Comparative Study for Phenol Removal from Wastewater by Adsorption and Ion Exchange

By

Nadia Isabella Bt Mohd Noor

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

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Chemical Engineering Programme
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Approved by,

(Dr. Usama Mohamed Nour El Demerdash)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2011

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.

(NADIA ISABELLA BINTI MOHD NOOR)

ABSTRACT

Nowadays, most of the wastewater produced as industrial effluent contain constituents where it needs to be treated prior discharge to environment. One of the constituents is phenol; an organic compound with the chemical formula C6H5OH which is generated in many of the steel industry's coking facilities as a precursor to many materials and useful compounds. Phenol can pose a severe health hazard whereupon it can affect the central nervous system and cause damage to the liver and kidneys. Phenol will stay in the air, soil, and water for much longer times if a large amount of it is released at one time, or if a steady amount is released over a long time. In advanced wastewater treatment, many methods have been applied such as adsorption using activated carbon, ion exchange using resin, using Fenton reagent and UV light degradation to remove phenol. So, in this systematic study, two methods have been chosen to be investigated for phenol removal efficiency, which is adsorption using activated carbon and ion exchange resin. A modification process is performed to modify the surface of activated chemically using KOH. The adsorptive capacity between modified activated carbon, non modified activated carbon and resin then is compared to determine which is better for phenol removal. From this study, it is proven that the modification on the surface of activated carbon improves the performance for phenol removal compared to non-modified and resin.

ACKNOWLEDGEMENT

First and foremost, I would like to express my praises to God for His blessing.

My deepest appreciation and gratitude is extended to my Supervisor, Dr Usama Mohamed Nour El Demerdash for being very encouraging, supportive and responsive throughout the whole process of completing this final year project to fulfil the university requirement. Without his constant supervision and guidance, I may not be able to complete this project successfully.

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Last but not least, I would like to acknowledge, my family members for keeping me motivated throughout the year.

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(NADIA ISABELLA BINTI MOHD NOOR)

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LIST OF ABBREVIATIONS

AC	Activated Carbon
BET	Bruneur-Emmett-Teller
FTIR	Fourier Transform Infrared
H2SO4	Sulphuric Acid
KOH	Potassium Hydroxide
MAC	Modified Activated Carbon
NaOH	Sodium Hydroxide
PAC	Purified Activated Carbon

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater Treatment

Wastewater treatment involves several stages which are pretreatment, primary treatment, secondary treatment and advanced wastewater treatment. Pretreatment steps is purposely added to remove large materials such as rags, logs and other large objects from the wastewater that could interfere the treatment process (Ludzack F.J. and Noran D.K., 1995). Coarse screening, grit chambers and flow equalization used to remove large materials in the wastewater. In the primary stage, a portion of the suspended solid and organic matter is removed from the wastewater. Sedimentation tank is used to remove the contaminant by gravity settling (Metcalf and Eddy, 2003). What settles out is called as sludge.

Meanwhile, secondary treatment removes soluble materials that require oxygen for decay, as well as further removal of suspended solids. Trickling filters, activated sludge and clarifiers normally used in secondary treatment (Ludzack F.J. and Noran D.K., 1995). In the advanced wastewater treatment, several processes are applied such as carbon adsorption, phosphorus removal and nitrogen removal. This level of wastewater treatment is so effective in removing pollutants so that the treated wastewater can be reused.

Figure 1: Wastewater treatment process

2.2 Phenol in Wastewater

Phenol, also known as carbolic acid, is an organic compound with the chemical formula C6H5OH. Although similar to alcohols, phenols have unique properties and are not classified as alcohols. Phenol was first extracted from coal tar, and its major uses involve its conversion to plastics or related materials. It is produced on a large scale since it is demand as a precursor to many materials and useful compound (Azni I. and Katayon S., 2003). However, phenol can pose a significant threat and severe health hazard and should be handled with extreme caution because it is highly corrosive to the skin and readily absorb through it where it can affect central nervous system and cause damage to liver and kidney.

Small, single releases of phenol do not stay long in the air and soil but it can stay in water for longer than 9 days. More phenol is usually found in the environment has been found in surface. Phenol compounds are considered to be hazardous wastes, which are released into the aquatic environment by industries such as coke ovens in steel plants, petroleum refineries, petrochemical, pharmaceutical and dye industries and have been reported in hazardous wastes sites (Ahmaruzzaman M. and Sharma D.K., 2004).

In industrial wastewater, the content of phenols usually is about 200–2000 mg/L which is higher than the standard limits set in regulation which is mostly less than 0.5 mg/L (Ahmaruzzaman M. and Sharma D.K., 2004). Due to its nature of highly toxic and biodegradability, phenol concentration in industrial effluent need to be reduced as low as applicable prior discharge to the environment. Following table shows the concentration of phenols from different industries:

Table 1: Phenol concentration in various industrial wastewater

Industry	**Concentration of phenol** (mg/l)
Coal mining	1000-2000
Lignite transformation	10000-15000
Gas production	4000
Petrochemicals	50-700
Pharmaceuticals	1000
Oil refining	2000-20000

2.3 Carbon Adsorption for Phenol Removal

In adsorption process, one or more components of a gas or liquid are adsorbed on the surface of the solid adsorbent and a separation process is accomplished. In commercial processes, the adsorbent is usually in the form of small particle size in a fixed bed. Many adsorbents have been developed for a wide range of separation. Typically, the adsorbents are in the form of small pellets, beads and granules ranging diameter from 0.1mm and 12mm. There are a number of commercial adsorbents such as activated carbon, silica gel, activated alumina, molecular sieve zeolites and synthetic polymer or resin (Geankoplis, 2003).

In wastewater treatment, adsorption is one of the most effective processes of advanced wastewater treatment employed by industries to reduce hazardous organic and inorganic wastes in effluents. Activated carbon normally used as an adsorbent in advanced stage to remove soluble organics which may still present after secondary treatment and filtration. It has a highly porous carbonaceous substance with a wide range of applications in gas, vapor, and liquid treatment. The refractory organic material will be adsorbed to the pores on the activated carbon surface. Once the activated carbon has reached exhaustion and all the adsorptive sites are filled, it must be regenerated by heating it at a temperature of 820 to 930 degC. Activated carbon is expensive, thus making regeneration is economically desirable.

There are few factors that may influence the performance of adsorption such as pH, dosage of adsorbent and adsorbate concentration. The adsorption of phenol at acidic pH does not give significant impact, except slightly increase with increasing pH. However, in the basic pH, the amount of phenol adsorbed decrease drastically (Carlos M.C., 2003). Besides that, the dosage of activated carbon and adsorbate concentration is directly proportional to the adsorption of phenol onto activated carbon (Fritz S. *et al,* 2003). The use of activated carbon as an adsorbent for industrial wastewater treatment also has several other problems such as regeneration of activated carbon, intraparticle resistance in adsorption processes in practice, and high cost of manufacture (Rengaraj S *et al,* 2001).

2.4 Ion Exchange for Phenol Removal

Ion exchange processes are basically chemical reactions between ions in solution and ions in an insoluble solid phase. The techniques used in ion exchange so closely resemble those used in adsorption. So, ion exchange process can be considered as a special case of adsorption. Most present today, ion-exchange solids used are synthetic resins or polymers (Geankoplis, 2003). The resins are prepared as spherical beads 0.5 to 1.0 mm in diameter.

In wastewater treatment, phenol can be removed efficiently by ion exchange process using anion resin (Geankoplis, 2003). In the vast majority cases, ion exchange process use to treat wastewater containing inorganic contaminants such as heavy metals. The kinetics of sorption of organic species from non-polar solvents by ion exchangers is typically unfavorable because ion exchangers which are resins not very effective against large organic molecules. This is due to the larger size of organic molecules which tends to reduce the exchange rate of the resins. However, ion exchanges process still effective in the treatment of specific organic compounds such as phenol.

Two kinds of resin most commonly used today is polystyrene with sulphonate groups to form cation exchangers or amine groups to form anion exchangers. Factors affecting the ion exchange process include the presence of oil and grease, contaminant concentration, exchange capacity of the resin and pH of the wastewater. Each type of resins has different affect towards pH. For example, strong acid cation resin is independent towards solution pH whereas weak acid resin has limited adsorption capacity for pH below than 6.0.

2.5 Activated Carbon

Activated carbon is a form of carbon that has been processed to make it extremely porous and has a very large surface area available for adsorption process and is produced from carbonaceous source materials like nutshells, wood, coconut shells and charcoal (Fritz S. *et al*, 2003). Activated carbon has three main forms which are powdered, granular and extruded. In wastewater treatment, activated carbon removes contaminant by adsorption process where activated carbon functions as adsorbent and contaminant or organic compound function as adsorbate. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption (Ahmaruzzaman M. and Sharma D.K., 2004).

