

REMOVAL OF ACRYLIC ACID FROM
PROCESS WATER BY USING ACTIVATED
CARBON BASED COCONUT SHELL

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ACTIVATED CARBON BASED COCONUT SHELL

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SUPERVISOR'S DECLARATION

We hereby declare that we have checked this project report and in our opinion this project is satisfactory in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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I hereby declare that the work in this report is my own except for quotations and summaries which have been duly acknowledged. The report has not been accepted for any degree and is not concurrently submitted for award of other degree.

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ABSTRACT

The presence of Acrylic Acid (AA) in process water is the major problem in many industries which are using AA. There are no proper methods available to remove AA from process water and hence the industries incinerating the process water containing AA to remove it. This method consumes large amount of natural gas and in turn leads to high energy consumption. This research attempt to remove AA via batch adsorption process by using activated carbon based coconut shell. The process water that taken from BASF Petronas Chemicals Sdn Bhd containing 4 wt % of AA is used as sample water in this study. The adsorption capacity was tested by varying different size of activated carbon (granular and powder), amount of activated carbon and contact time. The initial and final concentration of AA was tested by using High performance liquid chromatography (HPLC). The performance of adsorption process is modeled using three types of adsorption isotherms namely, Langmuir isotherms, Freundlich isotherm and Redlich-peterson isotherm. From the experimental results it was found that the activated carbon based coconut shell was good in removing AA from process water and Langmuir isotherm describe the process well compared to other two isotherms with value $R^2 = 0.94278$ %. The maximum capacity of adsorption by using activated carbon based coconut shell was found, $q_m = 94.3396$ mg/g with the dosage used of 400 g/L. In addition to that, the adsorption of acrylic acid onto powder activated carbon represents the favorable process.

ABSTRAK

Kewujudan asid akrilik di dalam air proses menjadi masalah besar kepada industri yang menggunakan asid akrilik. Tiada method yang tepat dan betul untuk memisahkan atau mengeluarkan asid daripada air proses. Sehubungan dengan itu, industri telah membakar air proses yang mengandungi asid akrilik dengan bertujuan untuk mengeluarkan asid akrilik tersebut. Kaedah pembakaran ini menggunakan gas asli dengan jumlah yang banyak dan seterusnya menyebabkan penggunaan tenaga yang tinggi. Oleh itu, kajian ini bertujuan untuk mengeluarkan asid akrilik ini dibuang melalui proses penjerapan secara berkumpulan dengan menggunakan serbuk karbon diaktifkan berdasarkan tempurung kelapa. Asid akrilik yang digunakan dalam kajian ini adalah dari air proses yang diperolehi daripada BASF Petronas Chemicals Sdn Bhd mengandungi asid akrilik sebanyak 4 peratusan berat. Kepekatan awal dan juga kepekatan akhir asid akrilik telah dikaji dengan menggunakan kromatografi cecair prestasi tinggi. Keberkesanan proses penjerapan ini dimodelkan dengan menggunakan tiga jenis penjerapan sesuhu model iaitu Langmuir, Freundlich dan juga Redlich-Peterson (R-P). Daripada kajian ini, keputusan menunjukkan bahawa serbuk karbon diaktifkan berdasarkan tempurung kelapa adalah bagus dalam mengeluarkan asid akrilik daripada air proses dan Langmuir sesuhu adalah model yang paling sesuai berbanding dengan sesuhu model yang lain dengan nilai sebanyak $R^2 = 0.94278$ %. Maksimum kapasiti penjerapan dengan penggunaan serbuk karbon diaktifkan telah dijumpai iaitu sebanyak 94.3396 mg/g dengan jumlah karbon teraktif yang digunakan sebanyak 400g/L. Tambahan itu lagi, keputusan menunjukkan bahawa penjerapan proses asid akrilik terhadap serbuk karbon diaktifkan adalah menggalakkan.

TABLE OF CONTENTS

	Page
SUPERVISOR’S DECLARATION	ii
STUDENT’S DECLARATION	iii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
ABSTRAK	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xii
LIST OF SYMBOLS	xiii
LIST OF ABBREVIATIONS	xiv
 CHAPTER 1 INTRODUCTION	
 1.1 Background of Study	1
1.2 Problem Statement	3
1.3 Research Objectives	4
1.4 Scope of Study	4
1.5 Significance of Study	4
1.6 Definition of Key Terms	5
 CHAPTER 2 LITERATURE REVIEW	
 2.1 Adsorption Process	6
2.1.1 Mechanism of Adsorption Process	6
2.1.2 Types of Adsorption	7
2.1.3 Factors Affecting the Rate of Adsorption	8
2.1.3.1 Size of Particles	8
2.1.3.2 Surface Area	8
2.1.3.3 Temperature	8
2.1.3.4 pH	9
2.2 Activated Carbon	9
2.2.1 History of Activated Carbon	9

2.2.2	Types of Activated Carbon Based	9
2.2.3	Properties of Activated Carbon	11
2.2.4	Classifications of Activated Carbon	13
2.2.5	Applications of Activated Carbon	14
2.3	Acrylic Acid	15
2.3.1	General Information of Acrylic Acid	16
2.3.2	Production of Acrylic Acid	18
2.3.3	Properties and Characteristics of Acrylic Acid	19
2.3.4	Applications of Acrylic Acid	20
2.3.5	Exposure and Toxicology of Acrylic Acid	21
2.4	Coconut Shell Based Activated Carbon	22
2.5	Adsorption Isotherms	24
2.5.1	Langmuir Isotherm Model	25
2.5.2	Freundlich Isotherm Model	27
2.5.3	Redlich-Peterson (R-P) Isotherm Model	28
2.5.4	Summary of Characteristics of Model Sorption Isotherm	30
2.5.5	Determination of Adsorption Capacity, q	30
2.6	Adsorption of Acrylic Acid	30
2.7	Instrumentation	31
2.7.1	High Performance Liquid Chromatography (HPLC)	32
2.7.2	UV-Visible Spectrophotometers (UV-Vis)	32

CHAPTER 3 METHODOLOGY

3.1	Introduction	34
3.2	Overall Research Methodology	34
3.3	Material	35
3.4	Adsorption Method	36
3.4.1	Preparation of Activated Carbon	36
3.4.2	Preparation of Acrylic Acid Stock Solution	36
3.4.3	Study on Effect of Activated Carbon Dosage	37
3.4.4	Study on Effect of Contact Time	37
3.4.5	Study on Effect Particle Types of Activated Carbon	37
3.5	Analysis Measurement	38
3.5.1	Condition on HPLC Analysis	39
3.5.2	Overall Methodology for Preparation of Solution for HPLC Analysis	40
3.5.3	Preparation of Stock Solution	40
3.5.4	Preparation of Sample Solution	42
3.5.5	Preparation of Mobile Phase	42

CHAPTER 4 RESULT AND DISCUSSION

4.1	Calibration Curve of Acrylic Acid	44
4.2	Batch Adsorption Study	45
4.2.1	Effect on Adsorbent Dosage	45
4.2.2	Effect on Contact Time	47
4.2.3	Effect on Particle Type of Adsorbent	49
4.2.4	Effect of Adsorbent Dosage and Contact Time	51
4.2.5	Changes in pH	53
4.3	Isotherm Study	55
4.3.1	Langmuir Isotherm	55
4.3.2	Freundlich Isotherm	57
4.3.3	Redlich-Peterson (R-P) Isotherm	59
4.4	Choosing the Best Isotherm Model	61

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1	Conclusion	63
5.2	Recommendations	64

REFERENCES	65
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APPENDIX	70
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LIST OF TABLES

