Production of Activated Carbon from Rice Husk and Its Adsorption Characteristics for Phenol

by

Muhd Anis Mohd Arsad

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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Approved by,

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Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
November 2005

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 work except as specified in the reference and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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Muhd Anis Mohd Arsad

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ABSTRACT

The objective of this report is to discuss the adsorption studies of Activated Carbon produced from rice husks. The common effluent of phenol in wastewater from industries is 10ppm while the allowed amount by regulations is 1ppm. Adsorption promises to be the cheapest and efficient of filling up this need of reducing unwanted chemicals into the environment.

Three different studies were carried out: Effects of Different pH of Activating Rice Husks on Adsorption Capacity, Effects on Contact Time on Adsorption Capacity and Effect of Different Medium of Adsorption Tests on Adsorption Capacity.

3 different samples of 0.5g carbonized rice husks were activated at different pH, 1, 3, and 5. Each sample was placed in each phenol samples of the same concentration. The sample containing rice husks activated at pH 1 prevails. 85% of the phenol in the solution was adsorbed. This is an adsorption of 0.8466mg of phenol out of 1.0mg per 0.1g of Activated Carbon/Rice Husks. This is a ratio of 0.008466g phenol/g AC.

3 samples of rice husks activated at pH 3 were placed in solutions of the same concentration. The Activated Carbon samples were left to adsorb for 6, 18 and 24 hours respectively. An almost equilibrium was achieved after 18 hours. 52% of the phenol was successfully adsorbed after 24 hours. This is 25.648mg out of 50mg. This is a ratio of 0.051296g phenol/g AC.

3 samples of rice husks activated at pH 3 were used to test the best medium to adsorb phenol: stirrer, shaker and stagnant conditions. All were left in each medium for 24 hours. This test is a qualitative test instead of quantitative test like the previous 2 tests. The results displays of the same results for all three mediums. An around 50% of phenol in the 3 samples managed to be adsorbed.

Conclusively, the objectives of this study was achieved and fulfilled.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

A number of studies on converting rice husk to activated carbon have been reported. Rice husk is agricultural waste, accounting for about one-fifth of the annual gross rice, 545 million metric tons of the worlds. As the demand using renewable resource for alternatives is rising rapidly with the decrement of renewable resource, the studies done on the potential of the rice husk is considered to be very essential and important.

Before it can be used as an adsorbent, a few methods have been identified to treat this rice husk. These treatment processes include the activation of the rice husk. There is no exact method has been proven to produce a high performance adsorbent from rice husk. The previous studies conducted show that the rice husk needs to be activated with acidic or basic solution. However, there are no studies done to compare between these two types of digestion solution on the rice husk.

There are no exact explanations of how the rice husk particles form its binding with its adsorbates. However, the formation of the surface complexes is most likely to be related to the predominant silica content of the samples. This is where the activation process takes place. The digestion process reduces the organic constituents and produced a highly porous cellulose-silica material which has a relatively good adsorptive in removing phenol. In all cases, rice husk is carbonized in an inert atmosphere (nitrogen or argon) in order to remove volatile matter.

1.2 PROBLEM STATEMENT

In wastewater treatment, the adsorption process is effective in the removal of organic matters at trace level. Conventional waste treatment methods like coagulation, chemical oxidation have not been successful because these methods are stable to organic matters, while adsorption has come out as the cheapest, most profitable and most efficient one. A lot of studies have been done in using the environmental waste as a potential adsorbent in removing organic matters, including studies on converting rice husks to activated carbon as the potential adsorbent. As Malaysia is rich with paddy, a thorough study in converting the rice husk to activated carbon will give a lot of advantage to the country.

The common amount of phenol content in wastewater in industries is around 10ppm. The allowed amount of phenol in wastewater into the environment is 1ppm [1]. With this stringent regulation, an economically feasible producible adsorbents need to be produced fast. In order to do this, the characters and behaviors of these adsorbents need to be known and investigated first. This way, these adsorbents can be applied to its maximum efficiency in the industries.

1.3 OBJECTIVES AND SCOPE OF STUDY

In order to complete this project within the time limit and scope given, three objectives have been identified as follows:

i. To activate rice husks by different pH solutions and determine its effects on the adsorption capacity of the Activated Carbon

ii. To determine which adsorption tests mediums is the most efficient among the shaker, stirrer and leaving the sample stagnant.

iii. To determine the effect of contact time on the adsorption capacity of the Activated Carbon

CHAPTER 2

LITERATURE REVIEW AND/OR THEORY

2.1 ADSORPTION STUDIES AND TESTINGS

Adsorption testing or studies of phenol is not a new topic. Various varsities and institutions have ventured into researching activated carbon produced from rice husks, particularly, to find the best conditions for the adsorption process to occur. Activated carbon from other types and form of carbon sources are also being actively researched all around the world specifically in developing countries. This is due to the abundance of agricultural waste available in these types of countries as agriculture is still one of the main economic engines for the population of these places.

Generally, adsorbents adsorb adsorbates with its micropores. The channel leading to these micropores are the opening of micropores, called the macropores. The corridors leading these macropores to the micropores are called the mesopores. For proper adsorption of phenol to occur, it is obvious that the openings of the macropores of the activated carbons, the mesopores and finally the micropores must be able to contain phenol. A direct way to ensure this is to have macropores, mesopores and micropores large enough to trap and hold phenol. An Activated Carbon usually has a few adsorbing spots. The bigger and more accessible these macropores, mesopores and micropores to the phenol molecules, the better adsorbents these Activated Carbon would make. A proper definition of macropores and mesopores respectively are as below:

- Macropores - provides accessible path for reactants to diffuse from outer surface pellet to the mesopores.
- Mesopores - provides a medium for preparing well-dispersed, small crystallites of metal. It also prevents migration and agglomeration of metal crystallites at high temperature.

Adsorption can be classified into two categories:

1. Physisorption
2. Chemisorption

Adsorption of phenol using Activated Carbon produced from rice husks is considered as physisorption. The main difference between the above classifications is that chemisorptions are much more appropriate for involvement of catalysts. This means that the chemical or substance adsorbed would be released later as a different object or product. For physisorption on the other hand, the chemical or substance adsorbed would be released later when the adsorbents are being regenerated as it is. Chemisorptions would not require any additional condition changes for it to release the chemicals or substances. These two types of adsorptions however shares about the same mechanism as follows from adsorbing to desorbing:

1. Bulk diffusion of adsorbate to the external adsorbent surface
2. Diffusion of adsorbate through porous network
3. Adsorption of adsorbate onto adsorbent surface
4. Desorption of adsorbate molecules from the surface. For physisorption, this process is termed as regeneration. Examples of regeneration includes by temperature increment and pressure reduction.
6. Diffusion of adsorbates through porous network to the pore mouth
7. Bulk diffusion of adsorbate from external surface through the stagnant gas film to the bulk gas stream

In a much obvious manner, the physicochemical of preparing the adsorbents or the manner the adsorption process is being carried out are studied. This is to know the conditions that encourages or supports the adsorbents in adsorbing phenol from any solution. These are the stimulation that would be applied in the industries for maximum performance of Activated Carbon produced from rice husks to adsorb phenol from its wastewater.

Thus, to produce an Activated Carbon with adsorption sites larger than the diameter of phenol and conditions that makes these adsorption sites more attractive to the phenol molecules would be the aim of the testing and studies to be done.

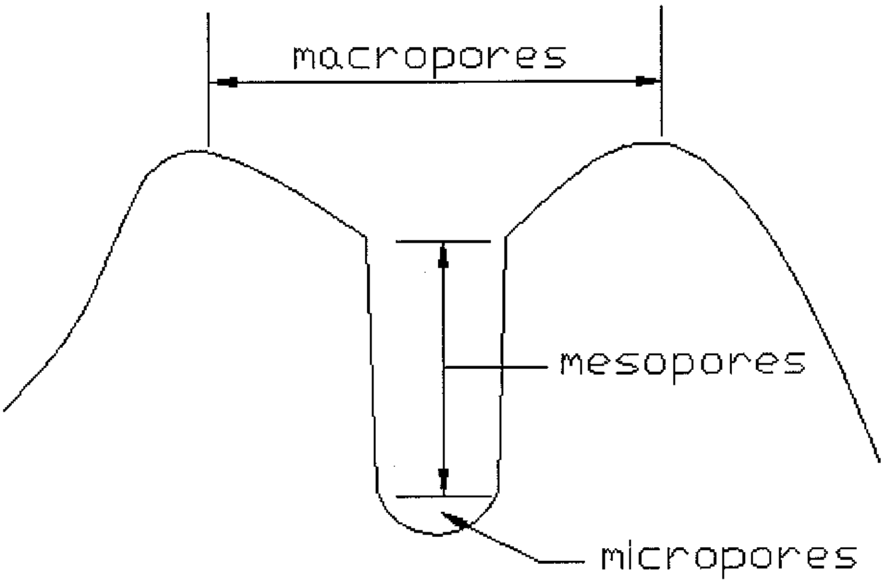

Figure 1: Macropores, mesopores and micropores

Phenol has a large amount of applications in the current existing industries. This makes this study much more relevant and meaningful. This also means that existence of phenol can be expected in the plant wastewater. Examples of such industries includes refineries, manufacture of phenol formaldehyde plastics e.g., Bakelite and production of cyclohexanol which is required for the production of Nylon. [2]

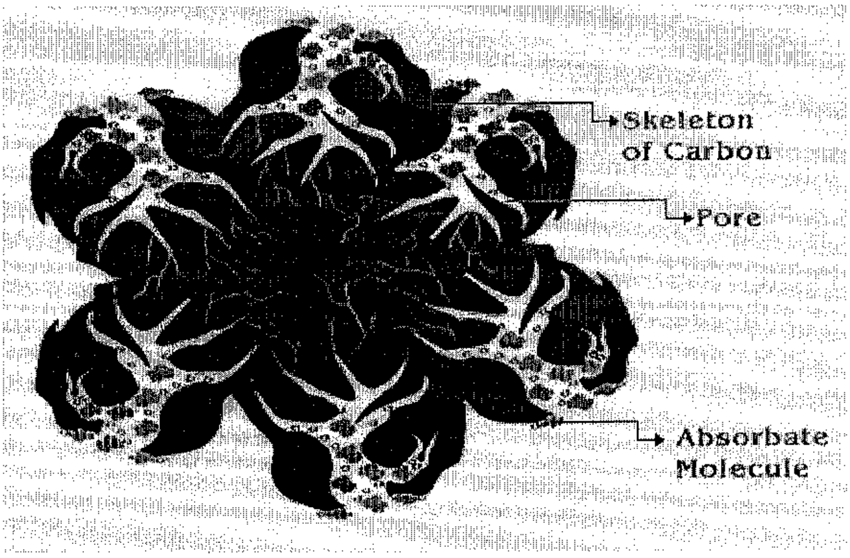

Figure 2: Structures of Activated Carbon

Hazards of symptoms of phenol include fire: combustible, explosion: above 78°C explosive vapour-air mixtures may be formed, inhalation: pungent, sore throat, coughing, shortness of breath, laboured breathing, dizziness, dullness, unconsciousness, skin: corrosive, may be absorbed, redness, pain, serious skin burns, eyes: corrosive, redness, pain, blurred visions and ingestions: corrosive, abdominal pain, vomiting, diarrhoea. [3]