There are several factors affect the size, number and chemical structure of organic acid molecules such as wastewater pH and temperature. Accordingly, there exist an infinite number of organics acids in wastewater and this cause difficulty in removing organics and consider as site specific. However, activated carbon's properties are used to remove organics like phenols. Generally, adsorption takes place because all molecules exert forces to adhere to each other. Activated carbon adsorbs organic material because the attractive forces between the carbons surface (non-polar) and the organic contaminant (non-polar) are stronger than the forces that keeping the contaminant dissolve in water (polar).

The organic molecules can be adsorbed by the activated carbon only when the molecules are close to carbon's surface. This is due to the adsorptive forces of the activated carbon are weak towards organic molecule. The large particle size as well as configuration of pores on the activated carbon surface also allows for the adsorption to take place. For activated carbon used in industrial wastewater treatment, its filter capacity towards organic molecules can be roughly estimated at 0.1pound of organics per 1 pound of carbon at a flow rate of 2gpm/cu.ft and carbon depth 3 feet (Frank D.S., 2000).

For this project, activated carbon in the form of granular is used because this form can be a particularly good adsorbent medium due to its high surface area to volume ratio. One gram of a typical commercial activated carbon will have a surface area equivalent to 1,000 square meters. This high surface area permits the accumulation of a large number of contaminant molecules.

2.6 Resin

An ion-exchange resin is an insoluble material that is normally in the form of small beads with 1 to 2mm in diameter. It is fabricated from an organic polymer substrate. Resin has highly developed structure of pores on the surface so that ions will be easily trapped and released. The process trapping of ions with simultaneous releasing of other ions is called ion-exchange process.

The functional group determines whether the ion exchange resin is a cationic type or an anionic type. Although an infinite quantity of functional groups can be attached to the polymeric matrix, the most commonly used in the industry are:

Table 2: Type of resin and their active group

Active Group	Structure	Type of Resin
Sulphonic	R-SO_3H	Strong acid cation (SAC)
Carboxylic	R-COOH	Weak acid cation (WAC)
Ammonium	R-$N(CH_3)_3Cl$ R-$N(CH_3)_3OHCl^-$ R-$N(CH_3)_2$	Strong base anion (SBA) type I Strong base anion (SBA) type II Weak base anion (WBA)
Chelating	R-SH R-CH_2 $N(CH_2COOH)_2$ R-CH_2 $NHCH_2$ CH_2 PO_3 H	Chelating resins

Strong acid cation resins contain exchangeable H+ cation which gives the resins the ability to behave very reactive insoluble acids. These resins not only can be used to exchange the H+ ion for the cation of a salt in solution but they can be used in place of soluble acid in many catalytic reactions as well.

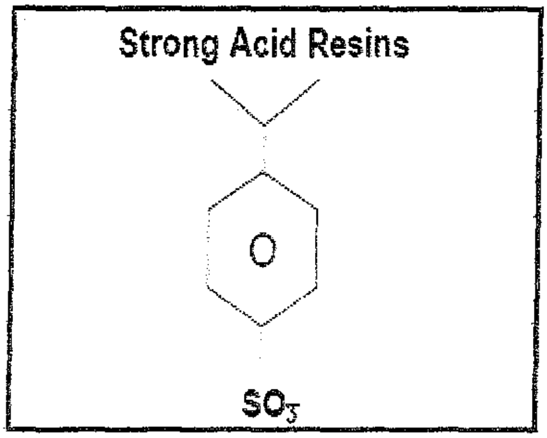


Figure 2 : Molecular structure for strong acid cation resin

For weak acid cation resin, it contains carboxylic acid groups which act as base adsorbers (Frank D.S., 2000). A typical weak acid resin has limited capacity below a pH of 6.0 conditions making it unsuitable for deionizing acidic metal in wastewater treatment (Rengaraj S. *et al.*, 2001). Strong base anion resins functional group is quaternary amine and has the ability to exchange anions. When in the OH- ionic form, this type of resins is capable to act like very strong insoluble bases in solution. Strong base anion resin can be divided to two types which are Type I and Type II. Type I resins incorporate quaternary methylamines as the functionality and behave as the strongest bases of the anion resins. For Type II resin, its basicity is lower than Type I is formed when the amine used in the reaction is dimethylethanolamine, which results in improved regeneration efficiency.

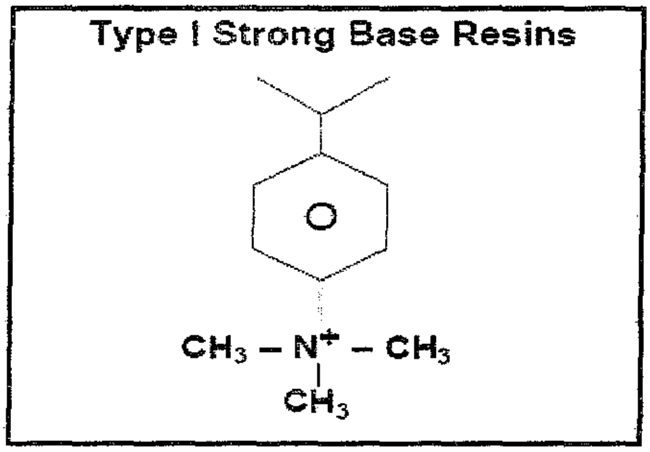


Figure 3: Molecular structure for Type I anion resin

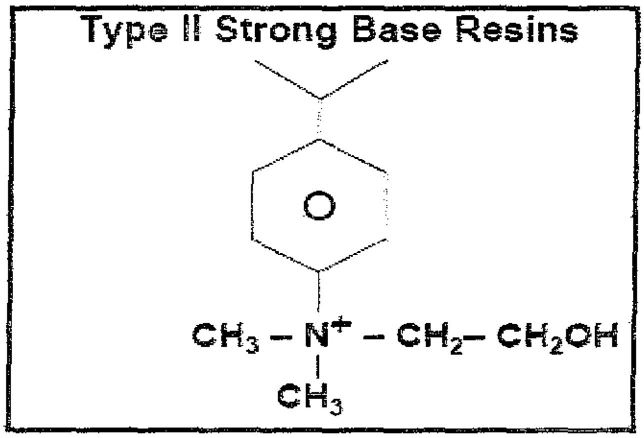


Figure 4: Molecular structure for Type II anion resin

Weak base anion resins contain tertiary amine functionalities which act as acid adsorbers. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0. The weak base resin does not have a hydroxide ion form as does the strong base resin (Rengaraj S. *et al.*, 2001).

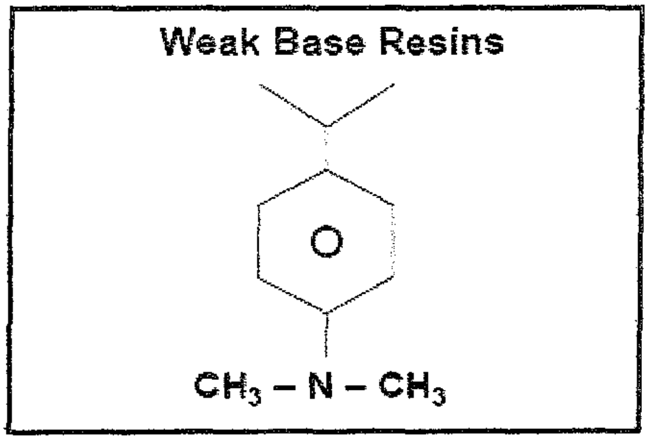


Figure 5: Molecular structure for weak base anion resin

For chelating resins, they have different types of functional group. They remove metals, boric acid or other ions selectively. They may have used in chromatographic separation and in removal and recovery of traces heavy metals from concentrated salt solution.

In this work, strong base anion resin Type I will be used to remove phenol. The solid exchange, as well as a high porosity on which molecular adsorption by hydrophobic interaction can take place (Rengaraj S. *et al.*, 2001). In this case the ion exchanger does not act as such but more as a conventional adsorbent. Plus, strong base anion resin also has high resistance to fouling (Frank D.S., 2000). Phenol can be efficiently removed from polluted wastewaters by using a strong-base anion exchanger. It was observed that its removal capacity was higher than that of other known adsorbents.

2.7 Activated Carbon Surface Modification

Based on the type and nature of the targeted impurities, the surface of activated carbon may be modified to enhance the affinity toward the desired impurity. As an inert porous carrier material having large specific surface area, activated carbon is capable of attracting a variety of chemicals onto it hydrophobic internal surface. Depending on the application, there are different methods to modify activated carbon, which make the surface accessible to a variety of reactants. The modification can be categorized in three classes:

a) Chemical modification
b) Physical modification
c) Biological modification

The chemical modification may further be divided into two broad groups, those resulting in acidic and basic surface. The third type of chemical modification is the surface impregnation of activated carbon with active metals and their oxides. The physical modification includes mainly heat treatment. The biological modification is a relatively newer approach, where biological methods of environmental control can be used for water treatment and other applications (Vivekand G. and Shankar P.A., 2008).