Table No.	Tittles	Page
1.1	Definition of Key Terms	5
2.1	Types and Properties of Activated Carbon	10
2.2	General Information of Acrylic Acid	17
2.3	Properties and Characteristic of Acrylic Acid	20
2.4	Exposure Limit of Acrylic Acid	21
2.5	Proximate and Element Analysis of Palm Shell and Coconut shell	23
2.6	Cellulose, Halocellulose and Lignin Contents on Palm Shell and Coconut Shell	24
2.7	Types of Isotherm Based on R value	27
2.8	Summary Characteristic of Model Sorption Isotherm	30
2.9	HPLC Condition for Identification of Acrylic Acid	32
2.10	UV-Vis Condition for Identification of Acrylic Acid	32
3.1	Condition for HPLC Analysis	39
3.2	Value of Initial Volume for Different Concentrations of Stock Solution	41
4.1	Percentage Removal of Acrylic Acid with Different Weight of Adsorbent	45
4.2	Percentage Removal of Acrylic Acid with Different Contact Time	47
4.3	Percentage Removal of Acrylic Acid with Different Particle Type of Adsorbent	49
4.4	Percentage Removal of Acrylic Acid with Different Particle and Different Contact Time	51
4.5	pH Values for Different Contact Time	54
4.6	Values of C_e , q_e and C_e/q_e	55
4.7	Differences of q_m in Removal Acrylic Acid	57
4.8	Values of $\log C_e$ and $\log q_e$	58
4.9	Values $\ln ((K_R C_e/q_e)-1)$ and $\ln C_e$	60

4.10	Summary Data for Langmuir, Freundlich and Redlich-Peterson Isotherm Model	61
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LIST OF FIGURES

Figure No.	Tittles	Page
2.1	Mechanism of Adsorption Process	7
2.2	Powder Activated Carbon	14
2.3	Granular Activated Carbon	14
2.4	Acrylic Acid Solution	16
2.5	Molecular Structure of Acrylic Acid	17
2.6	Coconut Shell	23
3.1	Overall Procedure for Adsorption Acrylic Acid from Process Water	35
3.2	BASF Petronas Chemical Sdn. Bhd. Process Water	36
3.3	Orbital Shaker	38
3.4	Overall Methodology for HPLC Analysis	40
3.5	Sonication Condition of Mobile Phase	43
3.6	High Performance Liquid Chromatography	43
4.1	Graph of Calibration Curve for Acrylic Acid	44
4.2	Graph of Percentage Removal of Acrylic Acid against Adsorbent Weight	46
4.3	Graph of Percentage Removal of Acrylic Acid against Contact Time	48
4.4	Graph of Percentage Removal of Acrylic Acid against Adsorbent Weight for Different Type of Particle	50
4.5	Graph of Percentage Removal of Acrylic Acid against Adsorbent Weight for 1 Hour and 10 Hours	52
4.6	Graph of pH Pattern against Contact Time	54
4.7	Graph of C_e/q_e against C_e	56
4.8	Graph of $\log q_e$ against $\log C_e$	58
4.9	Graph of $\ln ((K_R C_e/q_e)-1)$ against $\ln C_e$	60

LIST OF SYMBOLS

$^{\circ}\text{C}$	degree Celcius
%	Percentage
C_0	Initial concentration
C_e	Equilibrium concentration
g	gram
g/L	gram per liter
mg	Miligram
mL	mililiter
q_m	Maximum capacity of adsorption
R^2	Correlation Coefficient

LIST OF ABBREVIATIONS

AA	Acrylic acid
AC	Activated carbon
ACGIH	American Conference of Governmental Industrial Hygienists
C	Carbon
GAC	Granular activated carbon
H	Hydrogen
HPLC	High performance liquid chromatography
IUPAC	International Union of Pure and Applied Chemistry
N	Nitrogen
O	Oxygen
PAC	Powder activated carbon
ppm	Part per million
rpm	revolution per minute
S	Sulfur
TFA	Trifluoroacetic acid
Wt %	Weight percentage

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

In conjunction with rapidly changing technologies in Malaysia, there are increasing in amount of industrial company that directly will increase the amount of industrial products and as well wastes generated. In the industrial, the water is widely used especially in the process site that known as process water. Besides can be recycled in the process, process water also may discharge from the factory. When the process water is discharged, these not only could threaten the animals but also society's health as well environment. In addition to that, sometimes, the process chemicals mixed with process water and thus it is necessary for the industries to remove these chemicals before this process water is recycled or discharged as waste water.

The process water taken from BASF Petronas Chemical Sdn. Bhd., Gebeng, contains a lot of chemical components with different amount of weight percentages. In this process water, acrylic acid (AA) contains with high weight percentage compared to the other components. Acrylic acid with IUPAC name of prop-2-enoic acid is the simplest unsaturated hydrocarbon compound. It is a valuable industrial product that used for various important purposes in chemical factories. AA is widely used in many industrial processes and also consumer product. It is include detergent, paints, coating, synthetic fibers, adhesive and others (Kumar *et al.*, 2010). Acrylic acid is completely soluble in water and soluble in certain organic compound such as hexane, benzene. Because of having solubility property, an acrylic acid will cause harm for the water. Besides that, the amount of production acrylic acid cannot achieve the target of production.

Therefore, in order to remove the acrylic acid in the process water, it needs to be treated first before it discharged which called as water treatment. Water treatment can be divided into three types which are physical treatment, chemical treatment also biological treatment. The physical treatment can divided into screening, sedimentation, flotation, granular medium filtration. While for chemical treatment it is divided into chemical precipitation, adsorption, disinfection, dechlorination, ion exchange and other chemical applications. The biological treatments are done by treating with activated sludge process, aerated lagoon, trickling filters and biological nutrient removal. Besides that, the other methods such as coagulation-flocculation, electrochemical oxidation and membrane filtration also can be used in order to treat the unwanted contaminants in water.

For the treatment purpose by using physical treatment such adsorption process which used the adsorbent to adsorb unwanted contaminants in water. There are several adsorbents can be used such clay (Blockhaus *et al.*, 1997 and Hameed, 2007), alumina (Mao and Fung, 1997; Malgat *et al.*, 2004 and Roostaei and Tezel, 2004), silica gel (Roostaei and Tezel, 2004), alginate bead (Kim *et al.*, 2008), as well as activated carbon (AC) (Kumar *et al.*, 2008; Kim *et al.*, 2008; Kumar *et al.*, 2010 and Rivera-Utrilla *et al.*, 2011). The activated carbon adsorbent has been proved as an effective adsorbent in order to remove variety of organic and inorganic pollutants that dissolved in aqueous solution or from gaseous environment (Roostaei and Tezel, 2004; Dias *et al.*, 2007; Hameed *et al.*, 2008; Yuen and Hameed, 2009; Rivera-Utrilla *et al.*, 2011; and Kushwaha *et al.*, 2011). This adsorbent is considered as an effective adsorbent because of the properties like micro-porous nature, large surface area and others.

In the adsorption process whether kinetic process or isotherms process there are several models has been used to prove whether the process is acceptable or vice versa. For instance, there are Langmuir isotherms, Freundlich isotherm as well as Redlich-Peterson (R-P) equilibrium isotherm models have been reported by previous study (Kumar *et al.*, 2008; Kim *et al.*, 2008; Kumar *et al.*, 2010; Hameed *et al.*, 2008 and Ignatowicz, 2011).

1.2 PROBLEM STATEMENT

Acrylic acid is a compound that soluble in water (Kumar *et al.*, 2010) and also in several organic compounds such as alcohol, benzene, chloroform, ether, and acetone. Besides that, the acrylic acid that released in water will undergo microbial degradation, chemical and also photochemical reactions. At higher concentrations, it can affect human, living things and also the environment. Because of the solubility characteristic, the production of acrylic monomer is lower than the actual target of production.

In this research, the process water from BASF Pertronas Chemical Sdn. Bhd. not only contains the acrylic acid, but contains also the other compounds. Based on the data given on the BASF Pertronas Chemical Sdn. Bhd. process water, besides contain acrylic acid, there are also 23 others components present in this water. In this process water, the composition of water is approximately 87 weight percentage (wt %) and AA has the highest amount which is 4 wt %, followed with the other compounds like acetic acid, formaldehyde, maleic acid anhydride and others.

Currently, BASF Petronas Chemical Sdn. Bhd. is incinerating the process water to remove the acrylic acid and also other compounds that present in the process water. This incineration process consumes large amount of natural gas. So that, the removal of acrylic acid from process water will reduce the natural gas consumption and in turn will increase the profit of the process.