Known studies done on adsorption of phenol using Activated Carbon derived from Rice Husks:

1. Effects of Contact Time of adsorbents and phenol solution on adsorption capacity of adsorbents
2. Effects of Adsorbent Amount during adsorption process on adsorption capacity of adsorbents
3. Effects of Initial pH of solution on adsorption capacity of adsorbents
4. Effects of Adsorbent Sizes of adsorbents on adsorption capacity of adsorbents
5. Effects of Chemical Agents used to activate adsorbents on adsorption capacity of adsorbents

6. Effects of Carbonization Temperature used to carbonize adsorbents on adsorption capacity of adsorbents
7. Effects of Carbonization Duration of carbonizing adsorbents on adsorption capacity of adsorbents

All of these tests may have been done by different methods, for example, using different amount of adsorbents and adsorbate. However, its end interest is still similar which the difference in phenol concentration initially and finally. Due to this difference and personal expression, a converging formula has to be used so as to be able to compare all the data from all the different sources fairly. All of these tests were derived from different sources. Understandably, all these data were expressed accordingly to its sources' choice.

$$\text{Removal Efficiency} = \frac{(\text{Final Concentration} - \text{Initial Concentration})}{\text{Initial Concentration}}$$

2.1.1 Effects of Contact Time on Adsorption Capacity of Adsorbents [4]

Table 1: Contact Time Studies Important Parameters

Physicochemical Properties	**Rice Husk**	**Rice Husk Ash**
pH	7	7
Initial Phenol Concentration (μg/L)	150	700
Amount of Rice Husk/Ash (g)	5	0.12
Equilibrium Time Taken (h)	6	3

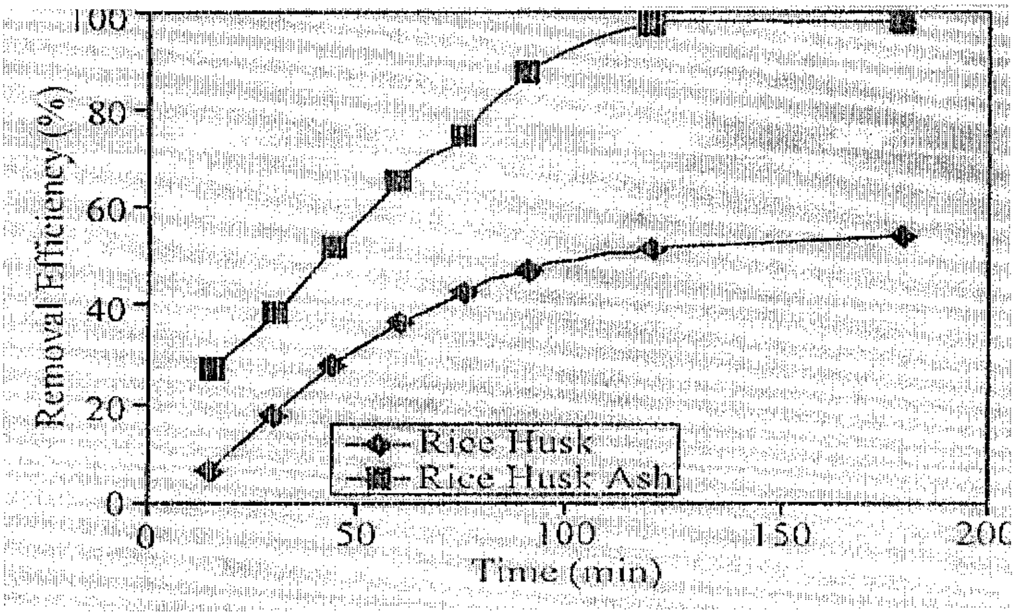

Figure 3: Graphs of Removal Efficiency VS Contact Time

From the graph above, the removal efficiency of rice husks ash is almost 100% while that of rice husks alone is around 40% only. Rice husks ash refer to carbonized rice husks which were is used in these studies, and it is not activated. As the table above states, it took 3 hours for rice husks ash to adsorb the phenol content of the solution and 6 hours for rice husks to reach equilibrium only.

The above experiment shows that the adsorption process actually occurs in a speedy manner, especially in the first 2 hours for the rice husk ash. This is because that is the period where the largest amount of phenol is being adsorbed. Rice husks ash is also shown as the better adsorbent compared to rice husks alone. Rice husks ash requires less residence time. Another obvious conclusion would also be that the longer the contact time of the adsorbents to the phenol solution, more adsorbate can be adsorbed. Numerically, it takes 3 hours for 0.12g of rice husks ash to adsorb

$$0.7\text{mg/L} * 0.1\text{L} = 0.07\text{mg of phenol}$$

0.7mg/L being the initial concentration of phenol used for the adsorption test and 0.1L is the volume of beaker used to run the test. From these values, future experimenters can estimate the maximum time required to adsorb a certain amount of phenol using a specified amount of rice husk ash or activated carbon.

The ratio of phenol adsorbed to the amount of rice husk ash is thus

0.07mg of phenol/0.12g rice husk ash = 7.0 X 10^{-5}g of phenol/0.12g rice husk ash

= 5.833 X 10^{-4} g phenol/g rice husk ash

This ratio can be taken as a standard for the relation of both phenol and rice husk ash.

2.1.2 Effects of Adsorbent Amount on Adsorption Capacity of Adsorbents [4]

Table 2: Adsorbent Amount Studies Important Parameters

Physicochemical Properties	Rice Husk	Rice Husk Ash
pH	7	7
Amount of Rice Husk/Ash (g)	1-7	0.1-0.5

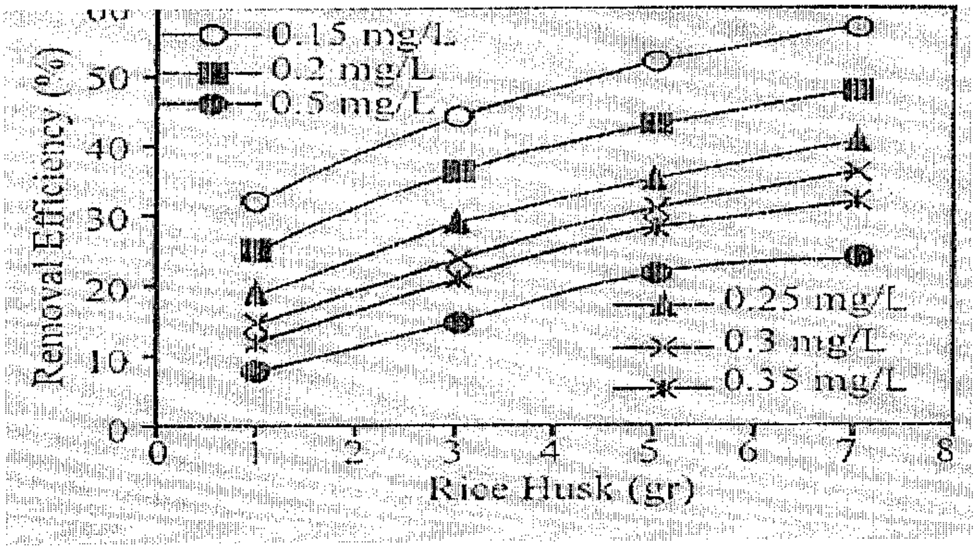

Figure 4: of Removal Efficiency VS Amount of Rice Husks

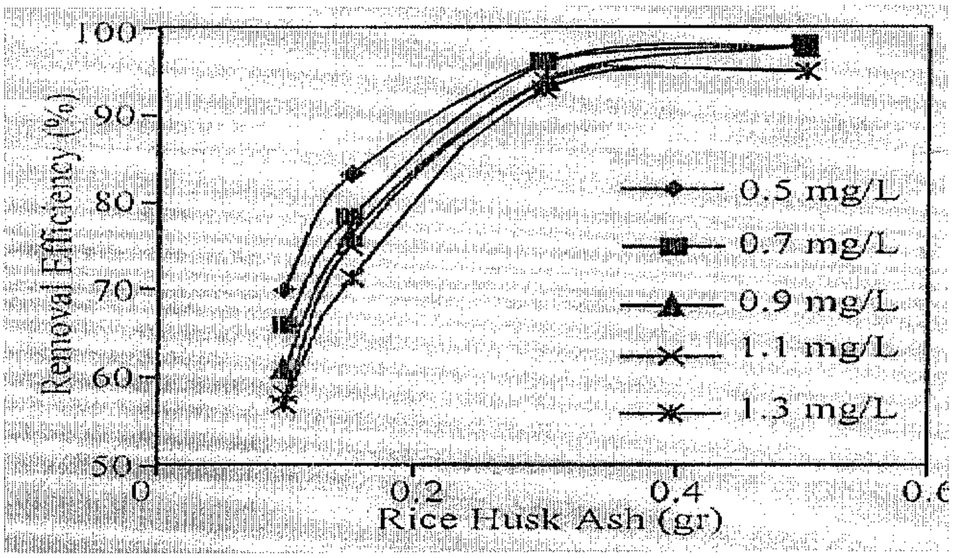

Figure 5: Graphs of Removal Efficiency VS Amount of Rice Husk Ash

The graph above shows for example, for a phenol solution of 500μg/L in a 100mL beaker, a minimum dosage of 0.3g rice husk ash is required to remove at least 96% of the phenol. It would require 5g of rice husks to remove 50% of a 150μg/L. Again, rice husk ash proves to be a better adsorbent compared to its natural state. The results also indicate clearly that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible, particularly for rice husks ash. Notice the converging point at the higher end of removal efficiency and higher amount of rice husk ash. The graphs also reflect that more adsorbents would adsorb more phenol, as expected. The graphs of rice husk ash are much steeper than that of rice husk alone. This means that a little difference in rice husk ash amount would bring a drastic performance in the adsorption process. This cannot be said with rice husks. 0.5g of rice husk ash would remove almost completely phenol solution of concentration 500μg/L in a 100mL beaker. This would be about

$$0.5\text{mg/L} * 0.1\text{L} = 0.05\text{mg}$$

of phenol. The above tests are done without considering the time factor. However, judging by the amount of rice husk ash used and the amount of time taken to completely remove phenol from the solution, it can be gauged that the time is shorter than the previous study, which is somewhere below 3 hours. Referring to the section before this, 70μg/L of phenol was successfully adsorbed in 3 hours using rice husk ash just by using 0.12g of rice husk ash. Combining these two types of information, the performance of the adsorbents can be improved by manipulating both types of physicochemical parameters.

