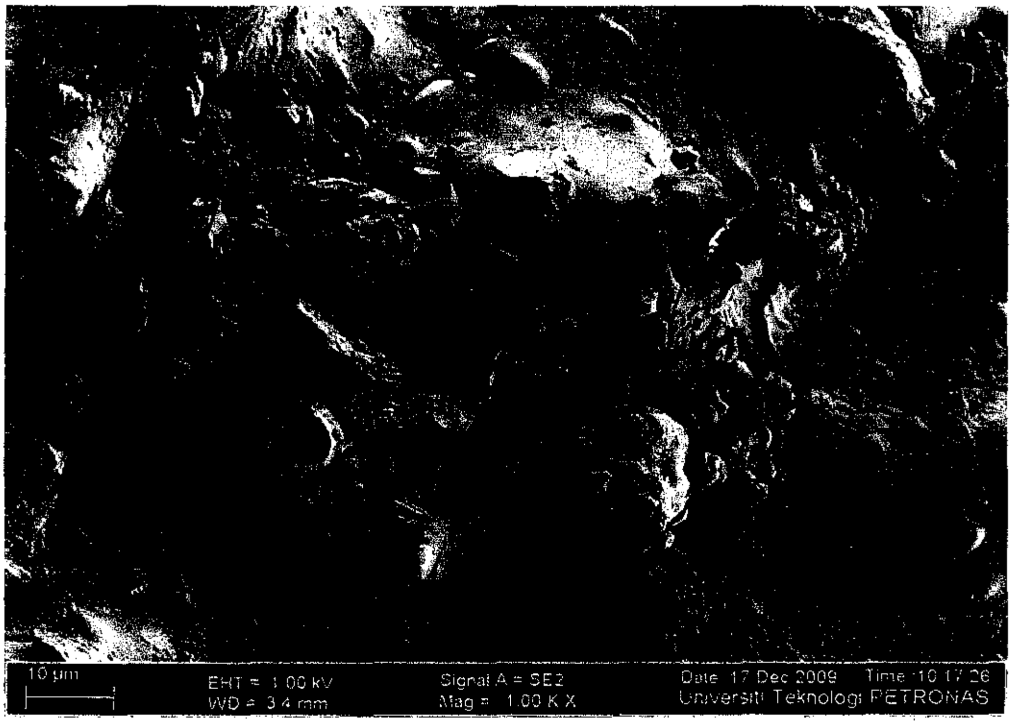

Figure G: Raw rice husk morphology

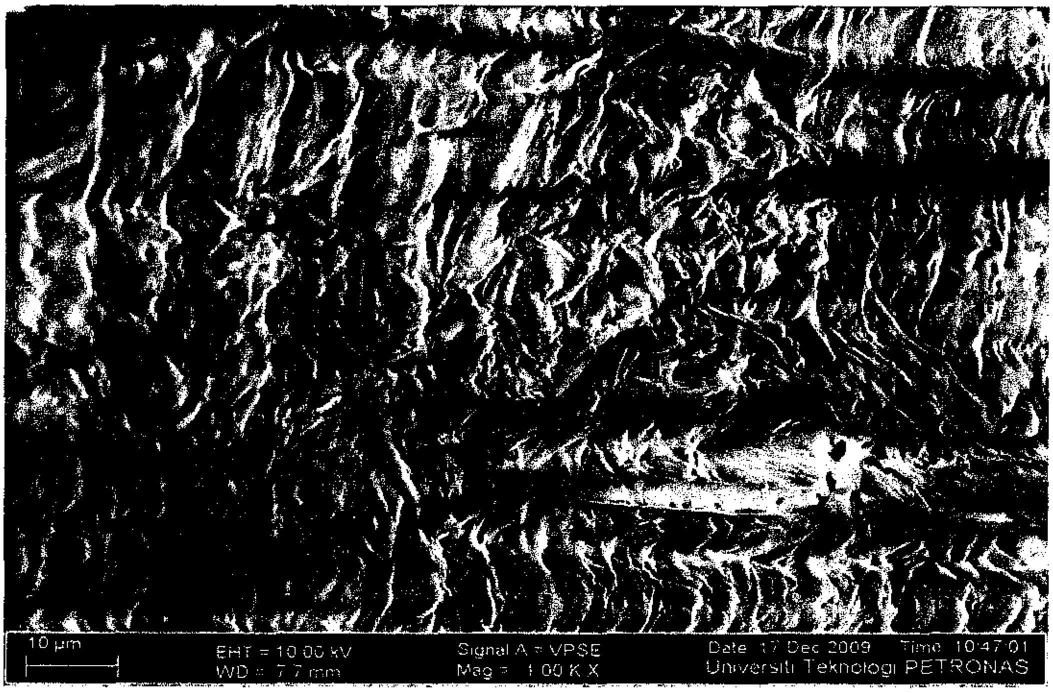

Figure H: Rice husk treated with NaOH

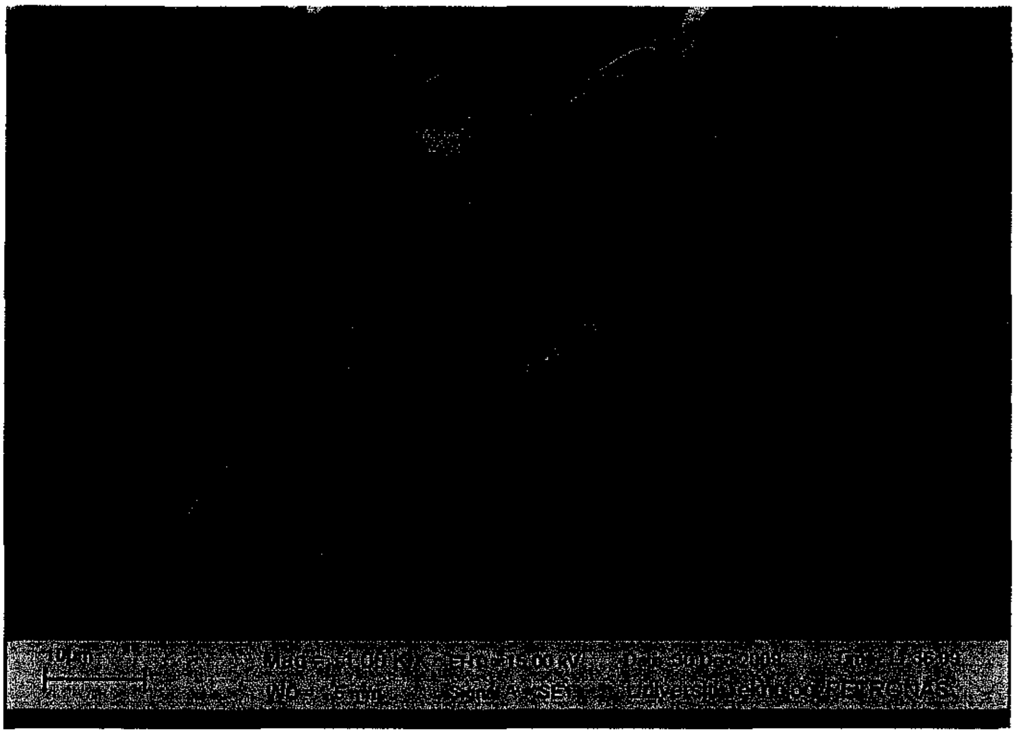

Figure I: Rice husk treated at 500 °C for 3 hours

APPENDIX III: GANTT CHART & KEY MILESTONES

Table A: Gantt chart and key milestones of FYP1

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13
1	Selection of project topic	▒	▒					Mid- Semester Break						
2	Preliminary research work		▒	▒	▒	▒								
	a) Research on literature review		■	■	■	■								
	b) Research on project methodology		■	■	■	■								
3	Submission of extended proposal defense						▒							
4	Proposal defense								▒					
5	Project work continues									▒	▒	▒		
	c) Getting workspace									■	■	■		
	d) Pre-treatment of RH									■	■	■		
6	Submission of interim draft report												▒	
	e) Treatment of RH (by physical)												■	
7	Submission of interim report													▒

Legend:

▒	Process
■	Milestone

Table B: Gantt chart and key milestones of FYP2

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								
	a) Adsorbent Preparation b) Test run performance c) Analysis of result																