Therefore, this research is aims to attempt the removal of acrylic acid by using adsorption technique. Adsorption process by using activated carbon as adsorbent provides low cost and more efficient in this treatment process (Dias *et al.*, 2007 and Acharya *et al.*, 2009). According to Acharya *et al.* (2009), commercial activated is usually used but because the price is expensive, there is a new alternative by producing activated carbon from the raw materials like agricultural waste. For instance, raw materials that has been used are palm kernel shell (Jumasiah *et al.*, 2005), bituminous coal (El Qada *et al.*, 2006), sawdust, baggasse (Ionnidou and Zabaniotou, 2006 and Gratuito *et al.*, 2008), nut shells and peat (Yang *et al.*, 2010) as well coconut shell (Sekar *et al.*, 2004; Amuda *et al.*, 2007 and Ignatowicz, 2011)

1.3 RESEARCH OBJECTIVES

The purposes of this research are:

- i. To remove acrylic acid from process water by using activated carbon based coconut shell.
- ii. To study the adsorption isotherms

1.4 SCOPES OF STUDY

In order to achieve the research objective, the scopes that considered are as below:

- i. The effect of activated carbon dosage.
- ii. The effect of contact time.
- iii. The effect of particle types of activated carbon

1.5 SIGNIFICANCE OF STUDY

The presence of acrylic acid in high concentration and higher toxicity can cause harm for environment and also human. So, treatment by using activated carbon can reduce the pollutions as well negative effects to the human, living things, and also environment.

Besides that, the water can recycle again in the plant and provide low cost for treatment process. It is because, by using a suitable activated carbon, it will indirectly reduce the cost of removal process. In addition to that, the production of acrylic acid will approximately achieved the factory's target by using desorption method to get back an acrylic acid.

1.6 DEFINITION OF KEY TERMS

Table 1.1: Definition of key terms

Terms	Definition
Hydrocarbon	Any class of organic compound which contains only of carbon and hydrogen atoms.
Unsaturated hydrocarbon	An organic compound that contain either double or triple carbon-carbon bonds.
Adsorbent	A material that has a capacity or tendency to adsorb other substance.
Adsorbate	A substance that has been or is capable for being adsorbed.
Adsorption	A chemical process that take places when a liquid or gas (adsorbate) accumulates on the surface of a solid (adsorbent), forming a molecular or atomic film

CHAPTER 2

LITERATURE REVIEW

2.1 ADSORPTION PROCESS

Adsorption process is known as attachment process of a substance either in gas phase or liquid phase to a solid particle. This process is occur when the gas or liquid phase substance are accumulates on the surface of solid. The solid that used is named as adsorbent. Meanwhile, substance that attached to the solid is known as adsorbate. There are a lot of advantages by using adsorption process when compared to the other process which are this process does not cause any pollution or harm for the system, easily regenerative and low cost of process.

2.1.1 Mechanism of Adsorption Process

In the adsorption process, it can be divided into three steps. These steps are started with the diffusion of a molecule to the adsorbent surface or across the liquid film surrounding the adsorbate particles. For example, it is known as external diffusion or film diffusion. Then, it followed by the migration from the external surface into the pores of adsorbent. In the other term, the second step occurs by diffusion of in the liquid contained in the pores or along the pore walls. This migration called as internal diffusion or also known as intra-particle diffusion. Lastly, the process is proceeding with the adsorption or desorption process between adsorbate and active site. In addition to that, monolayer is buildup of the adsorbate. The monolayer occur when the adsorbent is saturated which can't adsorb anymore of the molecule.

The figure 2.1 exhibits the mechanism of the adsorption process that occurs onto solid particles.

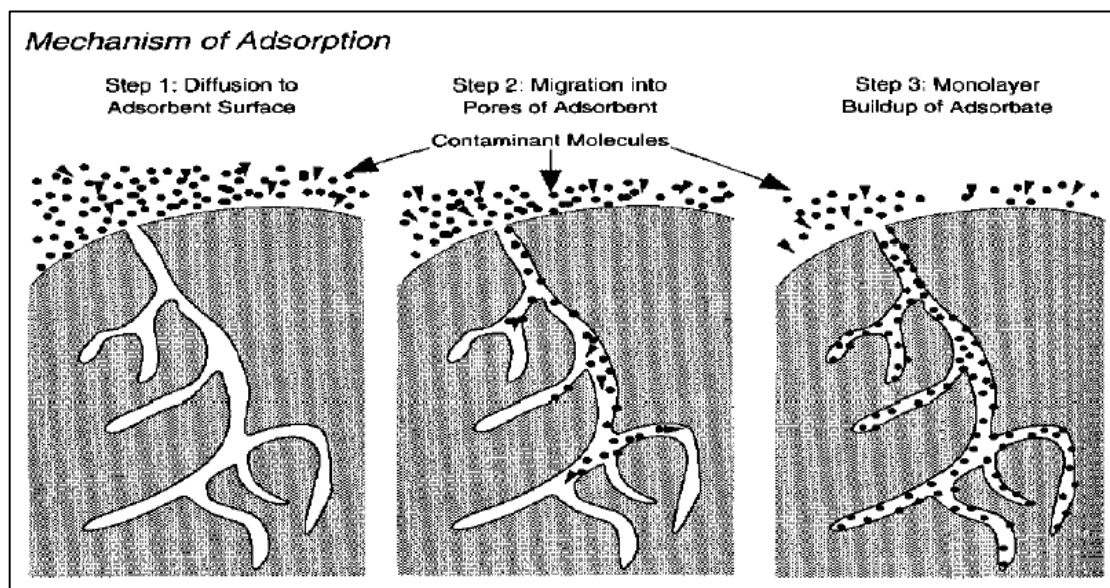


Figure 2.1: Mechanism of adsorption process

Source: Athappan (2008)

2.1.2 Types of Adsorption

Adsorption process can be divided into two types which are physical adsorption and chemical adsorption. The physical adsorption process will occur when the bonds exists between an adsorbate and adsorbent is weak which is the bonding occur from the van der Waals forces. For example of weak bonding is van der Waals, hydrogen bond as well dipole-dipole bond. For this type of bonding, this may cause the bond between adsorbate and adsorbent easily to broken if there is heating process of adsorbent or reducing the pressure are occurs.

Meanwhile, the chemical type of adsorption contains very strong bonding between the adsorbent and adsorbate. This strong interparticle bond occurs between adsorbate and adsorbent is due to an exchange of electron. For instance are ionic bond

and covalent bond. Therefore, with strong chemical bonding, the adsorbent used cannot be recovered again.

2.1.3 Factor Affecting Rate of Adsorption

In the adsorption process, the factors like particle sizes, surface area, temperature, and pH may affect the rate of process to occur.

2.1.3.1 Size of Particle or Molecular Size

Size of particle that may determine also as molecular weight of the particles is one of the factor and sources of energy for the movement purpose of particles. At a given temperature, the particle with smaller molecular weight or smaller molecules are able to move faster compared to the particle that has high molecular weight. Therefore, the rate of adsorption of smaller particles is faster compared to the largest one.

2.1.3.2 Surface area

Surface area of the adsorbent is also one of the important parameter that able to affect the adsorption rate. The surface area is directly proportional to the rate of adsorption. This means that, when the surface area is larger, the rate of adsorption is high. This is due to the large surface area contact occurring between adsorbate and adsorbent (Acharya *et al.*, 2009 and Kumar *et al.*, 2010).

2.1.3.3 Temperature

Adsorption process that taking place usually in exothermic condition, which is releasing heat. The rate of adsorption process is indirectly proportional to the temperature supplied during the adsorption process. This means, when the heat supplied is increase, the energy of the particles also increase as well this will increase the kinetic movement of the particles. Therefore, with the increasing of temperature, the rate of adsorption will decrease (Mao and Fung, 1997; Kumar *et al.*, 2008 and Kumar *et al.*, 2010).

2.1.3.4 pH

pH may determined as the degree of ionization process. This means that pH will determine either the solution is strong or weak of acid or base respectively. pH generally give inversely impact on the rate of adsorption which mean when pH value is lower, the rate of adsorption is increase (Hameed *et al.*, 2008 and Kim *et al.*, 2008).