Another obvious observation that can be made from the graphs above is the easiness to adsorb phenol of a lower concentration compared to a higher one. This is because that there are simply less phenol to be adsorbed compared to those at a higher concentration. Using the same amount of rice husk and rice husk ash, the amount of phenol able to be adsorbed decreases gradually as the concentration of phenol increases.

The ratio of amount of phenol adsorbed to the amount of rice husk ash is:

$$0.05\text{mg of phenol}/0.5\text{g rice husk ash} = 5.0 \times 10^{-5}\text{g of phenol}/0.5\text{g rice husk ash}$$
$$= 1.0 \times 10^{-4}\text{g of phenol/g rice husk ash}$$

2.1.3 Effects of Initial pH on adsorption capacity of adsorbents [4]

Table 3: Initial pH Studies Important Parameters

Physicochemical Properties	**Rice Husk**	**Rice Husk Ash**
pH	Various	
Initial Phenol Concentration (μg/L)	200	
Amount of Rice Husk/Ash (g)	3	0.5

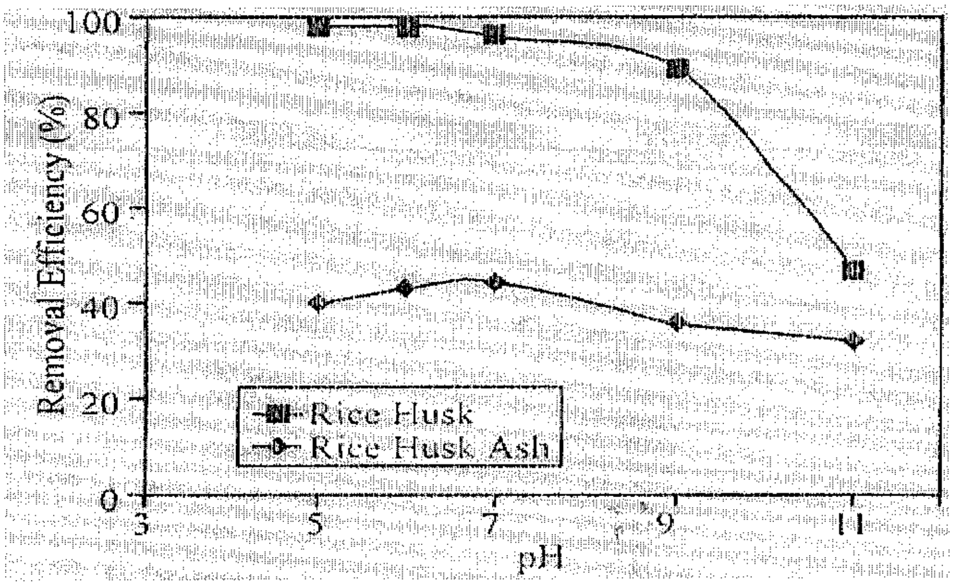

Figure 6: Graph of Removal Efficiency VS pH of solution

The results from the graph above show that with increasing initial pH, the amount of phenol adsorbed decreases. No time factor was considered. This means that the experiments were meant to see the maximum amount of phenol that can be adsorbed for each pH. For acidic pH, rice husk ash can adsorb phenol to an almost 100% removal. This denotes that pH of lower than 7 truly supports the adsorbents in adsorbing phenol. Once the pH crosses the neutral pH of 7, the removal efficiency steeply decreases. The removal efficiency for rice husk at every pH shows relatively not much difference. However, it does gradually show adsorption testing at a lower pH could adsorb phenol better than those in a higher pH.

The main difference between rice husk and rice husk ash is that rice husk ash is carbonized rice husk. From the above results, it is shown that rice husks need to be carbonized to be a better adsorbent. More about this would be discussed in a later section. When rice husks are carbonized, its surface area and micropores are increased, despite its overall volume is decreased from rice husk to rice husk ash or activated carbon. This can be easily imagined as rice husk itself has no or less lineage structure on its surface area. The network and structure of the links of macropores are also formed during carbonization.

Thus, at pH 5, 0.5g of rice husk ash would adsorb

$$0.2\text{mg/L} * 0.1\text{L} = 0.02\text{mg of phenol}$$

The ratio of phenol adsorbed is:

$$0.02\text{mg of phenol/0.5g rice husk ash} = 2.0 \times 10^{-5}\text{g of phenol/0.5g rice husk ash}$$

$$= 4.0 \times 10^{-5}\text{g of phenol/g rice husk ash}$$

Adsorption of phenol from aqueous solution is directly dependent on pH. pH affects the adsorption process by:

1. surface charge of the adsorbents
2. degree of ionization of adsorbate
3. speciation of adsorbate

The degree of ionization of phenol can be estimated using the following formula:

$$\Phi_{\text{ions}} = 1/ [1+10^{(\text{pKa} - \text{pH})}]$$

For example, we take conditions at two pHs, 1 and 5, to demonstrate the above formula.

For pH=1,

$$\begin{aligned}\Phi_{\text{ions}} &= 1/ [1+10^{(10 - 1)}] \\ &= 1/ [1+10^{9}] \\ &= 1/ [1 + 1000000000] \\ &= 1/ 1000000001 \\ &= 9.99 \times 10^{-10}\end{aligned}$$

For pH=5,

$$\begin{aligned}\Phi_{\text{ions}} &= 1/ [1+10^{(10 - 5)}] \\ &= 1/ [1+10^{5}] \\ &= 1/ [1+100000] \\ &= 1/ 100001 \\ &= 9.99 \times 10^{-6}\end{aligned}$$

As can be seen from the two calculations above, the degree of ionization of phenol is much lower at a lower pH. pKa for phenol is approximately 10 and phenol can be considered as a weak acid. It releases the H^+ ion instead of OH^- in aqueous solutions. This means at higher pH, phenolate ions exist instead of phenol molecules in the aqueous solutions. This alone already defeats the purpose of the whole experiment which is to adsorb phenol. Another factor to take note is at higher pH, the aqueous solution is filled with OH^- ions. Phenol is governed by its cyclic ring with circle of electrons in the middle. This makes phenol an overall negative behaving molecule. Thus, there will be constant repulsive force between phenol or phenolate ions and OH^- ions. This makes the condition in the aqueous solution very chaotic and unstable among the ions and prevents the adsorption of phenol and phenolate ions by the adsorbate. Furthermore, since phenol is a weak acid, at higher pH, it would tend to react with the base to form salts.

pH also affects the surface properties of the adsorbents, for example its surface charge. At very low pH, the surface of the adsorbent would be surrounded by hydronium ions. This enhances the phenol interaction with the binding site of the adsorbent with dipole-dipole forces of attraction. The figure below gives a simple idea of the stated point. As mentioned before, phenol is mostly governed by electrons circle. With positive charge of the Activated Carbon or adsorbents, it is logical and straightforward that the hydronium ions can be used to attract phenol.

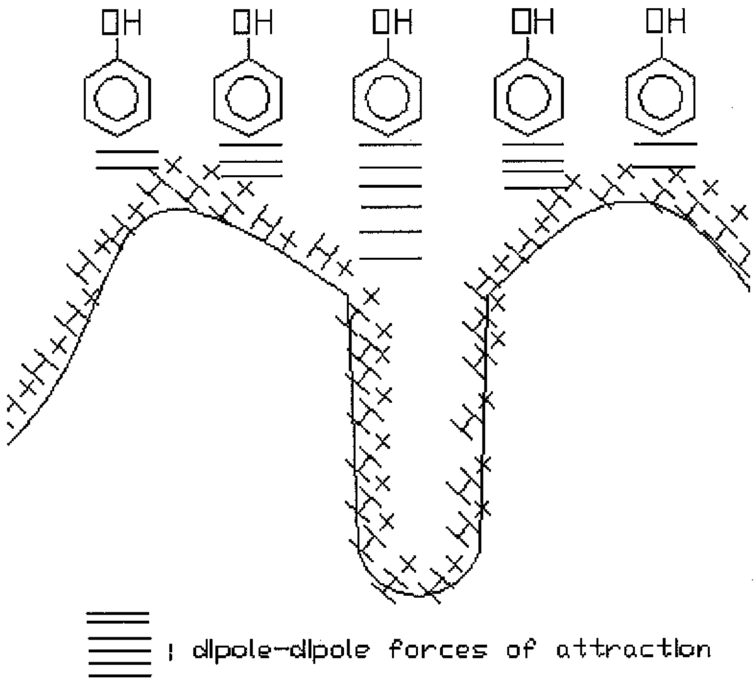

Figure 7: Activated Carbon in Acidic Solution

2.1.4 Effects of Adsorbent Sizes on adsorption capacity of adsorbents [5]

Table 4: Different Sizes Adsorption Studies Important Parameters

Physicochemical Properties	Rice Husk Activated Carbon
Amount of Activated Carbon(g)	0.5
Duration of Adsorption Test(h)	24
Sizes of Activated Carbon Tested(mm)	<1, 1-2, 2<
Activating Agent Used	$ZnCl_2$ or NaOH
Activation Duration(h)	24
Carbonization Temperature(°C)	500
Carbonization Duration(h)	1