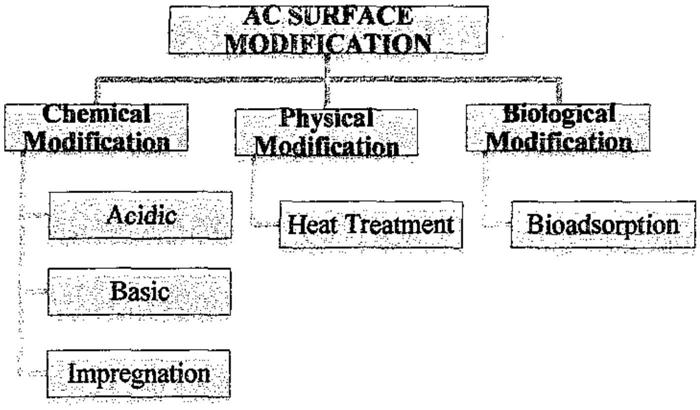


Figure 6: Type of AC surface modification

2.7.1 Chemical Modification

The chemical modification is carried out by impregnation the activated carbon with acid, basic or foreign metal depending on the targeted impurities. Acidic treatment will form acidic surface functional group such as carboxyl, quinine, hydroxyl, carbonyl, carboxylic anhydride and lactone as shown in following figure:

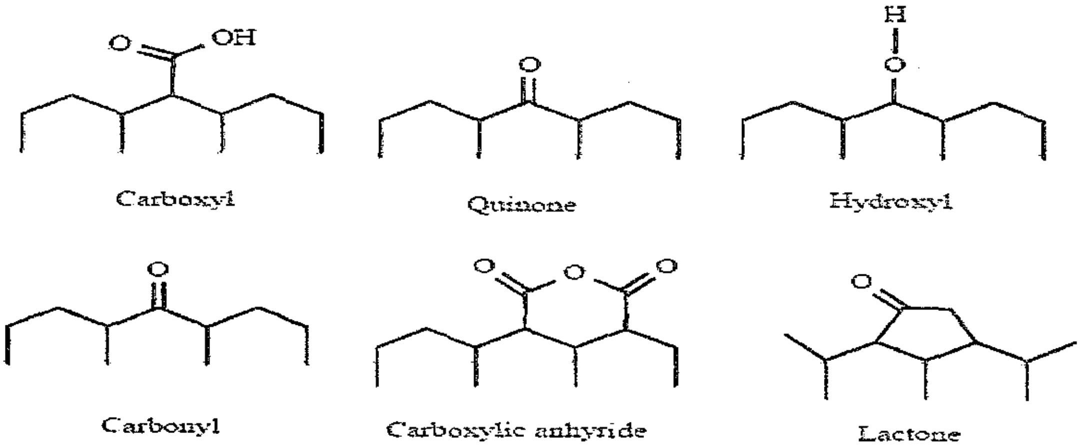


Figure 7: Some acidic surface group bonded to aromatic rings on AC

These functional groups will increase affinity towards metal ions since metal ions have a tendency to form metal complexes with the negatively charged acid groups. Figure 9 shows the cation exchange mechanism with the carbon surface carboxylic acid. Besides that, the existence of acidic group will promote hydrophilicity on the carbon surface.

Figure 8: Cation exchange mechanism with the carbon surface carboxylic group

Based on a study done by Chen, the maximum adsorption capacity for adsorption of copper increased from 6.14 mg Cu/g to 14.92 mg Cu/g after the activated carbon was treated with citric acid (Wengzhong S. *et al.*, 2008). Edwin reported that the maximum adsorption capacity treated with citric acid was enhanced from 0.5813 mg/g to 0.881 mg/g (Shunnian W. and Chen J.P., 2008). However, acidic modification has its disadvantages where it will reduce the BET surface area and pore volume. This is due to the destruction of porous structures within activated carbon during oxidation process. Besides that, the acid modification does give adverse effect on the uptake of organics contaminant. The adsorption capacity if benzene onto activated carbon treated with nitric acid is less than non-treated activated carbon.

As contrast to the acidic treatment, basic modification is highly favorable for adsorption of organic contaminant. A research conducted by Yamin shows that the activated carbon treated with KOH demonstrate better performance in adsorbing organic dye of methylene blue. Basic modification is commonly done by treating the activated carbon with aqueous ammonia and sodium hydroxide. Under basic solutions, it is expected that OH– ions react with the surface functional groups of activated carbon.

Surface impregnation is another method for chemical modification of activated carbon. The term 'impregnation' defined as fine distribution of chemicals and metal particles on the internal surface of AC (Vivekand G. and Shankar P.A., 2008). The rational for employing impregnation are to optimize the catalytic properties of activated carbon by promoting it's built in catalytic oxidation capability, to promote synergism between activated carbon and the impregnating agent and to boost the capacity of activated carbon as an inert porous carrier. Vivekand reported that the activated carbon impregnated with silver, copper, nickel, aluminum and iron has enhanced adsorption capacity towards fluoride, cyanide and heavy metals like arsenic in water.

For this project, chemical modifications of basic groups on the surface are carried out by treating activated carbon with potassium hydroxide (KOH) because the alkaline treatment of activated is beneficial in enhancing the adsorption of organic species like phenols.

2.7.2 Physical Modification

Heat treatment is the major method so far reported for physical modification that partly remove some of the humic acids lodged in the micropores; therefore result in increase surface area. Furthermore, the heat treatment of activated carbon under inert flow is favorable for enhancing adsorption of organic compounds since the basic characteristic of activated carbon is amplified at high temperature.

2.8 Adsorption Isotherm

Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature and the resulting function are called as adsorption isotherm. There are several equations that are often used to describe adsorption isotherm were develop, but the most commonly use to describe adsorption characteristic of the activated carbon used in wastewater treatment is Freundlich Isotherm, defined as (Metcalf and Eddy, 2003):

$$\frac{X}{M} = KC^{\frac{1}{n}}$$

Where X/M: Amount of contaminant adsorbed per unit mass of adsorbent, mg adsorbate/g activated carbon

C: Concentration of contaminant in the water stream

K,n: Empirical constants particular to the contaminant

The constant in the Freundlich isotherm can be determined by plotting log (X/M) versus log Ce and get a straight line with i/n is slope value and $logK_f$ as y-axis intercept. The equation written as:

$$\log(\frac{X}{M}) = logK_f + \frac{1}{n} logC_e$$

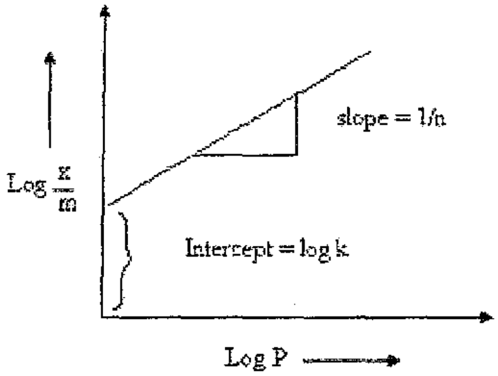


Figure 9: Freundlich Isotherm Curve

2.9 Characterization

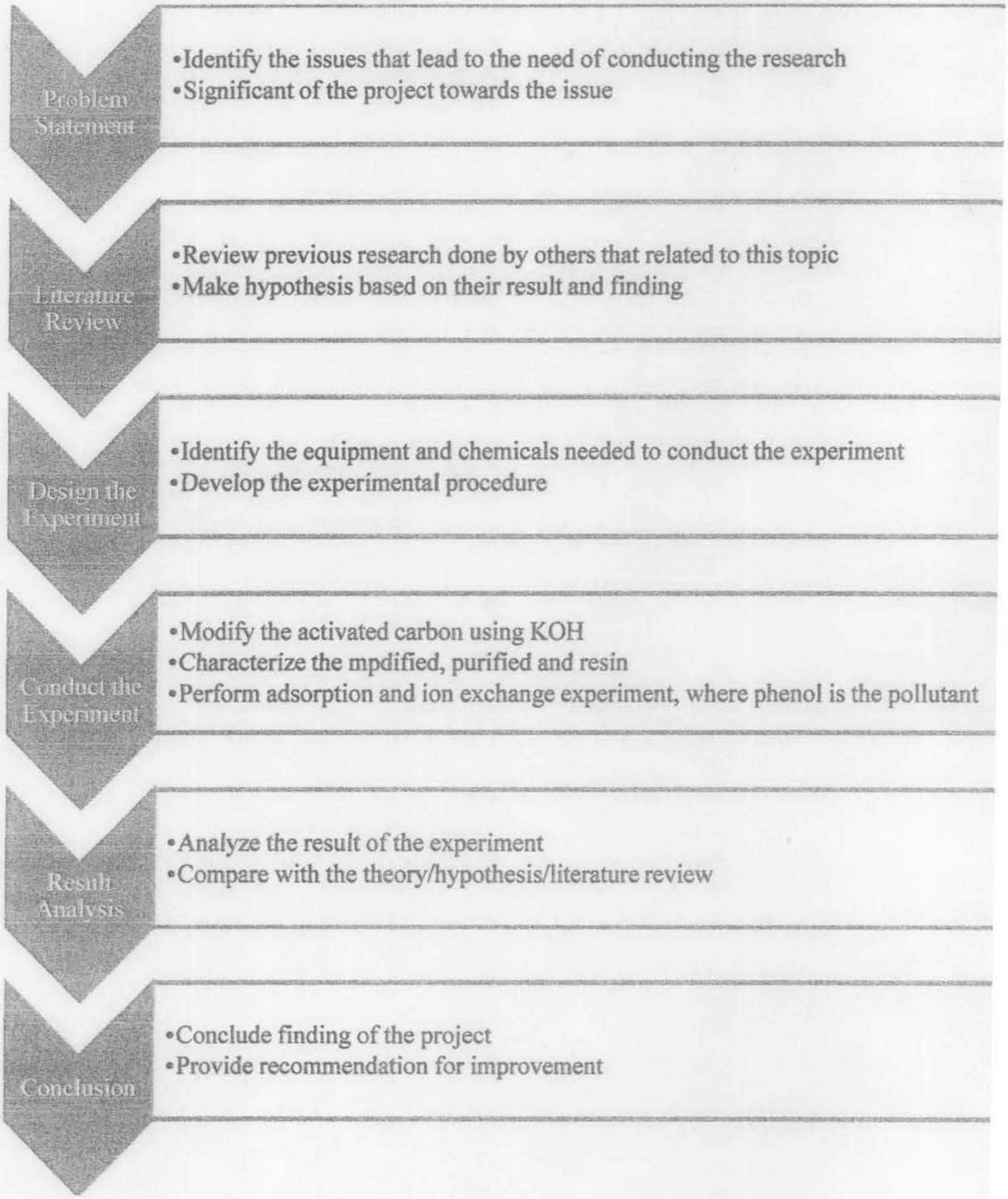
2.9.1 Fourier Transform Infrared Spectrum (FTIR)

FTIR analysis is used to investigate variations in the functional groups of the sample. The increase and decrease in the spectrum peaks shows how the experimental conditions affect the structure of material. FTIR is used to identify the chemicals either organics or not.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Research Methodology



Problem Statement

- Identify the issues that lead to the need of conducting the research
- Significant of the project towards the issue

Literature Review

- Review previous research done by others that related to this topic
- Make hypothesis based on their result and finding

Design the Experiment

- Identify the equipment and chemicals needed to conduct the experiment
- Develop the experimental procedure

Conduct the Experiment

- Modify the activated carbon using KOH
- Characterize the mpdified, purified and resin
- Perform adsorption and ion exchange experiment, where phenol is the pollutant

Result Analysis

- Analyze the result of the experiment
- Compare with the theory/hypothesis/literature review

Conclusion

- Conclude finding of the project
- Provide recommendation for improvement

3.2 Equipment and Chemicals

Following table shows list of equipments and chemicals used in this study:

Table 3: List of equipment and chemicals

Equipment	**Description**
Fixed Bed Activation Unit	To activate the modified activated carbon
Ion Exchange Unit	To allow ion exchange process between anion resin and phenol
Oven	To dry the activated carbon during modification process
Water bath shaker	To do adsorption process
UV Vis Spectrophotometer	To determine initial and final concentration of phenol
Chemicals	**Description**
Activated Carbon (R&M)	As adsorbent
Strong base anion Exchange Resin (Amberlite IRA420 Cl)	As ion exchanger
Potassium Hydroxide (R&M)	To modify surface of activated carbon
Phenol (R&M)	As contaminant or adsorbate

3.3 Project Gantt Chart

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Adsorbent Preparation	▨	▨												
2	Modified activated carbon			▨	▨										
3	Ion exchange studies					▨									
4	Adsorption studies						▨								
5	Sample analysis							▨	▨						
6	Adsorbent characterization									▨	▨				
7	Submission of progress report								●						
8	Project Work Continue											▨	▨	▨	▨
9	Poster exhibition											●			
10	Submission of draft report												●		
11	Submission of Dissertation (soft bound)												●		
12	Oral Presentation													●	
13	Submission of Project Dissertation (Hard Bound)													●	

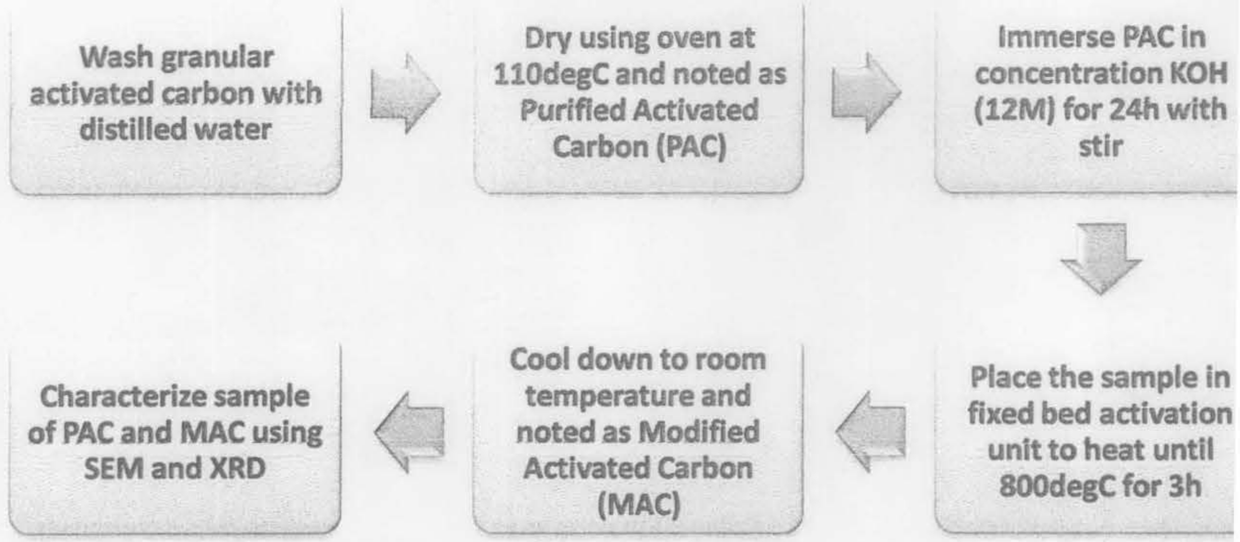
3.4 Experimental Procedure

Basically, three experiment procedures will be conducted in this project involves activated carbon surface modification, adsorption process using modified and purified activated carbon and also ion exchange process using anion resin. For adsorption and ion exchange, the effect of solution pH, adsorbent amount and initial adsorbate concentration will be investigated. This is due to pH of wastewater is differ depends on the process in the industry. The effect of adsorbent amount is studied to investigate its correlation with amount of phenol adsorbed. Different industry release different amount of phenol concentration in its wastewater. So, the effect of adsorbate concentration is very important to be investigated to determine its effect towards adsorption capacity. The effect of temperature is not taken into consideration because the process follow adsorption isotherm.

3.4.1 Preparation Modified Activated Carbon (MAC)

The commercial granular AC (R&M) is used in this study. Prior to use, it is washed with distilled water to remove ash and subsequently dried using oven at 110degC for 24 hours and noted as purified activated carbon (PAC).

Some of the PAC is immersed in concentrated KOH (12M) for 24 hours with stir. After completed, the resulting sample is repeatedly washed to neutralize the pH and remove any excess KOH. Subsequently, the sample is dried in oven for 24 hours at 110degC. Then, the sample is placed in the fixed bed activation unit and heated from room temperature until 800degC under inert condition. The sample is held at 800degC for 3 hours and cool down to room temperature under inert condition. Once it reaches room temperature, air is introduced. The sample is noted as modified activated carbon (MAC).



3.4.2 Characterization

All samples, the raw activated carbon, purified activated carbon (PAC) , modified activated carbon (MAC) and anion resin are sent for characterization using Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD).

3.4.3 Adsorption Studies

The adsorption of phenol by activated carbon is carried out using batch technique. The effect of solution pH, initial adsorbate concentration and adsorbate amount towards adsorption process are investigated. For the effect of pH solution, 0.2g of PAC and MAC are added into two different conical flasks containing 150mL of 150ppm phenol. The pH of the solution is adjusted using NaOH and H_2SO_4 to make it in range between pH 2 to 11 and shake for 60 minutes at 150 rpm. The sample for each value of pH is taken and concentration of phenol is determined using UV-Vis spectrophotometer by 4-Aminoantipyrine Method.