2.2 ACTIVATED CARBON

2.2.1 History of Activated Carbon

Most of all materials able to contain high carbon content which has the potential to be activated. Activated carbon start used in a long time ago. It is started used in 1500 BC when Ancient Egypt followed by Hippocrates used it as an adsorbent for medicinal purpose, purifying agent and also to remove odor. According to Bansal and Goyal (2005), an Ancient Hindu used charcoal or namely activated carbon for water filtration.

During First World War, the application of activated carbon used as a gas masks as a protection from hazardous gases and vapors. According to David (2005) in Shaharuddin (2009), the application of activated carbon is used widely in a various industry.

2.2.2 Types of Activated Carbon Based

In order to use activated carbon as adsorbent, there are a lot of types of activated carbon that has been determined. Usually the commercial activated carbon is used in adsorption process such in adsorption of micro pollutants or heavy metals (Dias *et al.*, 2007), removal of acrylonitrile (Kumar *et al.*, 2008), treatment of synthetic dairy wastewater (Kushwaha *et al.*, 2011). But due to the high and expensive of production, there is the new alternative which is produce activated carbon from the wastes that will produce a lower price of production (Hameed *et al.*, 2008 and Kumar *et al.*, 2008).

The activated carbon can be produced from different raw material such as sawdust, bagasse (Ionnidou and Zabaniotou, 2006 and Gratuito *et al.*, 2008), nut shells and peat (Yang *et al.*, 2010), bituminous coal (El Qada *et al.*, 2006), rice husk ash, bagasse fly ash, coal fly ash, straw dust (Kushwaha *et al.*, 2011), apricot stone (Kobya *et al.*, 2005), palm kernel shell (Jumasiah *et al.*, 2005). Besides that, coconut shell also has been noticed as the raw materials in the production of activated carbon (Sekar *et al.*, 2004; Amuda *et al.*, 2007 and Ignatowicz, 2011)

Table 2.1 below indicates the differences between various types of activated carbon such coconut, coal, lignite as well as wood activated carbon and the comparison of these activated carbons in the characteristic of size either micropores and macropores, hardness, amount of ash, the solubility of activated carbon in water, dust, the reactivations level and lastly on the apparent density.

Table 2.1: Several types and properties of activated carbon

Properties	Coconut AC	Coal AC	Lignite AC	Wood AC (Powder)
Micropore	High	High	Medium	Low
Macropore	Low	Medium	High	high
Hardness	High	High	Low	n/a
Ash	5 %	10 %	20 %	5 %
Water soluble	Good	Low	High	medium
Dust	Low	Medium	High	n/a
Reactivation	Good	Good	Poor	None
Apparent density	0.48 g/cc	0.48 g/cc	0.4 g/cc	0.35 g/cc
Iodine Number	1100	1000	600	1000

n/a – not available

Source: Carbochem (2009)

Based on the table above, it generally shows that activated carbon based on coconut more effective compared to the other types of activated carbon. This can be

seen according to the size of micropores of AC. Besides that, it also has good property soluble in water as well has high reactivation. According to Ignatowicz (2011) and Wei *et al.* (2006), activated carbon based coconut shell has properties of high surface area as well as larger adsorption capacity. It also contains the lowest percentage of ash where this contributes to the excellent property in adsorption process. This means, the amount of adsorption and the effectiveness of adsorption process by using coconut activated carbon is higher compared to other types of activated carbon.

In addition to that, when looking on the activated carbon based on coal and wood, the reactivation level of coal and it less soluble in water. Meanwhile, the reactivation of activated carbon based wood is too less or can be described as no reactivation. These two types of activated carbon have low surface areas as well as lower or poor properties in adsorption process. This has also has noted by Ignatowicz (2011) which state that the effectiveness by using activated carbon based on coal and wood is lower.

2.2.3 Properties of Activated Carbon

The adsorption capacity of activated carbon is related to its surface area, pore structure, and surface chemistry. (Ayranci *et al.*, 2005). All the activated carbon is divided into three types of pore sizes which are micropores, mesopores as well as macropores (Cameron Carbon, 2006). But, the size of micropores, mesopores and macropores of activated carbon is different between the others which are according on the types of raw material used in the production of activated carbon. This means that, different raw material used will produce different size of micropores, mesopores as well macropores of activated carbon.

The size for micropores is less than 40 Angstroms (Å), mesopores is in the range between 40 until 5000 Å and lastly is macropores is more than 5000 Å which is usually in the range of 5000 until 20000 Å (Cameron Carbon, 2006). Meanwhile, Wan Daud and Wan Ali (2004) have stated that the pore size for micropore is less than 2 nm or 20 Å, mesopores in between 2 until 50 nm and lastly macropore more than 50 nm. The

value of micropores, mesopores and macropores that stated by Wan Daud and Wan Ali (2004) is little difference and smaller when compared to the value stated by Cameron Carbon (2006). According to the sizes of pores having by activated carbon, the effectiveness of activated is higher when the amount of micropores size is large.

Therefore, in order to choose the suitable activated carbon used in the adsorption process, besides by choosing the lower cost of activated carbon, there are characteristics like iodine number, surface area, apparent density, types of particle size, and also ash contents needs to be considered (Carbochem, 2009).

The iodine number is the basic parameter that used to characterize the performance of activated carbon. Besides that, the iodine number is a parameter for the measurement of the activity level of activated carbon which is the level of activated carbon's activity is directly proportional to the iodine number having in the activated carbon.

Besides that, surface area of the particles also considered in the measurement for capacity of adsorption. The adsorption capacity of activated carbon is directly proportional to the surface area where when surface area is increase, the capacity of adsorption is increase. This is happen because, with the large surface area, there are more contact surface occurs between the adsorbent and adsorbate which this will make more adsorption occur.

In addition to that, the other parameter is apparent density. Density can be determined by mass of particle divided with volume or it also can be calculated by specific gravity of matter multiply with the volume of water which is 1000 kg/m^3 . In choosing suitable activated carbon, the activated carbon with higher density will provide a greater volume of activity. Therefore, the quality of adsorption process also directly proportional to the density of that activated carbon.

Besides that, the type of particles which is the particle size of activated carbon whether granular, powder, pellet or else. According to Carbochem (2009) and Kumar *et al.*, (2008), matter with smaller particle size will provide high adsorption rate compared

to the particle having larger particle size. The adsorption rate occurs higher with smaller size of particle because of the reduction of the required contact time between the adsorbent with the adsorbate.

Last but not least is the content of ash containing in activated carbon. Ash content means the mass of incombustible material that remain after combustion or burning process for a coal samples as the percentage of the original mass of the coal. Higher ash content in the activated carbon has a tendency to reduce the overall activity and reduce efficiency of reactivation level of the activated carbon. This means that the adsorption rate of the activated carbon that contains higher ash content is lowest.

2.2.4 Classification of Activated Carbon

When jump into the classification of activated carbon, it can be classified into powdered activated carbon (PAC), granular activated carbon (GAC), extruded activated carbon (EAC), impregnated carbon, and others. Most previous researchers used powder type of activated carbon (Kumar *et al.*, 2008; Kim *et al.*, 2008 and Kumar *et al.*, 2010) and granular activated carbon (Kumar *et al.*, 2008) for the research purpose especially in the uptake of unwanted constituents in desired solutions.

The size for powder activated carbon is less than 1.0 mm with average diameter between 0.15 mm and 0.25 mm. Meanwhile, granular activated carbon, GAC has a larger particle size compared to the PAC. For the extruded activated carbon (EAC) consist a cylindrical shaped with diameters from 0.8 mm to 40 mm. This is has high mechanical strength and low dust content.

All the types of this activated carbon have different characteristics that will affect the adsorption rate in the adsorption process. Figures 2.2 indicate the illustration of the powder activated carbon.



Figure 2.2: Powder activated carbon

Meanwhile, figure 2.3 shows the granular type of activated carbon.