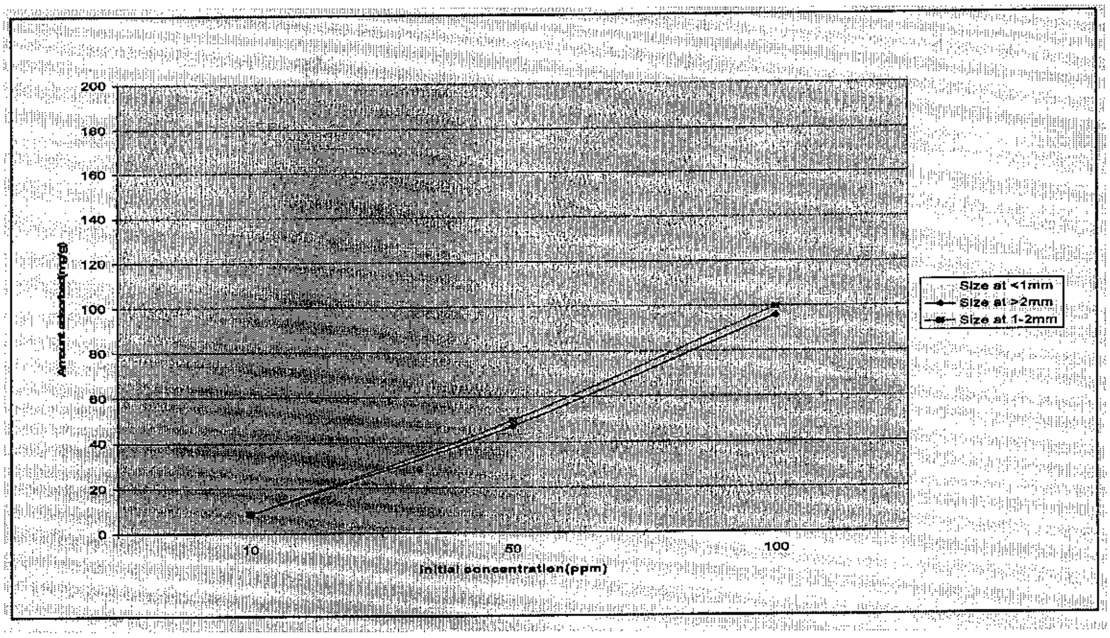

Figure 8: Graph of Amount Adsorbed against Initial Concentration for Activating Agent ZnCl2

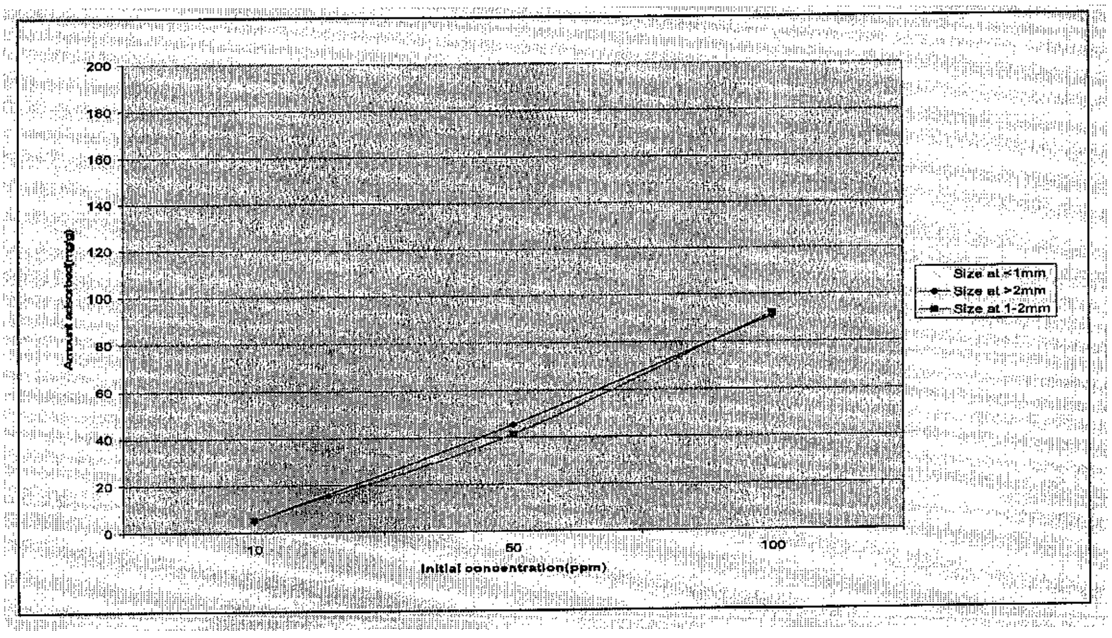

Figure 9: Graph of Amount Adsorbed against Initial Concentration for Activating Agent NaOH

The tests these time uses activated, carbonized rice husks instead of carbonized rice husk alone. Both $ZnCl_2$ and NaOH are used. The graphs above shows a linear pattern as the initial concentration and the amount of phenol adsorbed increased. From the graphs above, the results shows that for both type of activated carbon, the adsorption capacity increases as the size of activated carbon decreases.

The particle size at <1mm showed the highest adsorption capacity which varied between 0.016g of phenol/g activated carbon to 0.098g of phenol/g activated carbon.

This means that a removal efficiency of 98% was achieved and 49mg of phenol was adsorbed from 50mg of phenol.

Consider the figure below. Assume that it takes 36 of the smaller circles to match the volume and mass of the bigger circle. It can be seen roughly that the surface area of the smaller circles collectively is larger than that offered by the bigger circle. Since adsorption is about higher amount of surface area and developed pores network which involves pores distribution of micropores, mesopores and macropores, the smaller particles would offer a better option to fit the criteria stated.

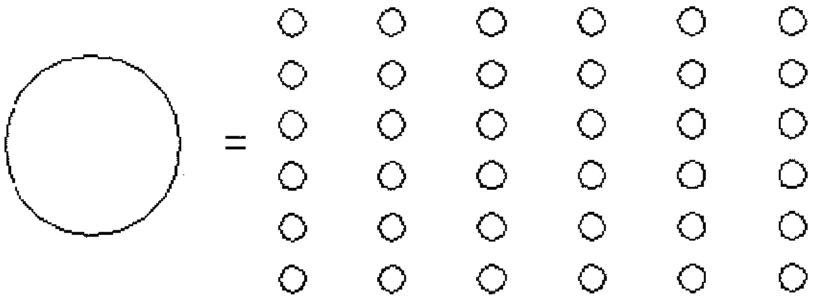

Figure 10: Comparison of sizes and its surface area

A higher amount of surface area allows the Activated Carbon to expose itself more to phenol. A much more developed pores distribution, network and volume give the Activated Carbon more spaces on itself to store phenol molecules. The manipulation of other physicochemical properties like the pH of the solution, the activating agent used further assist in making these adsorbents more 'attractive' to the phenol molecules.

2.1.5 Effects of Chemical Agents on adsorption capacity of adsorbents [5]

Table 5: Activating Agent Studies Important Parameters

Physicochemical Properties	Rice Husk Activated Carbon
Amount of Activated Carbon(g)	0.5
Duration of Adsorption Test(h)	24
Sizes of Activated Carbon Tested(mm)	<1, 1-2, 2<
Activating Agent Used	$ZnCl_2$ or NaOH
Activation Duration(h)	24
Carbonization Temperature(°C)	500
Carbonization Duration(h)	1