For the effect of initial adsorbate concentration, the adsorption will be carried out using different phenol initial concentration ranging from 50ppm to 400ppm and same amount of adsorbent is used which is 0.2g of PAC and MAC. All of the solutions are stirred for

60 minutes at 150 rpm. Samples are taken after 60 minutes to determine phenol concentration using UV-Vis spectrophotometer.

Meanwhile, for the effect of adsorbent amount towards phenol adsorption, various amount of adsorbent in the range of 0.2g to 2.0g are added to 150ppm phenol and shake for 60 minutes at 150 rpm. Then, the samples are taken to determined final concentration of phenol using UV-Vis spectrophotometer.

For the effect of contact time, 150ml of 150ppm phenol aqueous solution was added to two conical flasks containing 0.2g PAC and MAC. The solution is shaken at 150 rpm. The samples were withdrawn every 5 to 10 minutes. The experiment is done both for PAC and MAC.

3.4.4 Ion Exchange Studies

Batch technique is used for phenol removal by ion exchange process using anion resin. Before the ion exchange resin is used in the experiments, it is pretreated by immersed in deionized water for 3 to 4 hours. Then, the resin is dried at 40degC in vacuum condition for 24 hours before being used. The resin samples were stored in desiccators for experiments.

For the effect of pH solution, 0.2g of anion resin is placed into a conical flask containing 150ml of 150ppm phenol. The pH of the solution is adjusted using NaOH and H_2SO_4 to make it in range between pH 2 to 11 and shake for 60 minutes. The sample for each value of pH is taken and concentration of phenol is determined using UV-Vis spectrophotometer.

For the effect of initial adsorbate concentration, the ion exchange process will be carried out using different phenol initial concentration ranging from 50ppm to 400ppm and same amount of resin which is 0.2g is used. All of the solutions are stirred for 60 minutes. Samples are taken after 60 minutes to determine phenol concentration using UV-Vis spectrophotometer.

Meanwhile, for the effect of adsorbent amount towards phenol adsorption, various amount of anion resin in the range of 0.2g to 2.0g are added to 150ppm phenol and shake for 60 minutes. Then, the samples are taken to determined final concentration of phenol using UV-Vis spectrophotometer.

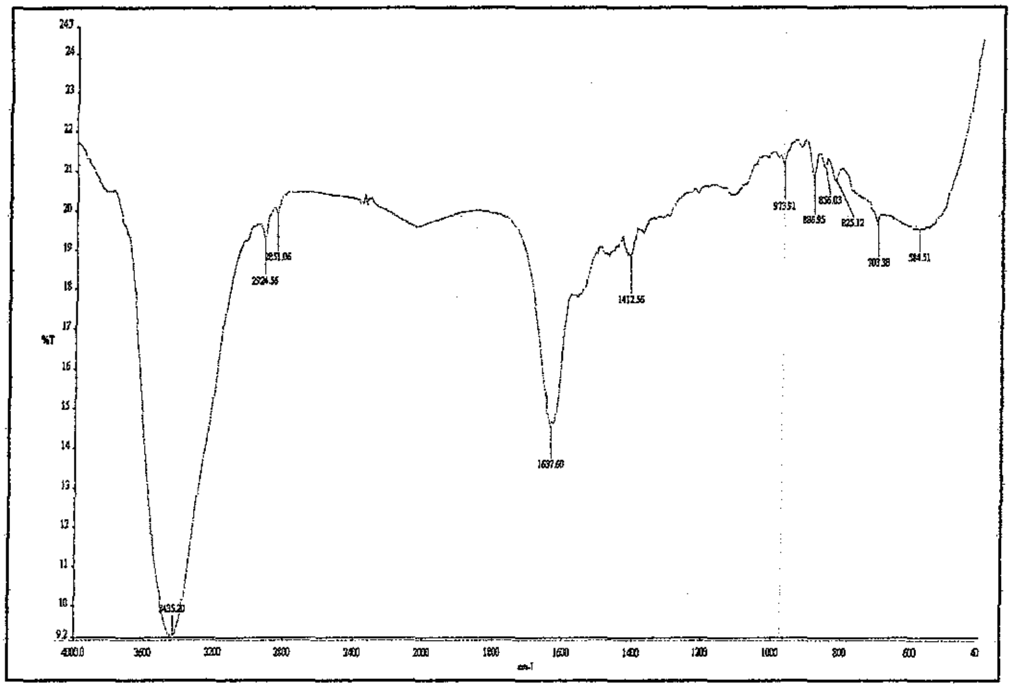
For the effect of contact time, 150ml of 150ppm phenol aqueous solution was added to a conical flasks containing 0.2g anion resin. The solution is shaken at 150 rpm. The samples were withdrawn every 5 to 10 minutes.

CHAPTER 4

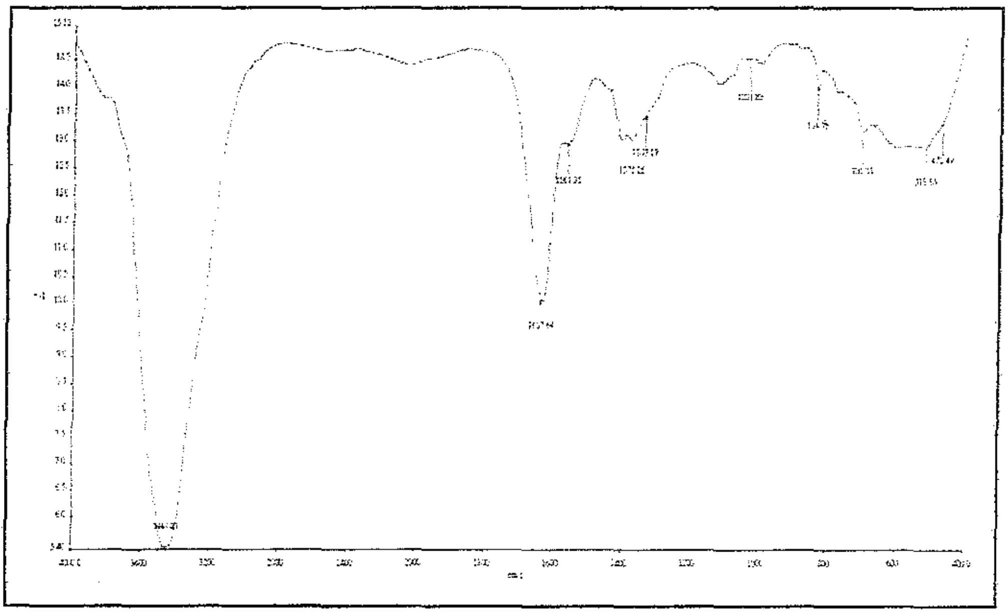
RESULT AND DISCUSSION

4.1 Characterization of Adsorbent

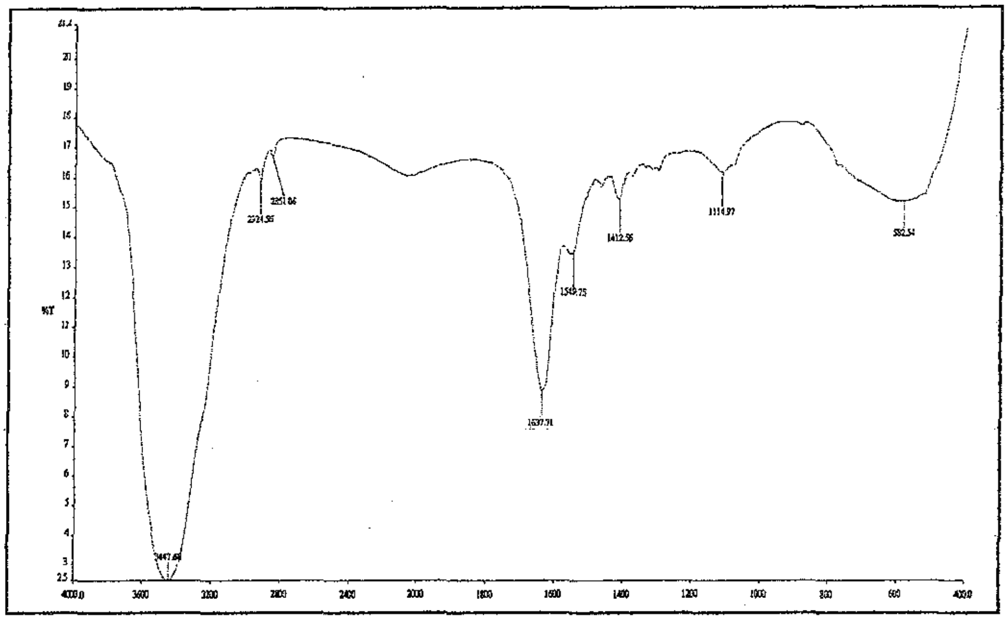
4.1.1 FTIR Analysis



(a)



(b)



(c)

Figure 10: FTIR image for (a) resin (b) PAC (c) MAC

A quantitative analysis for all adsorbents was conducted using FTIR. Based on the Figure 10, the FTIR spectra for PAC and MAC samples are almost similar. For the anion resin, some of the wavelengths are around 2800 cm-1. This might be due to OH- ions in the resin after pretreatment process. For PAC, there are some wavelength ranges between 3300 to 2500 cm^{-1}. This might be due to the OH- on the surface of activated carbon. For MAC, the wavelengths for hydroxyl group is less because some of the ions is remove when modification is performed on the activated carbon.