Figure 2.3: Granular activated carbon

2.2.5 Application of Activated Carbon

Activated carbon whether in the size of powder, granular, pellet as well extruded has been widely used in several applications since in 1500 BC. It has been realized commercially used in order to remove odor, colour, taste and also unwanted organic or inorganic compound from the water. These applications has been noticed by several researches such Goyal and Banzal (2005) as well Kim *et al.* (2008). Those applications

are applied by using activated carbon because of activated carbon able act as an excellent and versatile adsorbent.

In addition to that, because of abundant in wastewater problems, activated carbon is used to treat the wastewater before it is discharged to the river, ocean, or environment. It also has been used in the treatment of industrial waste water, air purification in inhabited spaces such as in chemical industries, restaurants and others. The major application of activated carbon has been applied in removal of unwanted chemical composition in the water (Dias *et al.*, 2007; Rivera-Utrilla *et al.*, 2011; and Kushwaha *et al.*, 2011) like copper ion and phenol (Kim *et al.*, 2008 and Roostaei and Tezel, 2004), dye like Basic Blue 9, Methylene Blue (Jumasiah *et al.*, 2005 and El Qada *et al.*, 2006), benzoic acid (Ayranci *et al.*, 2005), acrylonitrile (Kumar *et al.*, 2008), lead (II) (Acharya *et al.*, 2009), 2,4,6-trichlorophenol (Hameed *et al.*, 2008), pesticides (Ignatowicz, 2011) and others

Besides that, on other field like remedies, activated carbon is used for purification of bloods, removal certain of poisons or toxins. In addition to that, activated carbon also used in treatment of foods, beverage and also in pharmaceutical industries (Ayranci *et al.*, 2005).

In conjunction with the development of new technologies that applied on the application of activated carbon has been noticed by Zhang (2006) in Yang *et al.* (2010), activated carbon can act as a super-capacitors, electrodes, gas storage and others, widely used in process of separation and purification (El Qada *et al.*, 2006 and Yang *et al.*, 2010), as catalyst supports (Dias *et al.*, 2007 and Yang *et al.*, 2010).

2.3 ACRYLIC ACID

Acrylic acid solution known with other common names like vinyl formic acid and propene acid as indicates in figure below is usually commercial in two types of grade which are technical grade and glacial grade. Both types of grade are usually used with different purpose. The technical grade with the percentage of 94 % by weight is used for esterification process. Meanwhile, acrylic acid that contains 98 % until 99.5 %

by weight and maximum percentage of water about 0.3 % is known as glacial grade acrylic acid. This glacial grade commonly used for the production of water soluble resin.

Figure 2.4 represent the liquid acid aqueous solution at room temperature with colourless in colour



Figure 2.4: Acrylic acid solution

Source: <http://cnreachem.en.made-in-china.com/product/UeOnBAfygoYG/China-Acrylic-Acid.html> (2011)

2.3.1 General Information of an Acrylic acid

Acrylic acid is found in acidic solution is a moderately carboxylic acid. At room temperature, acrylic acid appears with colourless liquid. The smell of acrylic acid may be described as irritating, pungent as well rancid and sweet (WBK & Associates Inc, 2002)

Acrylic acid is the simplest of an unsaturated carboxylic acid with chemical formula of $C_3H_4O_2$. This compound contains both double bond and carboxyl group that linked to it C3. C3 means the double bond is linked at the third arrangement of carbon in chemical formula. Figure 2.5 below represents the molecular structure of acrylic acid.

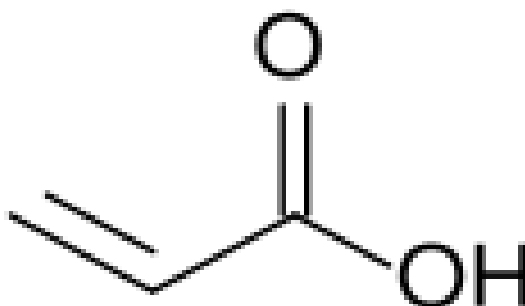


Figure 2.5: Molecular structure of acrylic acid

Source: <http://www.websters-online-dictionary.org/definitions/Acrylic%20Acid> (2011)

The general information of acrylic acid like common and synonyms names, CAS registry number, chemical formula as well conversion factor are as table 2.2 below.

Table 2.2: Names and general information of acrylic acid

Chemical name	Acrylic acid
Common name	Acrylic acid
Synonyms	Propenoic acid
	Acroleic acid
	Viinyl formic acid
	2-Propenoic acid (CAS name)
CAS registry number	79-10-7
Chemical formula	$\text{CH}_2=\text{CHCOOH}$
Conversion factor	$1 \text{ mg/m}^3 = 2.94 \text{ ppm}$

Source: WBK & Associates Inc. (2002) and Safety and Handling Acrylic acid, 3rd edition, BASF Corporation (2003)

2.3.2 Production of Acrylic Acid

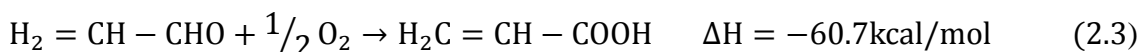
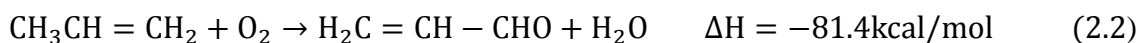
In production of acrylic acid, there are several methods that considered such as propylene method, carbonyl reaction, ethylene cyanohydrins method, acrylonitrile method, and others method. These methods are developed because of long valued commercial of acrylic acid and its ester. But, in order for environmental consideration, most of these methods are neglected.

For propylene method which also called oxidation of propene. In this reaction, propene is converted to acrylic acid with a presence of molecular oxygen. According to Lin (2001), this process can divided into two types which are one step oxidation of propylene or two steps oxidation. All of these reactions are exothermic reaction which is this process occur by releasing heat.

For the one step oxidation, propylene is converted straightly to the acrylic acid. The equation of one step oxidation is described in equation (2.1) as below:



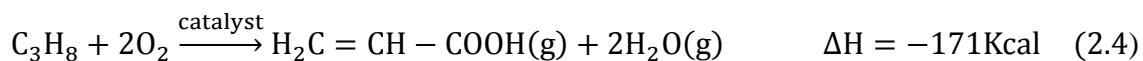
Meanwhile, for the two-step of oxidation of propylene, an acrolein is produce first for the first step process. Acrolein or called also as propenal is a simplest saturated aldehyde group act as intermediate product for oxidation process of propylene before it is converted onto acrylic acid. The two steps oxidation process is described as below where the equation (2.2) is the equation that represent the process for step 1 and equation (2.3) indicates the process for the step 2.



As the overall yield of acrylic acid achieved for both one-step oxidation and two-step oxidation process, it has been determined that yield of acrylic achieved is

higher when through two-step of oxidation process compared through one-step oxidation process. This is has been noted by Lin (2001)

On the other side, Lin also has been shown that acrylic acid also may produce through one-step catalytic oxidation (Lin, 2003). When compared to previous process, the type of process is still the same which is still oxidation process, but the new process has been developed by using catalyst in the process. This process is known as the catalytic oxidation which is involve gas phase with the molecular oxygen. In addition to that, by substituting raw material from propylene to propane also may reduce the cost of starting material in producing acrylic acid (Lin, 2003). The process is as indicates as equation (2.4) below:



2.3.3 Properties and Characteristic of acrylic acid

The properties of acrylic acid can be classified as the physical and chemical properties respectively. Table 2.3 below shows the properties and also characteristic of an acrylic acid:

Table 2.3: Properties and characteristic of acrylic acid

Properties	Information/Value
Formula weight	72.06
Physical form	Liquid above 13 ⁰ C
Boiling point	
760 mmHg	141 ⁰ C
10 mmHg	40 ⁰ C
Melting point	13 ⁰ C
Odor threshold (detect)	0.092 ppm
Density at 25 ⁰ C	1.046 g/cm ³
Solubility	
In water	Infinite
In organic solvents	Freely soluble in most solvents like alcohol, benzene, chloroform, ether, acetone
Flash point	
Tag closed up	50 ⁰ C
Tag open up	54 ⁰ C
Viscosity at 20 ⁰ C	1.19 cp
Light Sensitivity	Light promotes polymerization
Reactivity	Highly reactive between itself and with a wide variety of chemicals.