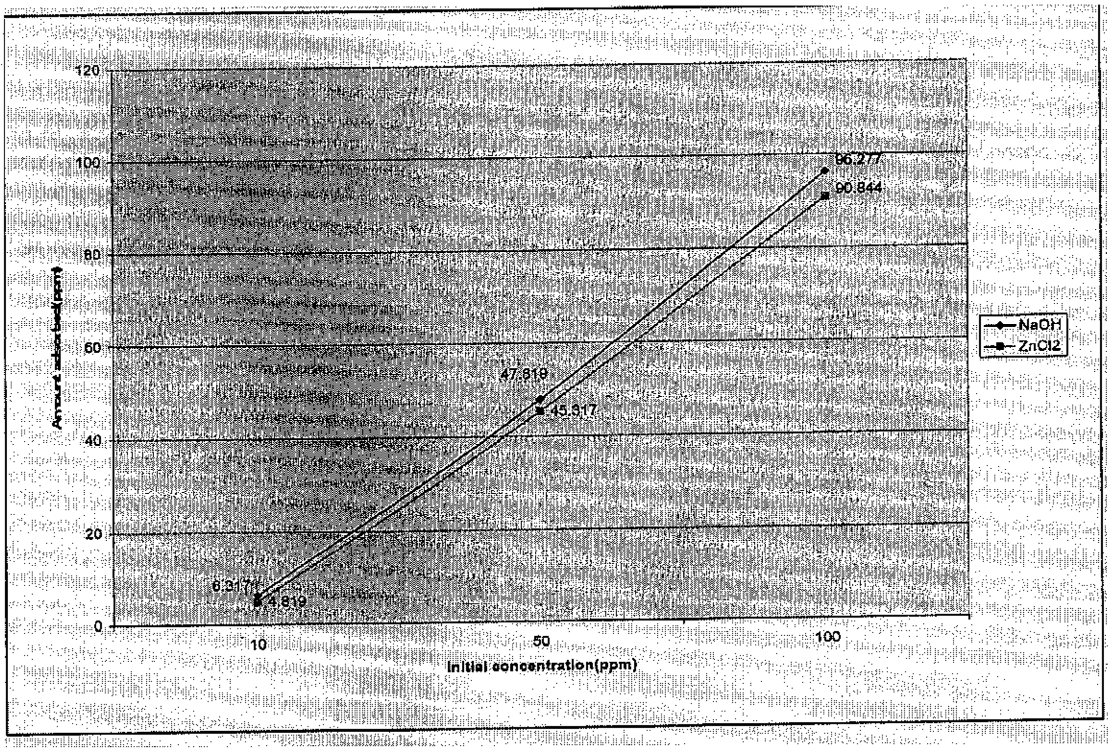

Figure 11: Graph of Amount Adsorbed against Initial Concentration for <1mm

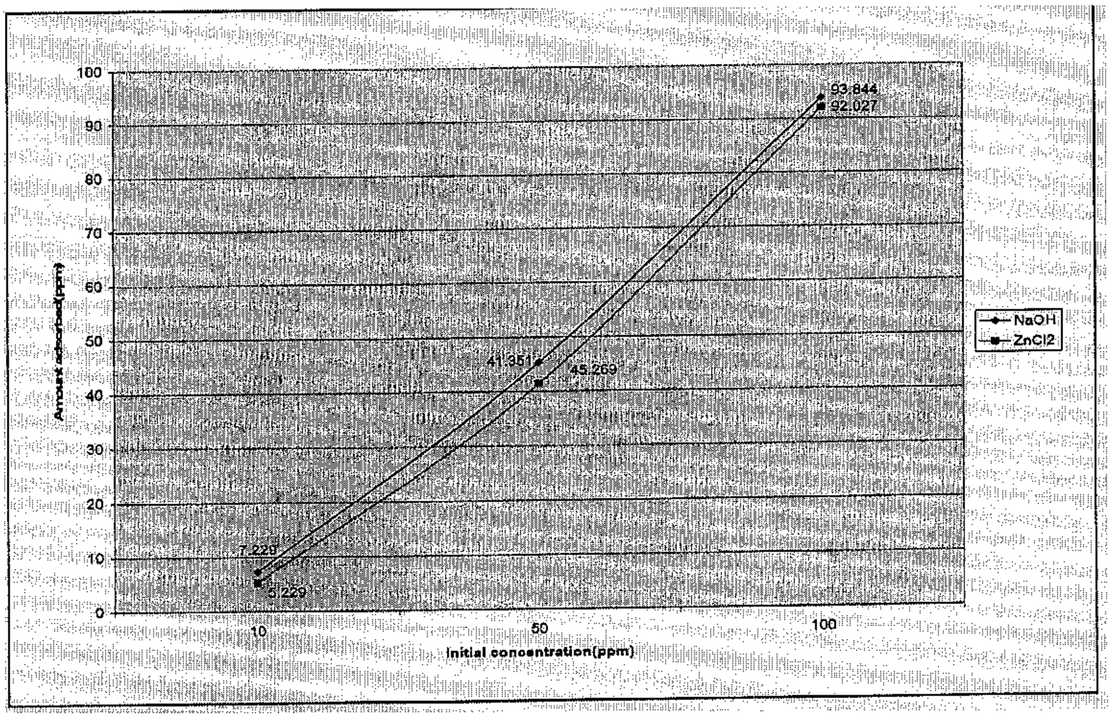

Figure 12: Graph of Amount Adsorbed against Initial Concentration for size 1-2mm

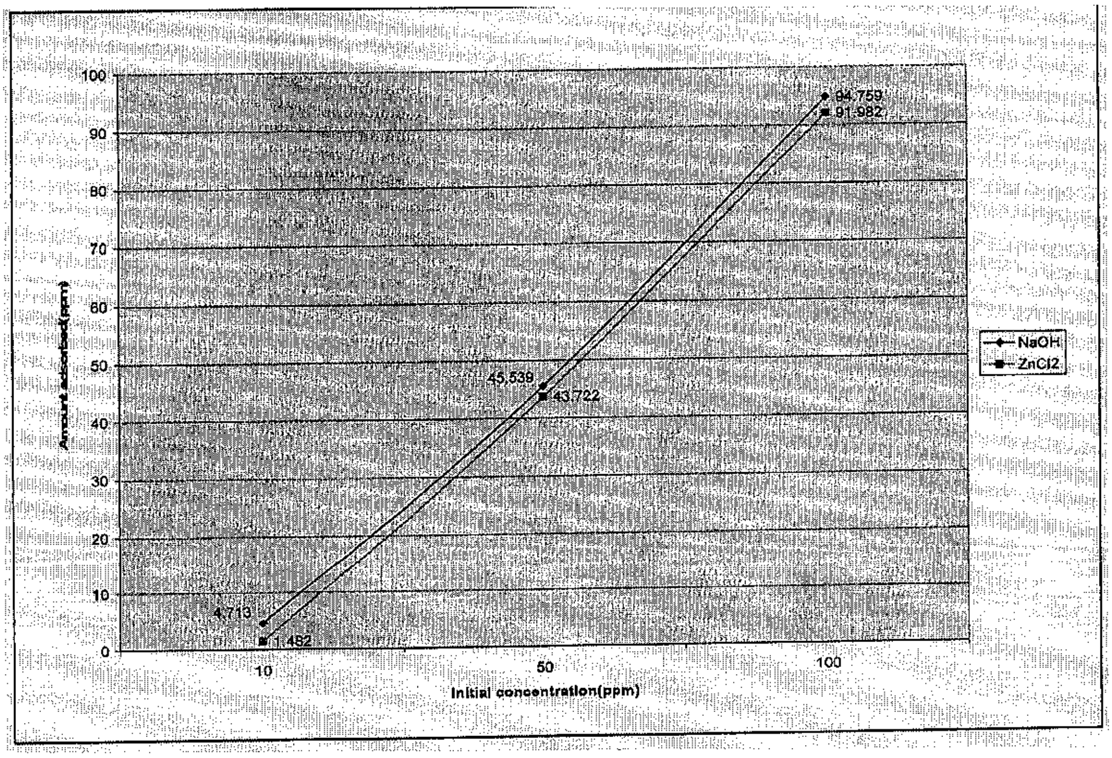

Figure 13: Graph of Amount Adsorbed VS Initial Concentration for size>2mm

The activating agents used are generally classified as base and salt. Another option would be acid. As the graphs above shows, Activated Carbon impregnated with NaOH can adsorb slightly more phenol than those impregnated with $ZnCl_2$. The results above are consistent as the previous statement can be applied to Activated Carbon of the three sizes. The graphs show a linear relationship as initial concentration and amount of phenol adsorbed increases.

The removal efficiency of Activated Carbon impregnated with NaOH was recorded up to 96%. This means 48.1385mgof phenol was adsorbed. The ratio of amount of phenol adsorbed to the amount of Activated Carbon used is

$$\begin{aligned} 48.1385\text{mg of phenol}/0.5\text{g AC} &= 0.0481385\text{g of phenol}/0.5\text{g AC} \\ &= 0.096277\text{g phenol/g AC} \end{aligned}$$

Eventhough Activated Carbon impregnated with NaOH performs better in adsorbing phenol, it is not significantly more compared to Activated Carbon impregnated with $ZnCl_2$. The explanation to this phenomenon can be referred to Section 1.3 where the effects of initial pH of between acidic and basic adsorbed solution are being discussed. The function of the impregnating agent is to minimize the formation of tars and any other liquids that can possibly block the pores and inhibit the development of porous structures in the Activated Carbon.

2.1.6 Effects of Carbonization Temperature on adsorption capacity of adsorbents [5]

Table 6: Carbonization Temperature Studies Important Parameters

Physicochemical Properties	**Rice Husk Activated Carbon**
Amount of Activated Carbon(g)	0.5
Duration of Adsorption Test(h)	24
Sizes of Activated Carbon Tested(mm)	<1, 1-2, 2<
Activating Agent Used	$ZnCl_2$
Activation Duration(h)	24
Carbonization Temperature(°C)	300, 500
Carbonization Duration(h)	1

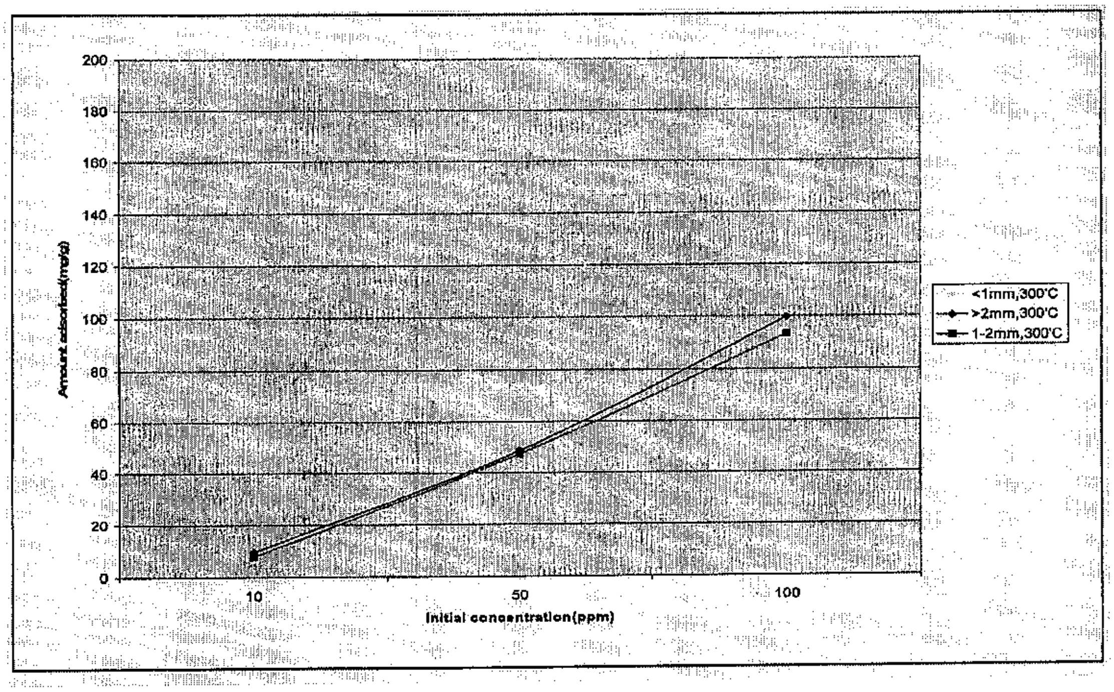

Figure 14: Graph of Amount Adsorbed against Initial Concentration for Carbonization Temperature 300°C

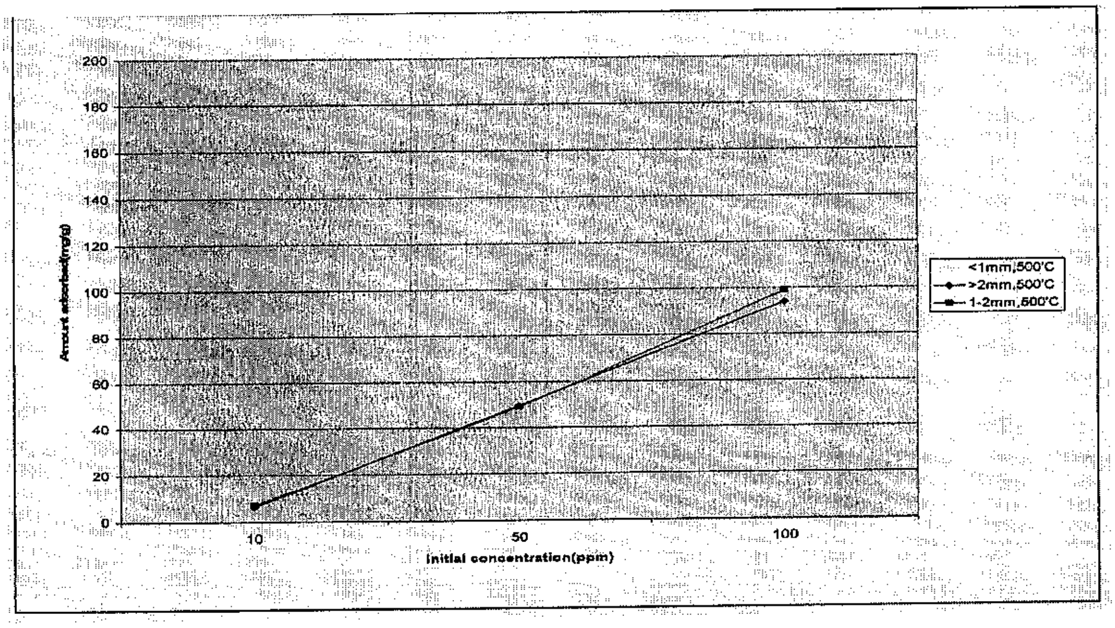

Figure 15: Graph of Amount Adsorbed against Initial Concentration for Carbonization Temperature 500°C

The graphs above shows that higher carbonizing temperature results in better adsorbents than those carbonized at a lower temperature. This result is consistent with all the three different sizes under test. Both graphs display a linear increase of both initial concentration and amount of phenol adsorbed.