2	Submission of Progress Report									▒							
3	Project Work Continues									█	█	█	█	█			
	a) Commencing test run b) Analysis of result																
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)																▒

Legend:

█	Process
▒	Milestone

APPENDIX IV: EQA 1974 (STANDARDS A AND B)

THIRD SCHEDULE

ENVIRONMENTAL QUALITY ACT 1974

ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS 1979

(REGULATIONS 8(1), 8(2), 8(3)

PARAMETER LIMITS OF EFFLUENTS OF STANDARDS A AND B

Parameter		Unit	Standard	
			A	B
(i)	Temperature	°C	40	40
(ii)	pH value	-	6.0 - 9.0	5.5 - 9.0
(iii)	BOD at 20°C	mg/ l	20	50
(iv)	COD	mg/ l	50	100
(v)	Suspended Solids	mg/ l	50	100
(vi)	Mercury	mg/ l	0.005	0.05
(vii)	Cadmium	mg/ l	0.01	0.02
(viii)	Chromium, Hexavalent	mg/ l	0.05	0.05
(ix)	Arsenic	mg/ l	0.05	0.10
(x)	Cyanide	mg/ l	0.05	0.10
(xi)	Lead	mg/ l	0.10	0.5
(xii)	Chromium Trivalent	mg/ l	0.20	1.0
(xiii)	Copper	mg/ l	0.20	1.0
(xiv)	Manganese	mg/ l	0.20	1.0
(xv)	Nickel	mg/ l	0.20	1.0
(xvi)	Tin	mg/ l	0.20	1.0
(xvii)	Zinc	mg/ l	2.0	2.0
(xviii)	Boron	mg/ l	1.0	4.0
(xix)	Iron (Fe)	mg/ l	1.0	5.0
(xx)	Phenol	mg/ l	0.001	1.0
(xxi)	Free Chlorine	mg/ l	1.0	2.0
(xxii)	Sulphide	mg/ l	0.50	0.50
(xxiii)	Oil and Grease	mg/ l	Not Detectable	10.0