Source: Safety and Handling Acrylic acid, 3rd edition, BASF Corporation., Technical Data Sheet of Acrylic Acid, BASF Corporation (2003)

2.3.4 Application of Acrylic Acid

Rapidly changing in technology causes the market of acrylic acid is increase and it application is widely used in a various sector. In the process of producing acrylic ester, acrylic acid being used as a raw material or reactant also as a monomer for polyacrylic and polymethacrylic acids and salts (WBK & Associates Inc, 2002). In addition to that, acrylic acid also may use as a co-polymer for the polymer, superabsorbent in diapers baby also in products for feminine hygiene.

According to WBK & Associates Inc (2002), acrylic acid also used in the manufacturing of plastics, in polymer solutions for coating process, paper coating, paint formulations for leather finishing, polishes, used in synthetic fibers process, detergent, cross-linked hygroscopic polymers and also adhesives (Kumar *et al.*, 2010 and Hellwig *et al.*, 1997). The usage of acrylic acid in other fields are like printing inks, floor

polishes, industrial primers, pharmaceutical binders, lacquers for automotive lubricating and fuel oil additives also for hot metal coating, chemical fibers, paper, adhesives, oil additives as well detergents (Silva *et al.*, 2004).

2.3.5 Exposure and Toxicology of Acrylic Acid.

An exposure to acrylic acid may occur through three different routes such as dermal, inhalation as well through ingestion (Kumar *et al.*, 2010). Vapor phase acrylic acid has a strong odor. It allows for initial detection of any potential releases. An exposure could happen during the loading, unloading, transportation of and other related on the acrylic acid. This exposure could happen to the worker and also society.

Table 2.4 below shows the values of exposure limit based ACGIH, OSHA exposure limit also odor exposure limit for acrylic acid. This limit is based on 8 hours time workday without harmful affects on people that exposure to acrylic acid

Table 2.4: Different exposure limit of acrylic acid

Types of Exposure Limits	Value
ACGIH threshold (Limit value, TLV-8hr)	2 ppm, skin
OSHA exposure limit	10 ppm
Odor exposure limit	0.1 ppm
ACGIH - American Conference of Government Industrial Hygienist	

Source: Technical Data Sheet of Acrylic Acid, BASF Corporation (2003) and Basic Acrylic Monomer Manufacturers, Inc. (2006)

In addition to that, acrylic acid is considered as a toxic compound. Because of property of toxicity, although in a low concentration, acrylic acid can cause burn the membranes when it was inhaled or swallowed. Basic Acrylic Monomer Manufacturer, Ins (2006) has stated that acrylic acid shown to be too high toxicity to algae as well does not accumulate in environment.

According to Technical Data Sheet of Acrylic Acid, BASF Corporation (2003), an exposure of acrylic acid can be divided into two which are acute exposure and chronic exposure. Acute exposure may cause injury or irritation symptom on eye, nose or long also may include respiratory inhalation (Kumar *et al.*, 2010). All the seriousness of injuries is depending on the amount and degree of exposure. Meanwhile, if acrylic acid is inhaled, it can effect on contact nasal, if swallowed it may cause gastrointestinal effect and if there is dermal contact, it may cause skin lesions. All these are determined as chronic exposure. Although in the dilute aqueous solution like only 1 % of acrylic acid, it also may cause injury of eyes. But, there is still no chronic effects on toxicity has been identified (WBK & Associates Inc, 2002 and Basic Acrylic Monomer Manufacturers, Inc, 2006)

Meanwhile, when looking on the animal, by repetition in inhaling acrylic acid vapor, it able causes negative effect on animal such as damaging on nasal tissue (Basic Acrylic Monomer Manufacturer, Ins, 2006). Besides that, acrylic acid also may affect common dosing site tissues although with low effect. For instance skin, kidney, stomach as well respiration tract. This has been covered in Fisher 244 rat as well Wistar rats (Black and Finch, 1995 and Hellwig *et al.*, 1997).

2.4 COCONUT SHELL BASED ACTIVATED CARBON

The application of coconut shell is widely used either commercially or traditionally. As traditionally, coconut shell is used as flower pots, heat insulation, brushes, aquarium filters and others. But, with the development of technology, coconut shell has been developed for the adsorption purpose. This coconut shell is activated first before used in adsorption process. For instance, coconut shell is widely used in removal heavy metal such as Cr(VI) (Babel and Kurniawan, 2004), lead (Sekar *et al.*, 2004 and Amuda *et al.*, 2007), zinc (Amuda *et al.*, 2007), phenol (Mohd Din *et al.*, 2009), chromium, pesticide (Ignatowicz, 2011) and others.

Figure 2.6 shows the picture of coconut shell that usually gets from the agricultural waste like oil industry.



Figure 2.6: Coconut shell

Source: http://www.alibaba.com/productfree/114883167/Crushed_Coconut_Shell.html
(2011)

According to Wan Daud and Wan Ali (2004), study on comparison between coconut shells with the palm shell has been conducted in order to find which raw material will produced high efficiency when it was activated. Therefore, there are comparisons on pore development between activated carbon that produced from coconut shell and palm shell.

The differences between coconut shell and palm shell based has been compared in term of amount of carbon (C), hydrogen (H), nitrogen (N), sulphur (S), oxygen (O) moisture, ash as well volatility of compound as indicates in table 2.5.

Table 2.5: Proximate and ultimate analysis of palm shell and coconut shell

Sample	Proximate Analysis (Wt %)				Element Analysis (Wt %)				
	Carbon	Moisture	Ash	Volatile	C	H	N	S	O
Palm shell	18.7	7.96	1.1	72.47	50.01	6.85	1.90	ND*	41.15
Coconut shell	18.6	8.21	0.1	73.09	48.63	6.51	0.14	0.08	44.64

ND* - not detectable

Source: Wan Daud and Wan Ali (2004)

From the overall, it shows that value of ash contained by coconut shell is lower compared to palm shell. This is verify hat coconut shell is having higher reactivation level and more effective as raw material in produce adsorbent as the efficiency of adsorption is higher when the ash amount is lower (Wan Daud and Wan Ali, 2004)

In addition to that, comparison also has been analyzed on the percentage amount of cellulose, halocellulose as well lignin as shown in table 2.6.

Table 2.6: Cellulose, halocellulose and lignin contents on palm shell and coconut shell

Material	Cellulose (%)	Halocellulose (%)	Lignin (%)
Palm shell	29.7	47.7	53.4
Coconut shell	19.8	68.7	30.1

Source: Wan Daud and Wan Ali (2004)

As the overall, the removal process by using activated carbon based on coconut shell is more effective compared to the other activated carbon. Besides consider the efficiency of the adsorption process, the other factors like low operating cost, as well engineering applicability and other factors are taking also as consideration in choosing the type of activated carbon used.

2.5 ADSORPTION ISOTHERMS

The mechanism of adsorption process is too complicated and this means that there is no simple theory may adequate in order to explain the characteristics of adsorption process. When looking on the expression on this process that has been reported, there are majority describes and explains the equilibrium relationship between adsorbent and adsorbate. For instance, the model that has been determined are Langmuir (1918), Freundlich (1894) and others. But, Langmuir and Freundlich isotherm equation model are widely used to show the equilibrium adsorption data obtained (Kumar *et al.*, 2008 and Ignatowicz, 2011). All the types of models are used in order to evaluate the maximum saturation of adsorbent

2.5.1 Langmuir Isotherm Model

The derivation of a semi-empirical isotherm for the purposed of kinetic mechanism study is known as Langmuir isotherm. This isotherm model was found in 1918. According to Ignatowicz (2011), the Langmuir isotherm model is a model that used for the monolayer localized of physical adsorption on homogenous surface. This condition also has been stated also by Kumar *et al.* (2008). In addition to that, this also may be extended to the other type of effect, which is heterogeneity effect as well on multilayer effect.