The carbonization process is a very complicated phenomenon involving many coupled mechanisms, both mechanically and chemically. Stress and strain generation and crack estimation have been included in the model to account for deformation during carbonization though limited in geometry and analysis methodology. Carbonizing process can be imagined as the self-cracking of rice husks. Pressure can also be considered as a form of carbonizing rice husk eventhough no studies have been done yet. This cracking process is the characterizing of the rice husks where the surface area is cracked open to form the pores, micro, macro and meso and the volume associated with the pores are developed by increasing in sizes. Thus, at a higher temperature, a higher cracking force is available compared to one at lower temperature.

The micropores are well-developed in the produced Activated Carbon and the total pore volume increase with an increase in carbonization temperature. Current findings have also proven that at higher carbonization temperature, the BET surface area and micropores volume increases. Increasing the carbonization temperature indirectly makes the micropores size distribution to become wider. The increase in the micropores volume can be recognized to a higher internal rate of carbonization in creating more pore volume as a result of rearrangement of the carbon layer resulting in the creation of better pore sizes. Thus, the higher carbonization temperature, the micropores volume developments are more prominent, focus, concentrated and dominant than mesopores and micropores.

Low carbonization temperature results in lower volatilization. Carbonized rice husks would lose mass and these losses are considered to be due to vaporization of volatile organic compound, which would then leave behind pure carbonized carbon, carbonized rice husks. Therefore, the higher the carbonization temperature, the higher the carbon content in the adsorbent produced. At low temperature, the basic microstructure starts to form at the same time the pores were blocked by the paralysis products.

The optimum temperature studied so for carbonization to occur is at 700°C. At this temperature, the surface area of Activated Carbon from rice husks is considered the largest with well-developed micropores.

2.1.7 Effects of Carbonization Duration on adsorption capacity of adsorbents [5]

Table 7: Carbonization Duration Studies Important Parameters

Physicochemical Properties	Rice Husk Activated Carbon
Amount of Activated Carbon(g)	0.5
Duration of Adsorption Test(h)	24
Sizes of Activated Carbon Tested(mm)	<1, 1-2, 2<
Activating Agent Used	$ZnCl_2$
Activation Duration(h)	24
Carbonization Temperature(°C)	500
Carbonization Duration(h)	1, 3

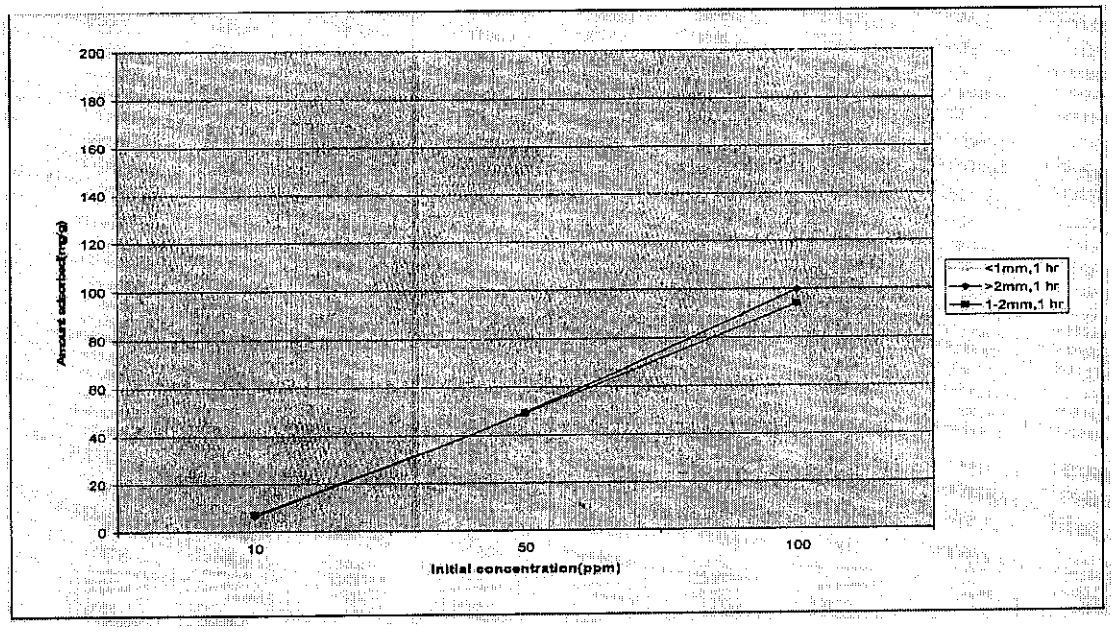

Figure 16: Graph of Amount Adsorbed against Initial Concentration for carbonization duration of 1 hour

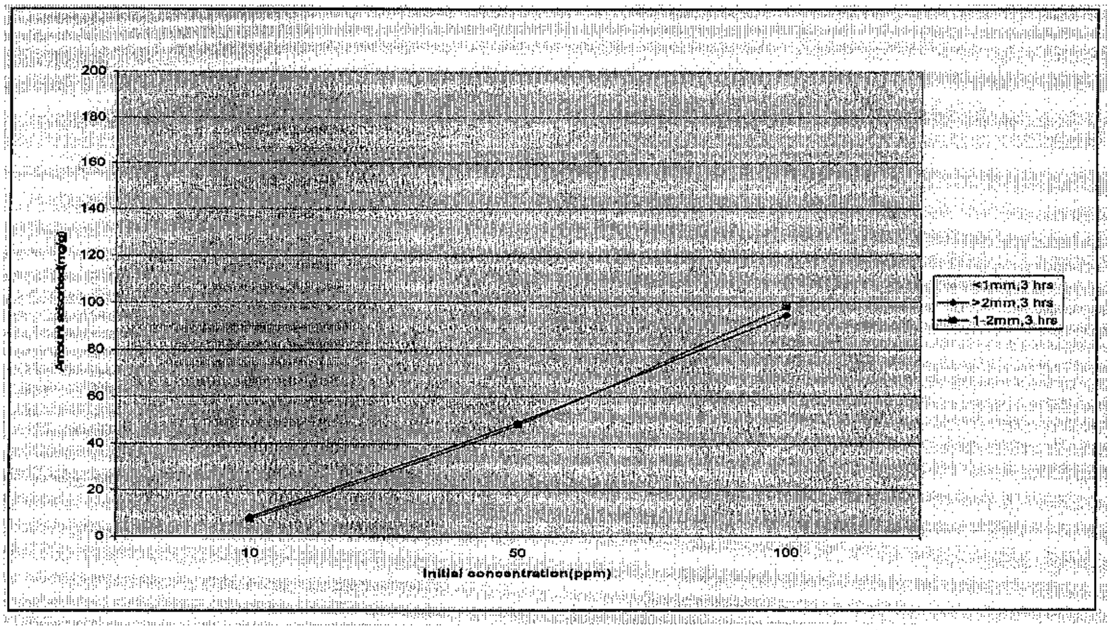

Figure 17: Graph of Amount Adsorbed against Initial Concentration for carbonization duration of 3 hour

The results displayed by the graphs above shows that the longer the rice husks were carbonized into Activated Carbon, the better adsorbents these Activated Carbon were. The graphs also show that the amount of phenol adsorbed is linearly related to the initial concentration of phenol tested. The results states that for sizes 1-2 and 2<mm, they are closely correlated. However, size 1<mm demonstrates that it is the best adsorbents by far by having the steepest graph in both carbonization duration of 1 and 3 hours respectively.

The explanation for this phenomenon is as the same as the previous section, Section 2.1.6. Imagine temperature or heat as a force used to crack open and characterize rice husk. At a certain temperature, the longer the force could work on the rice husk, the better the rice husk is characterized.

Carbonization involves thermal decomposition of the carbonaceous material, eliminating noncarbon species and producing a fixed carbon mass and a rudimentary pore structures. It is during this carbonization time that the pore size is widened by the burning effect of carbon in the pores resulting in the increase of pore size. Thus, the micropores volume and surface area increases with increasing carbonization time.

The ratio of phenol adsorbed per Activated Carbon used is 98mg phenol/g AC. This makes a removal efficiency of 98% as 49mg of 50 mg of phenol in the solution has been successfully adsorbed.

CHAPTER 3

METHODOLOGY

3.1 PREPARATION OF STANDARD PHENOL SOLUTION

To make future experiments easier, a standard phenol solution was made first. Any other concentrations that would be used later can be diluted or derived from the standard phenol solution. This phenol solution would later be used in the adsorption testings or studies. The concentration and amount of this standard phenol solution depends on the amount and concentration of the phenol used in the future experiments. Experimenters should therefore be able to gauge and budget the amount of phenol to be used for the adsorption studies and make a little more extras to allow cases of needs, spills, accidents and mistakes.

In this case for example, the concentration of phenol to be tested is in 10ppm and 100ppm. Thus, the standard phenol solution has to be more than 100ppm in concentration. Take note:

$$1\text{mg/L} = 1\text{ppm}$$

Thus 500ppm was chosen. This is due to the ease and accuracy of weighing 0.5g of phenol crystals compared to any lower value of phenol mass. 1L of the standard phenol solution was chosen as it is deemed sufficient amount to cover up for all the phenol solution to be used during the later tests and etc.

$$0.5g/L = 500mg/L$$
$$= 500ppm$$

To make this standard phenol solution, simply dilute 0.5g of phenol crystals in 1L of distilled water. Remember to label this standard solution.