4.2 Effect of Contact Time for Phenol Removal

The effect of contact time on the amount of phenol adsorbed was investigated at the optimum initial concentration of phenol which is 150ppm. The samples were withdrawn every 5 to 10 minutes time interval and the phenol concentration was determined using UV-Vis spectrophotometer. Figure 11 shows the phenol percent uptake after 60 minutes:

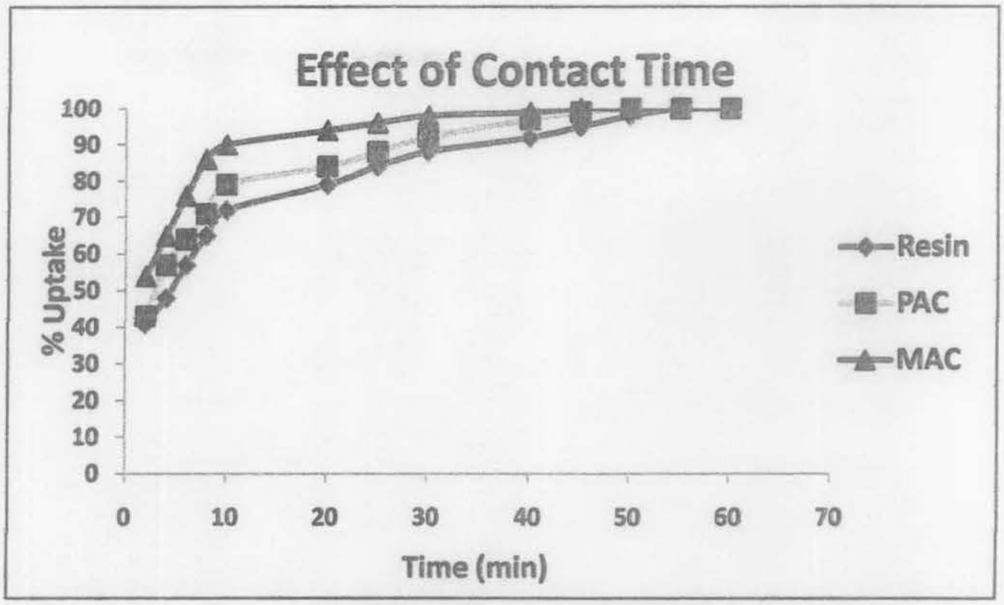


Figure 11: Effect of contact time

The percentage uptake is calculated using the following equation:

$$\% \, Uptake = \frac{Cinitial - Cfinal}{Cinitial} \times 100\%$$

From the above figure, it shows that MAC reach equilibrium fastest compared to PAC and resin after 60 minutes agitation. For MAC, it reached equilibrium at 45 min meanwhile for resin at 55 min and for PAC at 50 min. Between PAC and MAC where phenol is removed from aqueous solution by adsorption separation, MAC reached equilibrium faster. This might be due to greater surface area after the modification of activated carbon using KOH. The change in the surface morphology of the activated carbon will lead to better phenol adsorption. By treating the activated carbon with basic solution, it is expected that the OH- ions react with the surface functional groups of AC creating basic functional groups on the surface of the AC. This will lead to increase in efficiency for activated carbon to remove phenol. So, the alkaline treatment of activated carbon is beneficial in enhancing the adsorption of organic species such as phenol from water ((Vivekand G. and Shankar P.A., 2008).

This result also is parallel to Yamin's study where modified activated carbon with KOH reached equilibrium earlier than the non modified activated carbon in adsorbing ethylene blue (Yamin Y. *et al.,* 2007). The equilibrium time for activated carbon in this study is supported by Bestamin study where the activated carbon starts to saturate with phenol after 1 hour (Bestamin O., 2006).

The PAC achieved equilibrium faster than anion resin. This might be due to the different adsorption capacity between activated carbon and anion resin. The activated carbon adsorption capacity (350 mg/g) is higher than resin adsorption capacity which is only 317 mg/g (Lin S.H. and Juang R.S., 2009). The size of the phenol molecule also probably cause the equilibrium time for resin is more than PAC equilibrium time. It is difficult for the large organic molecule to penetrate inside the resin beads to the interior exchange sites. This means that the ion exchange reaction between the resin charged functional group and the phenol molecule occurs quickly only at the surface of the resins but the process getting slow as the organic gradually penetrates into the resin beads. So, there is a limit resin exchange rate because most of the ions exchange sites are not on the surface of the resin beads.

4.3 Effect of pH

The phenol removal process is greatly influenced by the pH of the solution. In this study, solutions contain 150 ppm phenol with pH 2, 3, 5, 6, 7,9 and 11 are agitated for 60 minutes. The pH is adjusted using NaOh and H2SO4. The following figure illustrated the effect of varying the pH on the phenol uptake from aqueous solution:

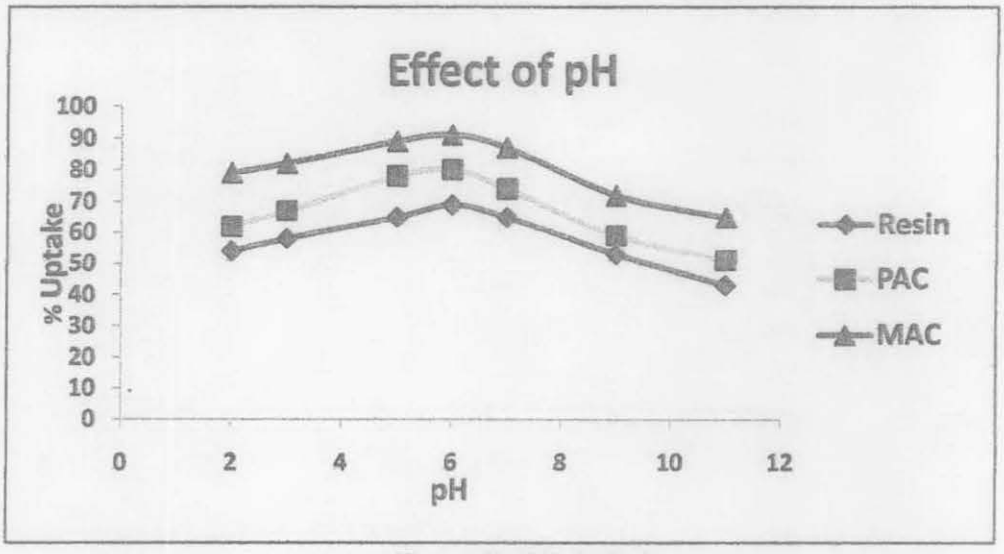


Figure 12: Effect of pH

From the above figure,it is clear that the maximum uptake percentage is between pH 5 to 7 for all adsorbents. From the result, it shows take the amount of phenol removed increase slightly with the acid and at a certain pH, the amount of phenol removed start to decrease while the pH increases. The influenced of the pH has been interpreted in terms of phenol dissociation. The phenol compounds starts to dissociate at a pH higher than pKa value which is 9.89 and ionize into water-soluble phenolate ion, C6H5O- (Carmona. *et al.*, 2006). Hence, the solubility of phenol in water increased and it tend to remain in the solution rather than been adsorbed onto activated carbon. At acidic pH, the phenol percentage removal is higher because phenol was not dissociated yet and easily adsorbed by activated carbon.

For phenol removal by anion resin, at pH higher than pKa, the multi component exchange between hydroxyl and phenolate ions will occur. Subsequently, the ions need to compete to be exchanged by the anion resins. Hence, the adsorption and ion exchange process will achieve good efficiencies for phenol removal if it has been conducted at several pH units where the pH is below than pKa.

Abburi in his study explained that phenols act as weak acids in aqueous solution and the dissociation of hydrogen ion from phenols strongly depends on the pH of the solution (Gao H.J. and Jiang, 2010). In acidic solutions the molecular form dominates and in alkaline medium the anionic form is the predominant species. That explains the experimental results show that the phenol is removed effectively by anion resin at around pH 6. The phenol molecules exist predominantly as neutral at pH 6. Therefore, the interaction between the resin and phenols is considered mainly as non-polar and the forces responsible for adsorption are physical van der Waals forces and phenols can be easily removed by resin.