In order to use the Langmuir Isotherm model, there are several assumptions that have been assumed. First, the surface of the adsorbent is uniform. With the uniform properties of adsorbent, therefore, all the adsorption sites are known as equivalent or same. Secondly is, the adsorbed molecules do not interaction each other, the mechanisms of the adsorption process that occur are considering the same and last but not least, at the maximum or optimum of adsorption process, only monolayer is formed. This means that the molecules of adsorbate is not deposit to each others, adsorbate molecules also already adsorb.

There are a lot of researches that use Langmuir model isotherm as a basic of model equation. For instance, it has been used by Malik (2003), Roostaei and Tezel, (2004), Ayranci *et al.* (2005), El Qada *et al.* (2006), Eren and Acar (2006), Amuda *et al.* (2007), Kumar *et al.* (2008), Hameed *et al.* (2008), Kumar *et al.* (2010), Ignatowicz, (2011), and others. The equation of the Langmuir model isotherm is as below where equation (2.6) is the non-linear equation

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2.6)$$

Where, q_e is amount of adsorbate that adsorbed by adsorbent or known also as adsorption capacity (mg/g), K_L is Langmuir constant (L/mg), C_e is concentration adsorbate at equilibrium (mg/L) and q_m is maximum saturation capacity at the isotherm temperature (mg/g).

By taking reciprocal equation (2.6) and rearrange the final linear equation is as equation (2.7)

$$q_e(1 + K_L C_e) = q_m K_L$$

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

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

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (2.7)$$

$$y = mX + c$$

By plotting the graph of C_e/q_e against C_e , the straight line graph will be appears. Hence, the value slope indicates of $1/q_m$ and intercepts indicates value of $1/q_m K_L$. According to Amuda *et al.* (2007), the essential of the Langmuir isotherm model may explain in the terms of dimensionless constant separation factor or called also as equilibrium parameter, R where R value is determined by equation (2.8) below:

$$R = \frac{1}{1 + K_L C_0} \quad (2.8)$$

According on the equation in calculating of R value, there are several types of isotherm that indicates the shape of the isotherm as shown in table below.

Table 2.7: Types of isotherm based on R value

Value (R)	Types of Isotherm
$R > 1$	Unfavorable
$R = 1$	Linear
$0 < R < 1$	Favorable
$R < 0$	Irreversible

Source: El Qada *et al.* (2006); Amuda *et al.* (2007) and Hameed *et al.* (2008)

2.5.2 Freundlich Isotherm Model

Freundlich model is the first mathematical model that fitted according the isotherm study and was published by Freundlich in 1894. According to Ignatowicz (2011), the Freundlich model is a purely empirical formula that used for the microporous as well heterogeneous adsorbates. Meanwhile, Kumar *et al.* (2008) has stated that Freundlich isotherm model equation is suitable for the highly heterogeneous surface but only over a restricted range of concentration of adsorbate. However, for condition of highly of heterogeneous surface and extremely low concentration of adsorbate, the Henry's law is invalid.

There are a lot of researches that use Freundlich model isotherm as a basic of model equation. For instance, it has been determined by Roostaei and Tezel (2004), Amuda *et al.* (2007), Kumar *et al.* (2008), Hameed *et al.* (2008), Ignatowicz, (2011), and others. The equation (2.9) shows the non-linear equation of the Freundlich model isotherm

$$q_e = K_F C_e^{1/n} \quad (2.9)$$

Where, q_e is amount of adsorbate that adsorbed by adsorbent or known also as adsorption capacity (mg/g), K_F is Freundlich constant (mg/g)/(dm³/mg)ⁿ, n is heterogeneity factor, and C_e is concentration adsorbate at equilibrium (mg/L)

By taking logarithms for both sides of equation (2.9) and rearrange the equation. Therefore, final linear equation is as equation (2.10)

$$\log q_e = \log K_F C_e^{1/n}$$

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

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (2.10)$$

$$y = mX + c$$

By plotting the graph of $\log q_e$ against $\log C_e$, the straight line graph will be appears. Hence, the value slope indicates of $1/n$ and intercepts indicates value of $\log K_F$. According to Eren and Acar (2006), for the adsorption process that produce beneficial adsorption, the value of Freundlich adsorption constant, or intensity of heterogeneity, n should in the range of 1 – 10

2.5.3 Redlich and Peterson (R-P) Isotherm Model

The Redlich-Peterson isotherm model has been published by Redlich as well Peterson. This type isotherm model having three parameters and this equation is the combination of the features having by Langmuir and Freundlich isotherms (Redlich, and Peterson, 1969). This is also has been stated by Kumar *et al.* (2010) as well Hong *et al.* (2009). The Redlich-Peterson equation usually used to shows the adsorption data of solute on the heterogeneous surface. In addition to that, Redlich-Peterson isotherm model reduces the Freundlich equation at high concentration and to Henry's equation at very low concentration (Kumar *et al.*, 2010).

There are a lot of researches that use Langmuir model isotherm as a basic of model equation. For instance, it has been determined by El Qada *et al.* (2006), Kumar *et al.* (2008), Kumar *et al.* (2010) and others. The non-linear equation of Redlich-Peterson model isotherm is as equation (2.11) below.

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^\beta} \quad (2.11)$$

Where: K_R is modified of Langmuir constant (L/g), α_R is constant (L/mg) and β is constant or exponent

By taking reciprocal of non-linear equation (2.11) and rearrange, therefore, the final linear equation is as equation (2.12)

$$\frac{K_R C_e}{q_e} = 1 + \alpha_R C_e^\beta$$

$$\frac{K_R C_e}{q_e} - 1 = \alpha_R C_e^\beta$$

$$\ln \frac{K_R C_e}{q_e} - 1 = \ln \alpha_R C_e^\beta$$

$$\ln \frac{K_R C_e}{q_e} - 1 = \beta \ln C_e + \ln \alpha_R \quad (2.12)$$

$$y = mX + c$$

By plotting the graph of $\ln ((K_R C_e/q_e)-1)$ against $\ln C_e$, the straight line graph will be appears. Hence, the value slope indicates of β and intercepts indicates value of α_R .

According to this equation, there are three unknown parameters which are K_R , β and lastly α_R . Because of there are three parameters unknown, therefore, the value of K_R is assume with various value which that can maximize value of correlation coefficient, R^2 as well the exponent value is still in the range of $0 \leq \beta \leq 1$.

2.5.4 Summary Characteristic of Model Sorption Isotherm

Table 2.8 below shows the summary of the characteristic for the different sorption isotherm models such Langmuir and Freundlich.

Table 2.8: Summary characteristic of model sorption isotherm

Isotherm	Formula	Linear Formula	Formula Constant	Method of Estimation
Langmuir	$q_e = \frac{qbc}{1 + bc}$	$q_e = \frac{1}{b} \frac{a}{c} + q$	$A = \frac{ac}{1} + kc$	Gauss-Newton
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$A = ac^{\frac{1}{k}}$	Gauss-Newto

Source: Kim *et al.* (2008) and Ignatowicz (2011)

2.5.5 Determination of Adsorption Capacity, q_t

The amount of adsorption capacity, q may determined by using equation (2.13). This has been determined by Eren and Acar (2006), Kumar *et al.* (2008), Ayranci *et al.* (2005) and others.

$$q_t = \frac{(C_0 - C_e)V}{W} \quad (2.13)$$

Where q_t is amount of adsorbate is adsorbed on the adsorbent surface at time (mg/g), V is volume of adsorbate in flask (L), W is mass of adsorbent used (g)

2.6 ADSORPTION OF ACRYLIC ACID

The adsorption of acrylic acid has been found treated y using adsorption process for different types of adsorbent like alumina (Eshiduki and Esumi, 1997 and Mao and Fung, 1997), aluminium (Bournel *et al.*, 1996), titanium oxide (Esumi *et al.*, 1998), clay minerals (Blockhaus *et al.*, 1997) and activated carbon (Kumar *et al.*, 2010).

Through the study in adsorption of acrylic acid by using all these type of adsorbent, adsorption process by using commercial activated carbon in the powder types (Kumar *et al.*, 2010) shows more effective adsorption process. For this treatment, the synthetic water is used where the acrylic acid was prepared by their own for several different concentrations about 50 to 500 mg/L. Synthetic water means that in that solution only contain acrylic acid compound. This experiment was conducted by varying the parameter like adsorbent dosage (w), contact time (t), temperature (T) and remain constant the pH value.