Table 8: Making Standard Phenol Solutions Requirements

Equipments/Glasses/Chemicals	Quantity	Purpose
Mass Balance	1	To weigh the amount of phenol crystals
Conical Flask, 1L	1	To place the phenol crystals in and dilute it with 1L of distilled water
Petri Dish	1	Used to put phenol crystals on to weigh on the mass balance
Spatula	1	To transfer phenol crystals from its container to other equipments like petri dish and conical flask
Phenol	0.5g minimum	-
Distilled water	As required	-

3.2 DILUTION OF PHENOL STANDARD SOLUTION

For future use or dilution, use the following formula:

$$C_1V_1=C_2V_2$$

Where C_1 is the initial concentration in ppm or mg/L, V_1 is the initial volume in L, C_2 is the final concentration in ppm and V_2 is the final volume in L. The concern is usually how much volume of the 500ppm solution is to be used in making the solution used for tests. The following examples are hoped to assist in a way or another.

For 10ppm:
$C_1 = 500\text{ppm}$ $C_2 = 10\text{ppm}$

Both initial and final concentration has already been known and decided. It is now up to the experimenter to decide the volume of the 10ppm phenol solution to be used during the adsorption studies. In the following experiments, 80mL has been decided for 10ppm phenol solution and 500mL for 100ppm. Thus, $V_2 = 0.08\text{L}$.

$$C_1V_1=C_2V_2$$
$$500\text{ppm}*(V_1) = 10\text{mg/L}*(0.08\text{L})$$
$$V_1 = 1.6 \text{ X}10^{-3}\text{L}$$
$$= 1.6\text{mL}$$
$$= 1600\mu\text{L}$$

Table 9: Dilution of Standard Phenol Solutions Requirements

Equipments/Glasses/Chemicals	Quantity	Purpose
Micropipette	1	To withdraw a very small amount of standard phenol solution from the conical flask
Measuring cylinder	1	To measure the amount of standard phenol solution for 100ppm phenol solution

Erlenmeyer flask, 200mL	13	To contain the 100ppm phenol solution for adsorption testings
Beakers, 80mL	7	To contain 10ppm phenol solutions for backup adsorption testings
Standard phenol solution	As Required	-
Distilled water	As Required	-

3.3 PRETREATMENT OF RICE HUSKS

The pretreatment part of the experiment is where the rice husks were prepared before they were used for the adsorption studies. This includes:

- Washing
- Drying
- Carbonization
- Activation

Rice husks were first washed with distilled water. This was to remove any sand and dust particles off the rice husks. Rice husks were placed preferably in a gauze basket as distilled water was run over it.

Drying the washed rice husks were next. The wet rice husks were placed on a tray and put inside the oven for 24 hours at a temperature of 110°C. A scenario that might surface would be that the oven needs to be shared by a few users. This need not affect the drying of the rice husks. The objective of this step is to dry the rice husks. Thus, even at different temperature and duration is also acceptable as long as the main objective is fulfilled.

Carbonization temperature and duration were determined in this set of adsorption studies. Carbonization temperature of 600°C and duration of 3 hours were chosen. The particular temperature was chosen because this set of experiments has no objective of studying carbonizing temperature and it is known that the optimum carbonizing temperature currently is 700°C. Thus, a safe option of 600°C was chosen. The duration of 3 hours is chosen as it is the optimum carbonizing duration known at the moment. Carbonization duration is also not in the agenda of adsorption studies in the following experiments. The dried rice husks were placed in a crucible before being placed into the furnace. The crucible must be covered with its lid when placed in the furnace so as not to convert the rice husks into ash instead of carbonized carbon. The furnace was heated up to the desired temperature before the crucible filled with dried rice husks were input into the furnace. Safety aspect that has to be taken note here is the usage of glove at all time when dealing furnace at a high temperature. After 3 hours of carbonizing, a pair of tongs was used to transfer the very hot crucible from the furnace to the dessicator. The dessicator was used to let the crucible and its content to cool down before it was ready to be handled by hand. It was also to prevent any other particles like dust and moisture to be mixed up with the newly carbonized rice husks. The cooling down usually takes a few hours.

Table 10: Washing, Drying and Carbonizing of Rice Husks Requirements

Equipments/Glasses/Chemicals	Quantity	Purpose
Gauze Basket	1	To place the rice husks in while washing it with distilled water
Distilled Water	As required	-
Trays	2	To place the wet rice husks to be put into the oven
Oven	1	To dry the moist rice husks

Crucibles	2	To place the dried rice husks in before being put into the furnace
Furnace	1	To carbonize dried rice husks
Tongs and gloves	1 pair	For safety reasons while handling crucibles in and out of furnace
Dessicator	1	To cool down and protect the carbonized rice husks from moisture, dusts and any other particles.

Activation of the carbonized rice husks was the most complicated and time consuming process of the pretreatment process. First, a series of solution with pH of 1, 3, 5, 7, 9, 11 and 13 were prepared. In order to prepare these 200mL pH solutions, 0.1M of HCl and NaOH solutions were made first in order to be able to manipulate the pH of these solutions later. For pH below 7, a certain very small amount of 0.1M HCl was placed in a 200mL Erlenmeyer flask. The Erlenmeyer flask was then filled up to almost its 200mL content with distilled water. pH meter was always placed throughout the process in the Erlenmeyer flask in focus to monitor the pH of the solution. Depending on the pH displayed by the pH meter, a dropper was used to increase the pH with the 0.1M NaOH solution or decrease the pH with the 0.1M HCl solution. In another words, making the different pH solutions is a form of trial and error process. It has no direct manner to form a solution with the accurate desired pH. The Erlenmeyer flask also has a magnetic stirrer in it and placed on a stirrer so as drops of acid or base were mixed into the solution, it would be quickly blended in.

The same method was also applied to solutions with pH than 7. This time around, an amount of 0.1M NaOH solution was used in the Erlenmeyer flask and then filled up with distilled water up to an almost 200mL point. Droppers were used to drop droplets of 0.1M NaOH or HCl solution to manipulate the pH of the solution to the desired value.

Once all the pH solutions were prepared, approximately 2.0g of carbonized carbon was placed in each of the different pH solutions. These mixtures of carbonized rice husks and different pH solutions were then sealed with plastic film each. Then these sealed Erlenmeyer flasks containing different pH solutions each with 1.0g of carbonized rice husks were placed on a plate shaker for 24 hours at a 125rpm.

After 24 hours, each of these solutions was filtered using filter papers to separate the Activated Carbon and the used pH solutions. Each of different pH impregnated Activated Carbon were then dried in a dessicator before being able to be used for adsorption testings.

Table 11: Activation of Rice Husks Equipments

Equipments/Glasses/Chemicals	Quantity	Purpose
Erlenmeyer Flask, 200mL	7	To contain all the different pH solutions
Distilled Water	As Required	-
NaOH	As Required	-
HCl	As Required	-
pH Meter	1	To monitor the pH of the solutions prepared to activate the carbonized rice husks
Stirrer	1	To stir the pH solutions while being prepared

3.4 ADSORPTION TESTINGS

3.4.1 Effects of Different pH of Activating Rice Husks on Adsorption Capacity

This test determines if different pH used in activating rice husks affects the adsorption capacity of the Activation Carbon. 0.5g of Activated Carbon of every solution with different pH prepared were mix with 100ppm and 0.1g for 10ppm of phenol solution. The purpose of having these two types of concentration is mainly for backups and comparison. One experiment might not produce a logical result or if both tests produce the same result, then it strengthens the result of the experiment. The mixtures of solid Activated Carbon and phenol solution of each pH were then sealed with a plastic film at the mouth of the flask and placed on the plate shaker for 24 hours.

3.4.2 Effects on Contact Time on Adsorption Capacity

This test determines the effects of the difference in duration of Activated Carbon left in the phenol solution. 0.5g and 0.1g of Activated Carbon activated by pH 3 was used in this experiment each in the 3 Erlenmeyer flasks and beakers respectively. Each flask represents 3 different durations, 6, 18 and 24 hours. The mixture of Activated Carbon and phenol solution of 100ppm and 10ppm were put on the plate shaker for 24 hours. The mouth of these flasks and beakers were sealed with plastic film before they were left on the shaker.

3.4.3 Effect of Different Medium of Adsorption Tests on Adsorption Capacity

The purpose of this test was to determine the best form of medium to adsorb phenol. Currently the most common medium is the shaker. The other two doable forms are the stirrer and letting the Activated Carbon and the phenol solution stagnant as it is. 0.5g of Activated Carbon of pH 3 was placed in each of the 3 200mL Erlenmeyer flasks containing 100ppm of phenol solution. The mouth of these flasks were sealed with parafilm film and then one were left on the plate shaker, one were placed on a stirrer with a magnetic stirrer in the mixture of Activated Carbon and phenol solution and the last one was just left as it is on the laboratory bench for 24 hours.

3.4.4 UV-Vis Spectrophotometer

Once all the above tests were completed, equipment called the UV-Vis Spectrophotometer was used to determine the remaining phenol left in the solution. However, before using the equipment a wavelength used to check the absorbance capability of the remaining solution has to be determined. The UV-Vis operates on correlating the amount of light a solution can adsorb to its concentration. Thus, a calibration test must be performed to determine what adsorbance reflects the concentration of the solution.

5 standard concentration solutions were prepared, 20, 40, 60, 80 and 100ppm. These 5 solutions were placed in the UV-Vis for two purposes:

- To determine the wavelength to be used during the light absorbance test to determine the remaining concentration of the phenol solution
- To calibrate the linear graph of light absorbance against the concentration of phenol in ppm. This graph can be referred to in Appendix II.

The wavelength to be used was found to be 269.5nm.

Upon completing the duration of the experiments, the samples were filtered using filter paper and the remaining solutions were placed in vials to be used in the UV-Vis.