4.4 Effect of Adsorbent Dosage

Adsorbent dosage is one of the significant parameter in determining the percentage of phenol removal. Following figure shows the percentage of phenol removal at various amount of adsorbent:

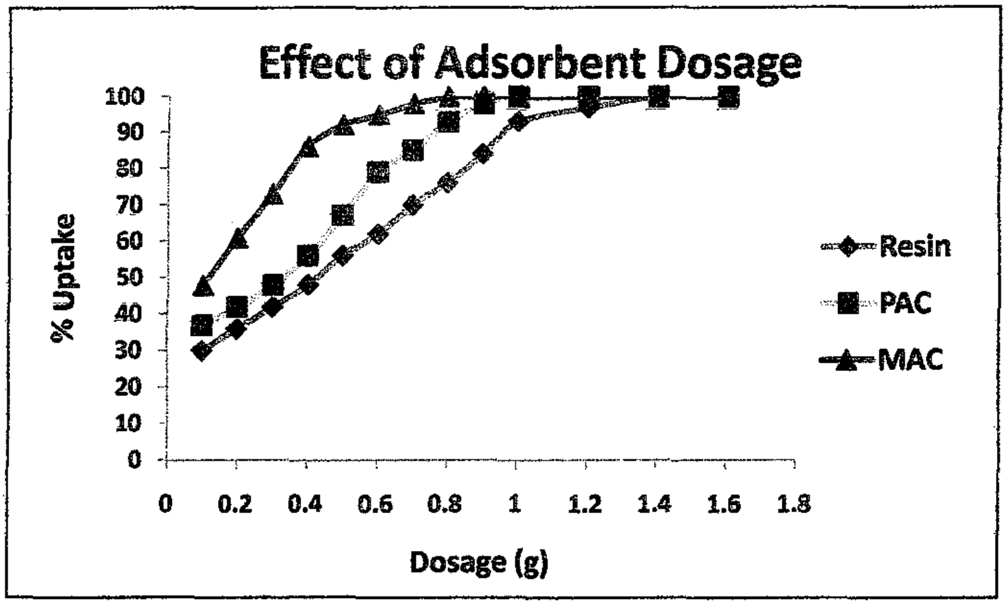


Figure 13: Effect of adsorbent dosage

From the above figure, it can be concluded that the phenol removal efficiency increasing by in by an increasing in dosage of adsorbent. The amount of adsorbent determines the number of surface area available for separation process to occur. This can be explained by the fact that the number of available adsorption sites increases as adsorbent dosage increase. Besides that, the result of the study by Hamzah et al. is same where the Nickel removal efficiency increases by increasing the adsorbent dosage (Hamzah M. and Ujang Z., 2003). Even though the adsorbate is different, however the pattern of the result is still same. Besides that, Mahdi also obtained similar result as this study for boron removal using ion exchange process (Mahdi. *et al.,* 2011).

From the result above, activated carbon adsorbed more phenol compared to anion resin at the same amount. This might be due to the activated carbon's properties which are used to remove organics. Generally, adsorption takes place because all molecules exert forces to adhere to each other (Frank, 2000). Activated carbon tends to adsorbs organic material because the attractive forces between the carbon surface (non-polar) and the contaminant (non-polar) are stronger than the forces keeping the contaminat dissolved in water (polar). Plus, the large surface of the activated carbon due to its particle size and pore configuration allows for the adsorption to takes place.

For phenol removal by ion exchange, the removal efficiency is less compared to activated carbon. The reason is most probably because during the ion exchange process, only selective ions will be displaced with certain selective ions. The ion exchange only continues as long as there are enough selective ions available for the resin to exchange. Once most of the functional groups are saturated with the selective ions, the process will become slow and more resin needed to remove the organic molecule.

4.5 Effect of Initial Concentration

Batch experiments were conducted for 150 minutes at 23°C to evaluate the effect of initial concentration of contaminant (phenol) removal from aqueous solutions. The effect of initial concentration of phenol was examined for concentrations of 50, 60, 100, 150, 200, 250, 300, 350 and 400 mg P/L at constant operating temperature of 23 °C. The pH value was kept constant at the original value of the solutions. The results obtained are illustrated in Figure 14:

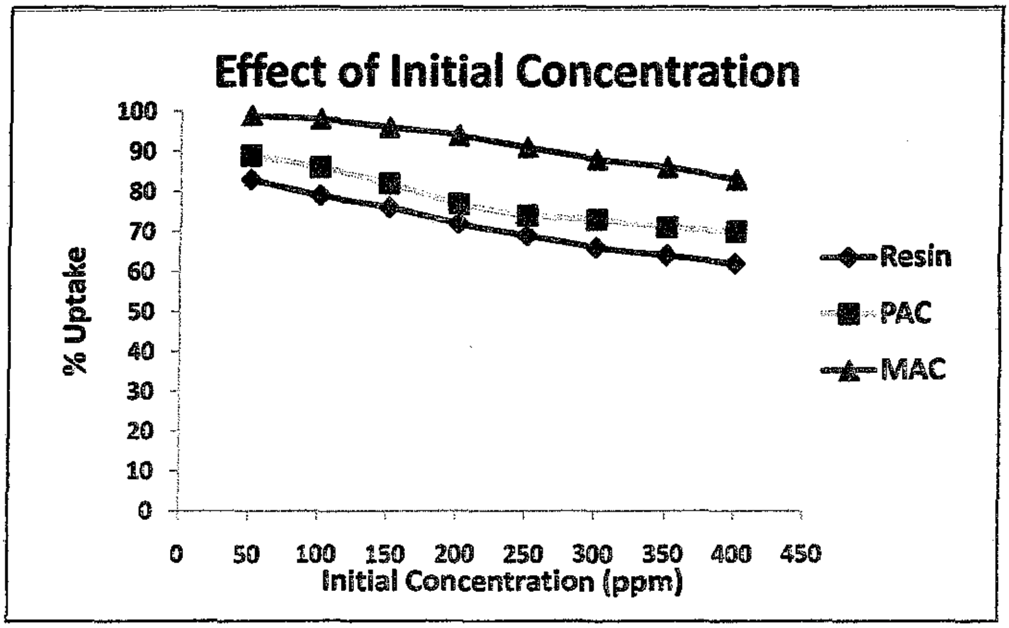


Figure 14: Effect of initial concentration of aqueous solution

Based on the result obtained, phenol percentage removal decreases with increasing initial adsorbate concentration at constant temperature, pH and resin amount. This might be due to the fact that for a fixed adsorbent dosage, the amounts of ion allowable for ion exchange process to occur is limited, resulting in a decrease of percentage removal corresponding to an increased in initial adsorbate concentration. According to Ho, the equilibrium would be reached faster at lower initial concentration, probably because the more sorption sites are available to catch the available ions, which means faster adsorption in lower concentrations. As a result, reaching the equilibrium condition increased when the initial concentration of the solution increased.

For activated carbon adsorption, it is clearly shown that as the initial concentration increase, the adsorptive capacity also increases. The same result also was achieved by Afshin et al. in their research on adsorption of phenol in aqueous solution (Afshin. *et al.*, 2007). This is due to the mass transfer driving force increasing as the initial concentration increase. Hence, the rate for phenol molecules passes from the bulk solution is higher, leads to easier adsorption process to occur. However, the percentage of phenol uptake decreasing as the initial concentration increases. This might be due to the adsorbent already saturated with phenol after shaking for 1 hour.

4.6 Adsorption Isotherm

There are several models have been reported in the literature to describe experimental data as adsorption isotherms. Analysis of the isotherm data is important in order to develop equations that represent the results which could be used for design purposes. In this study two models, which are Freundlich and Langmuir were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration for all adsorbents.

For Freundlich Isotherm, it is expressed as:

$$q_e = k_f(C_e)^{1/n}$$

Where, qe is the amount adsorbed at equilibrium (mg/g), Ce is equilibrium concentration of the adsorbate (mg/l), and k and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity respectively of the adsorbent. The values of k and 1/n can be obtained from the intercept and slope respectively of the linear plot of log qe versus logCe.

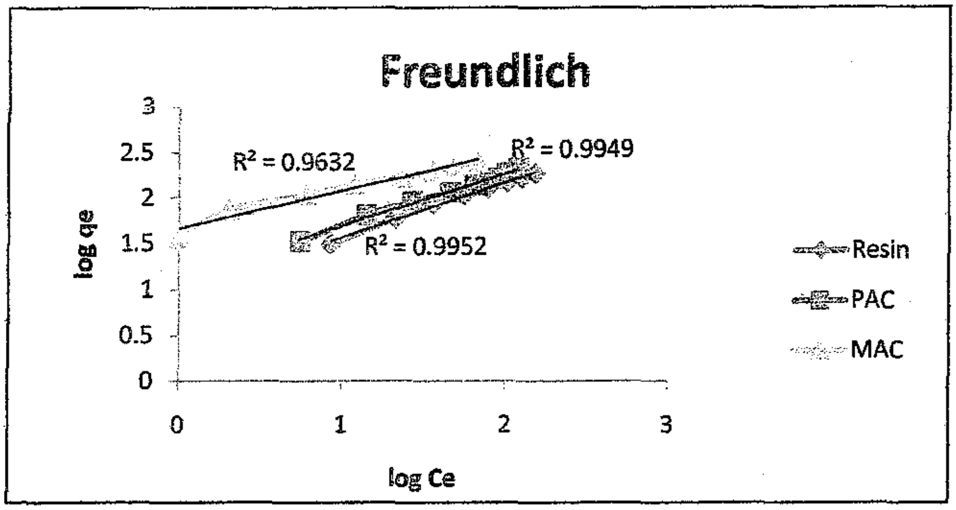


Figure 15: Freundlich Isotherm

The linear form of the Freundlich isotherm model is given by the following relation:

$$\log q_e = \frac{1}{n} log C_e + \log k$$

For Langmuir Isotherm, it is expressed as:

$$q_e = \frac{C_m b C_e}{1 + C_m C_e}$$

Where qe is the amount adsorbed at equilibrium (mg/g), Ce is equilibrium concentration of the adsorbate (mg/l), and cm(mg/g) and b (l/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and slope of the linear plot experimental data of 1/qe versus 1/Ce.

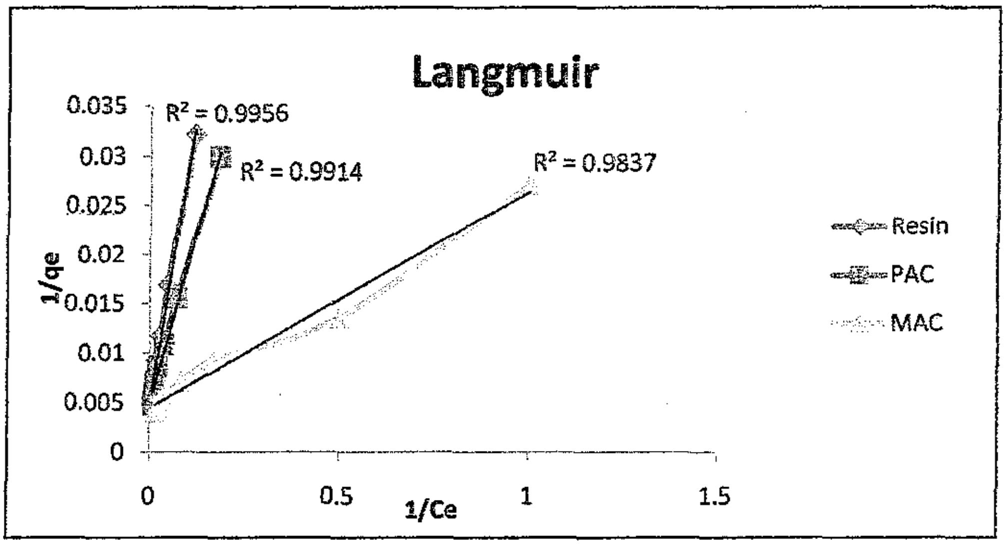


Figure 16: Langmuir Isotherm

Based on the adsorption isotherms above, the results reveal that for MAC and resin obey Langmuir isotherm whereas PAC obeys Freundlich isotherm. This might be due to greater porosity for MAC after undergoing the surface treatment.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The systematic experiment discuss in this paper shows that activated carbon surface modification can be done using KOH. After modification process, the adsorption efficiency is improved and the activated carbon removes phenol better compared to non-modified activated carbon and resin. This is proven that surface modification can be used to improve the adsorption efficiency for the activated carbon. From the adsorption study, it shows clearly phenol percentage uptake is directly proportional with adsorbent dosage used to remove phenol. The optimum pH is between 5 to 7 and 50 minutes contact time with the adsorbent to get the best efficiency of phenol removal. Both Freundlich and Langmuir adsorption models are suitable to describe the adsorption process of phenol removal from aqueous solution.

5.2 Recommendation

For future works continuation, the BET and porosity analysis should be done to analyze the surface and porosity of activated carbon before and after modification with KOH as well as for the resin. The study on the effect of KOH concentration used to modify the activated carbon shall be investigated to determine the effect on the activated carbon. For the operating parameter, the effect of operating temperature towards the phenol removal efficiency by the adsorbent should be studied to get better operating parameter for phenol removal process. Since this experiment is conducted by batch process, the next experiment should be done by continuous process to determine the differences between batch and continuous process. Another method for surface modification also can be done in the future study. It is recommended to perform the adsorption and ion exchange process on different pollutant, both organic and heavy metals ion to confirm whether it is applicable to be used for other contaminant.

REFERENCES

Lin, S.H. and Chery, M. J., (2002) Adsorption of phenol & m-chlorphenol on organobentonites and repeated thermal regeneration, Waste Management, 22, pp. 595-603

He F.,and Lei L., (2004) Degradation kinetics and mechanisms of phenol in photo-Fenton process, J. Zhejiang Univ. Sci., 5(2), pp. 198-205

Mark et al., (2008) Science and Technology for Water Purification, Nature Publishing Group

Carmona, M., De Lucas, A., Valverde, J. L., Velasco, B., and Rodrıguez, J. F., (2006) Combined adsorption and ion exchange equilibrium of phenol on Amberlite IRA-420, J. Chemical Engineering, vol. 117, pp. 155–160

Parka Y., Skellandb, A.H.P., Forneyb, L. J. and Kim, J. H., (2006) Removal of phenol and substituted phenols by newly developed emulsion liquid membrane process, Water Res., 40, pp. 1763–1772

Stavropoulos, G. G., Samaras P., and Sakellaropoulos G. P., (2008) Effect of activated carbons modification on porosity, surface structure and phenol adsorption, J Hazard Mater, Mar 1, Volume 151, Number 2-3, p.414-21

Michelle C., Cesar V., and Adriana F., (2009) Phenol removal from aqueous solution by adsorption and ion exchange mechanisms onto polymeric resin, Journal of Colloid and Interface Science, p.402–409

Ludzack, F.J., Noran, D.K., , (1995) Tolerance of Conventional Wastewater Treatment Process, J. Water Pollution Control, pp 1404-1416

Metcalf and Eddy, (2003) *Wastewater Engineering, Treatment and Reuse*, 4th Edition, McGraw Hill, New York

Azni, I, Katayon, S., (2003) Anoxic Oxidation of Phenol in Wastewater Treatment, J. Applied Electrochemistry, pp703-708, Ahmaruzzaman, M and Sharma, D.K., (2004) Adsorption of phenols from wastewater, J. Colloid Interface Sci., pp 14-24

Geankoplis, (2003) *Separation Process Principles*, 4th Edition, Prentice Hall, New Jersey

Carlos, M.C., (2003) Adsorption of organic molecules from aqueous solutions on carbon materials, J. Carbon, ElSavier, pp 83-94

Fritz, S., Victoria, M., Carlos, M.C., (2001) Adsorption of Phenolic Compounds from Aqueous Solutions by Activated Carbons, J. Langmuir, pp 3301-pp3306

Rengaraj, S., Cheol, K.J., Kim, Y., (2003) Removal of Chromium in Water by Ion Exchange, J. Hazardous Material, pp257-275

Frank, D.S., Activated Carbon Filtration, published in Water Quality Product Magazine Jan 2000

Rengaraj, S., Yeon, K.H., Moon, S.H., (2001) Removal of Chromium from Wastewater by Ion Exchange Resin, J. Hazardous Material, pp273-287

Vivekanand, G., Shankar, P.A., (2008) Surface modification of activated carbon for the removal of water impurities, J. Carbon

Wengzhong, S., Zhihie, L., and Yihong, L., (2008) Surface Chemical Modification of Porous Carbon, J. Chemical Engineering, pp 27-40

Shunnian, W., Chen, J.P., (2008) Modification of a commercial activated carbon for metal adsorption by several approaches, J. Materials of Chemistry, pp 22-26

Yamin, Y., Zobir, H., Faujan, A., (2007) Adsorption of methylene blue onto treated activated carbon, J. Malaysian Studies

Bestamin, O., (2006) Adsorption and desorption of phenol on activated carbon and a comparison of isotherm models, J. Hazardous Material, pp 158-163

Lin, S.H., Juang, R.S., (2009) Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents, J. Environmental Management, pp 1336-1349

Gao, H.J., Jiang, Xin., (2010) Effect of initial concentration on adsorption desorption characteristics and desorption of Hexachlorobenzene in soils, J. Pedosphere, pp 104-110

Hamzah, M., Ujang, Z., Dahalan, F.A., (2003) Removal of Nickel (II), Zinc (II) and Plumbum (II) by Dowex 50W, J. Water Research, pp 311-320

Mahdi, P., Mohsean, S.G., Mahmoud, M.N., (2011) Adsorption study for removal of Boron using ion exchange resin in bacth system, J. Environmental Science, vol. 6

Afshin, M., Bagher, M., Seied, A., and Ebrahimi, R., (2007) Application of commercial powdered activated carbon for adsorption of carbolic acid in aqueous solution, J. Biological Science, pp 2348-2352,