Chapter 4

RESULTS AND DISCUSSION

4.1 EFFECTS OF DIFFERENT pH OF ACTIVATING RICE HUSKS ON ADSORPTION CAPACITY

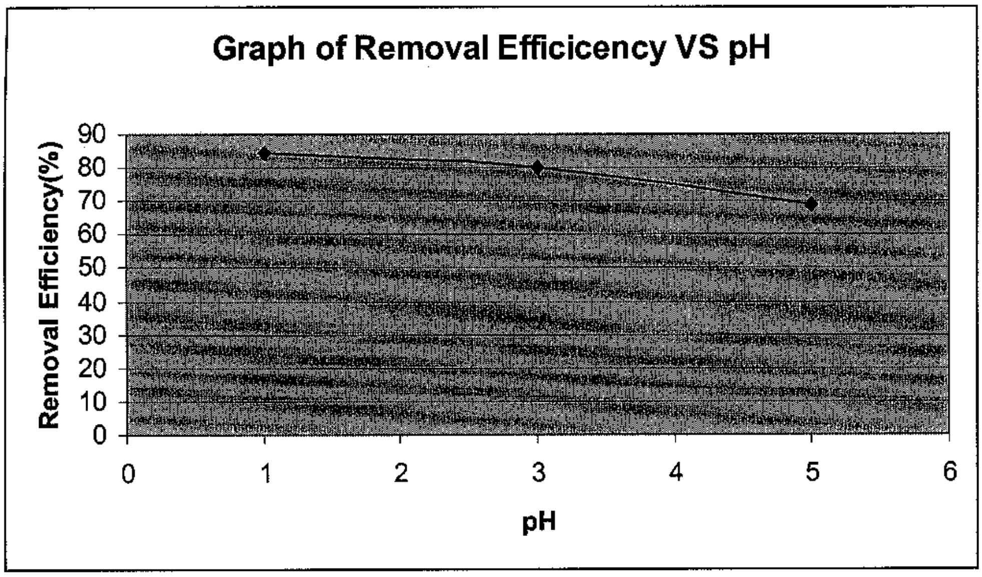

Figure 18: Graph of Removal Efficiency against pH

The graph above displays the results of Removal Efficiency for the Activated Carbon as the pH of its Activating Agent increases. As the result shows, adsorption capacity decreases as pH increases. The graph has an almost linear relation. The best pH to be activated, pH 1, has its Activated Carbon adsorbs an almost 85% performance. This is an adsorption of 0.8466mg of phenol out of 1.0mg per 0.1g of Activated Carbon. It gives a ratio of 0.008466g phenol/g AC.

The explanation behind this phenomenon is similar to that from Section 2.1.3. Thus the results above are consistent with other forms of adsorption studies. Future studies should include Activated Carbon activated at pH higher than 7 and manipulation of the duration time of the activation period

4.2 EFFECTS ON CONTACT TIME ON ADSORPTION CAPACITY

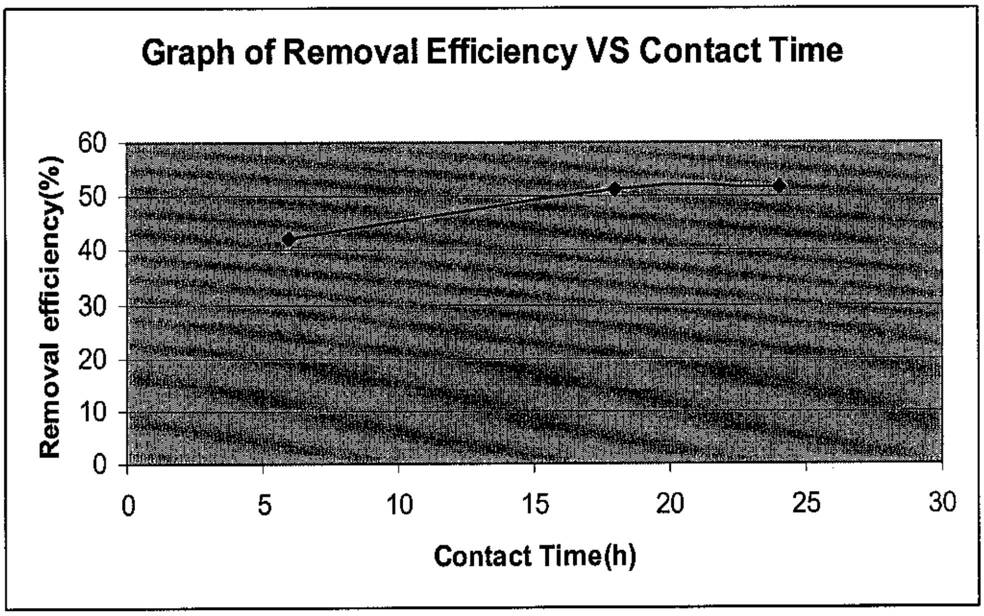

Figure 19: Graph of Removal Efficiency against Contact Time

The graph above displays the results for the removal efficiency of Activated Carbon activated at pH 3 with respect to time. Logically, the longer the adsorbent were allowed to adsorb, the more adsorbate it could adsorb. However the above also shows that the adsorbents reach an equilibrium state after 18 hours. The amount adsorbed after 24 hours was 52% of the phenol in the solution, which was 25.648mg out of 50mg. this makes it with a ratio of

25.648mg of phenol/0.5g of AC = 0.025648g of phenol/0.5g of AC
= 0.051296g phenol/g AC

Comparing the values of the studies here and those discussed in Section 2.1.2, the values here shows much more promising figures. This is because that the adsorbents used in this experiment were activated compared to the rice husk ash used in that section and the adsorption test duration was very lenient here compared to the studies done in the stated section. That is the main purpose of conducting long hours of adsorption tests and activation period which is to allow the entire possible amount to be adsorbed and the AC be as saturated impregnated by the activating agent.

4.3 EFFECT OF DIFFERENT MEDIUM OF ADSORPTION TESTS ON ADSORPTION CAPACITY

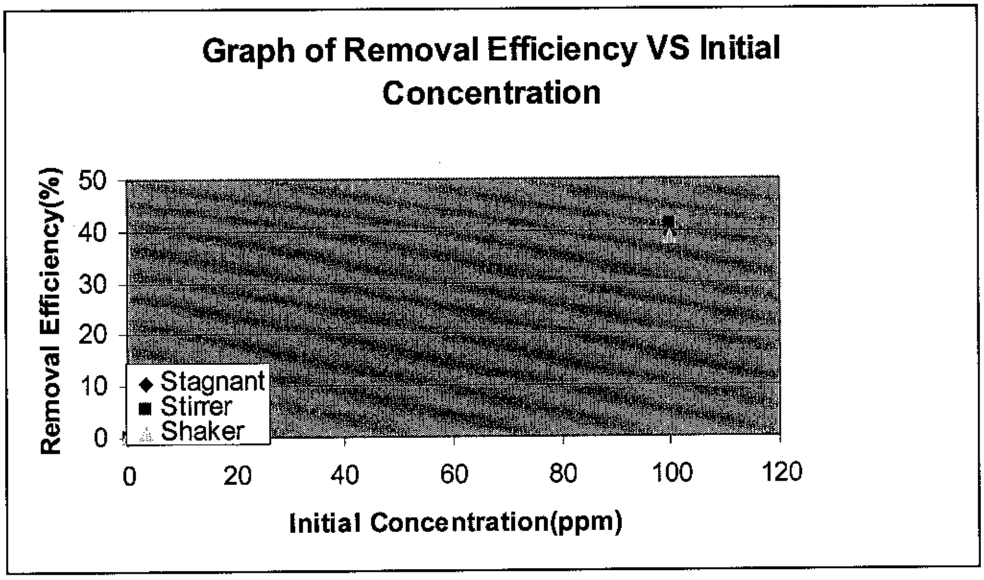

Figure 20: Graph of Removal Efficiency VS Initial Concentration

The graph above shows the results of removal efficiency of three different ways of adsorbing phenol. It shows that the stirrer is the best medium to be used to adsorb phenol and shaker is the least efficient. However, the difference among them is not significant. The commonly used medium at the moment is the shaker. The amount of phenol adsorbed quantitatively is not important here as the main objective here is to demonstrate the best medium to be used during experiments to adsorb phenol.

Despite the above results, the shaker will continue to be the choice of medium for future experiments. This is because since not much difference was registered during the tests. Furthermore, a plate shaker could run a few tests at the same time as it keeps the solution homogenous throughout the experiment. In order to use a stirrer, a few stirrers and its magnetic stirrer would be required. Leaving the samples stagnant could result in a non-homogeneous adsorption to occur.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION AND RECOMMENDATIONS

The three objectives that have been stated in the earlier part of this report have been achieved. Carbonized rice husks were activated in 3 different pH solutions and then used to adsorb phenol from its solutions. The findings state that Activated Carbon that was activated at a lower pH makes much better adsorbents. It managed to adsorb up to 84.66% of phenol in a 100mL of 10ppm phenol solution using only 0.1g of Activated Carbon. This makes it having a ratio of 0.008466g phenol/g AC. 0.8466mg of phenol was adsorbed from a total of 0.1mg.

To take this study further, it is recommended that future experiments include testings of activating rice husks at pH above 7. It is already known that base makes better activating agent than salt. Now, it is to compare if base or acid makes better activating agent and at which pH specifically would the adsorbents be at its best.

A qualitative study was also done to determine the most appropriate medium to do the adsorption testings. Adsorption testings have been done for quite some time with only the reliance of a shaker. The other two possible mediums are letting the samples stagnant on its own and the stirrer. The reason stagnancy was considered was because it was noticed that the Activation Carbon were swirling around gently at the bottom of the flask during the adsorption testing process on the shaker. The stirrer promises to be the best medium as it increases contact time between the adsorbents and adsorbate in a little bit more vigorous manner.

The results produced were both surprising yet expected. Stirrer did come out to be the best medium followed by stagnant and then shaker. However, the values by all these 3 mediums were close that it has no significance which medium is the best to be used during adsorption testings. Thus, shaker or stagnant will continue to be the choice of adsorption test medium. This is because both can run a few tests at the same time. Stirrer on the other hand can only run 1 test at a time.

A study on effects of contact time on adsorption capacity was also run. The difference between the experiments run for this study and the one discussed in Section Literature Review was that everything done in this study was done in excess. The duration of activating the carbonized rice husks was done in 24 hours. It is believed that the time required for this process is shorter but it was preferred to have the carbonized rice husks saturated and impregnated with the activating agent. Even the ratio of amount of activating agent to the adsorbents was understandably in excess. It is recommended that one of the future studies to be determining the optimum duration to activate the adsorbent.

The adsorption process was left for 24 hours, also in excess as the results agrees. Equilibrium was reached within 18 hours and the following values were obtained. Removal efficiency of 52% was obtained. 25.648mg of phenol was successfully adsorbed out of 50mg of phenol which gives the following ratio, 0.051296g phenol/g AC. 0.5g of Activated Carbon was used in this experiment.

A suggestion to be made to future experimenters is to standardize the studies that have been discussed in this report. All of the studies discussed in this report have various sources but as much as the results give the readers some clues of the characteristics of rice husks or activated carbon, more profound information would be required. For example, it is now understood and accepted that lower pH solutions promotes adsorption, but the rice husk ash used in that particular study was not activated in the first place. After all these studies have been standardized, it is much more accurate and straightforward to compare the results to one other.

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