Based on that research, it shows that the removal of acrylic acid is increase with the increasing of the dosage of powder activated carbon used, as well with the increasing contact time. As the result, the equilibrium state was achieved from this experiment by using 20 g/L powder activated carbon for 6 hours of process. From this study, it shows the percentage of acrylic acid removal approximately about 93 %. Based on this, it shows that activated carbon is an effective adsorbent used in the removal of acrylic acid from the aqueous solution.

Meanwhile, while looking on the isotherm study that conducted like Langmuir isotherm, Freundlich isotherm and Redlich-Peterson, the results shows that removal of acrylic acid onto powder activated carbon was followed Langmuir isotherm model with the meaning this adsorption process occur at monolayer condition.

But due to the high and expensive of production, there are the new alternative which to produce activated carbon from the wastes which is will produce a lower price of production (Hameed *et al.*, 2008 and Kumar *et al.*, 2008). Therefore, as the other initiatives, the treatment of acrylic acid from the process water will be done with the adsorption process of acrylic acid onto powder activated carbon based coconut shell.

2.7 INSTRUMENTATION

During previous methods of experiment, there are a few instrumentations that have been used in order to determine the concentration of acrylic acid after having adsorption process. For example, there is High Performance Liquid Chromatography

(HPLC) (Ishiku and Esum, 1997 and Kumar *et al.*, 2010), as well UV-Visible Spectrophotometer (UV-Vis) (Mao and Fung, 1997 and Liufu *et al.*, 2005)

2.7.1 High Performance Liquid Chromatography

In Kumar *et al.* (2010), High Performance Liquid Chromatography was used to determine the peak of acrylic acid. In determination of acrylic acid's peak, the conditions of HPLC used are as exhibit in the table 2.9. The detection of acrylic acid's peak is depending on the type of column as well type of mobile phase used. When column C₁₈ is used, acrylic acid's peak appear at for the time in interval 6 minutes to 7 minutes.

Table 2.9: Condition of HPLC for identification of acrylic acid

Parameters	Conditions
Column	18 (3.9 mm x 150 mm)
Mobile phases	1) 4 % acetonitrile 2) 0.1 % H ₃ PO ₄
Flow rate	1.0 mL/min

Source: Kumar *et al.* (2010)

2.7.2 UV-VIS Spectrophotometer

Mao and Fung (1997) have used the other instrument like UV-VIS Spectrophotometer for the purpose of calibration curve as well determines the peak of acrylic acid. The condition's of UV-VIS Spectrophotometer used is as in the table 2.10.

Table 2.10: UV-VIS condition for identification of acrylic acid

Parameters	Conditions
Stock solution	0.1 M phosphate buffer
Absorbance wavelength	211 nm

Source: Mao and Fung (1997)

According to both types of instrumentations used, the results indicate that High Performance Liquid Chromatography is more suitable and more accurate in detection of acrylic acid. This is because, High Performance Liquid Chromatography can detect multi-component components in a solution. This is shown that HPLC is a suitable instrument in detection of acrylic acid in a solution that contains a lot of the other components.

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

The experiment is divided into three major scopes of studies which are study on effect of adsorbent's particle type, effect on adsorbent dosage and effect of contact time between adsorbate and adsorbent. The methodology of this experiment is about preparation of activated carbon, preparation of stock solutions, batch adsorption process and also analysis process by using high performance liquid chromatography (HPLC).

3.2 OVERALL RESEARCH METHODOLOGY

Flow chart below indicates the general process of removal of acrylic acid from process water by using activated carbon coconut shell based.

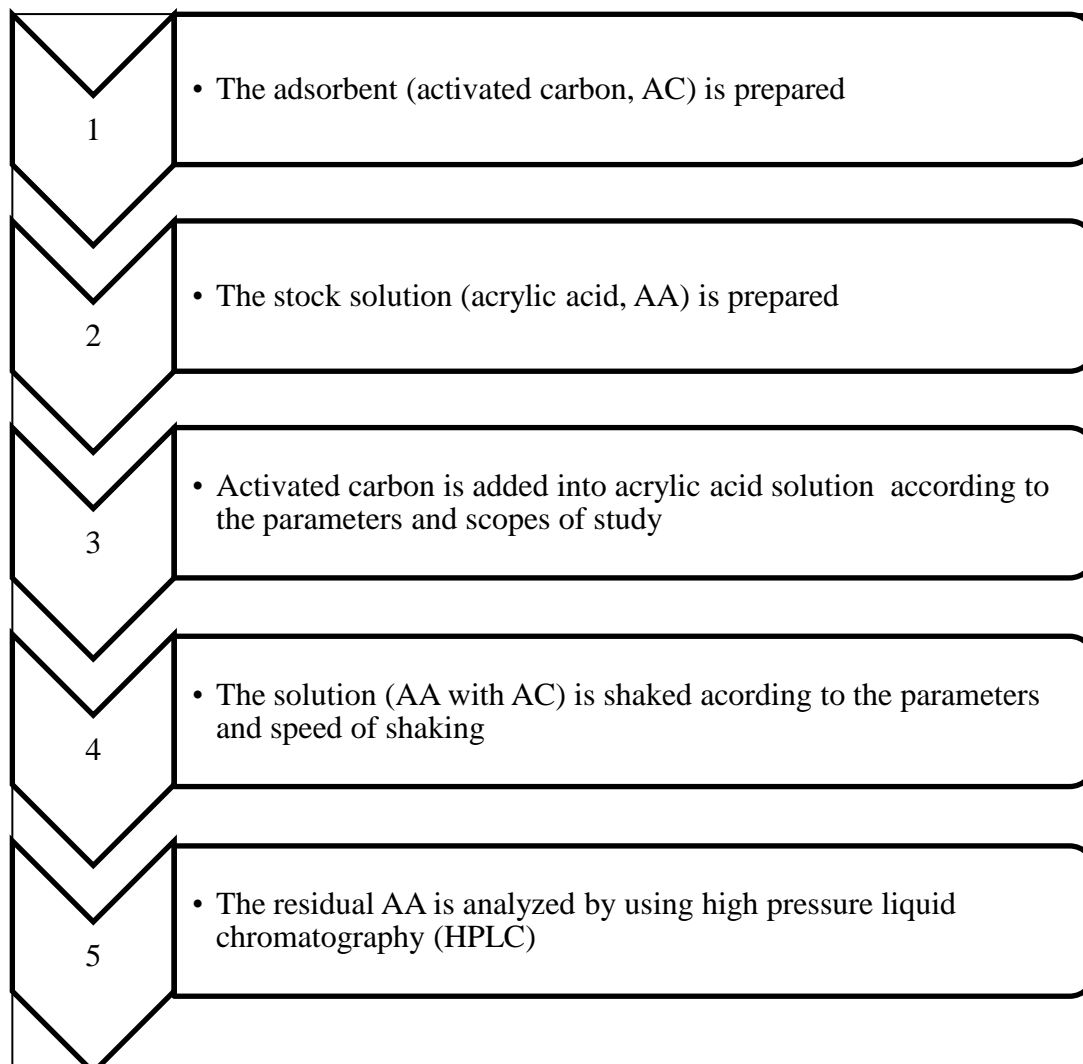


Figure 3.1: Overall research methodology on removal of acrylic acid from process water

Source: Kumar *et al.* (2010)

3.3 MATERIAL

There are two types of materials that used in this research which are adsorbent like activated carbon based coconut-shell in the size of powder and granular. Meanwhile, the other material is adsorbate which is acrylic acid that prepared from BASF Petronas Chemical Sdn. Bhd., Gebeng, Pahang. The initial concentration and

volume taken of acrylic acid for whole experiments is remain constant which is 40 000 part per million (ppm) and 100 mL respectively

3.4 ADSORPTION METHOD

3.4.1 Activated Carbon Preparation.

Based on the objectives of study, activated carbon based coconut shell was used to see the performance of removal process of acrylic acid. The AC used is in granular and powder type. Activated carbon was put in dry condition and closed plastic container in order to avoid activation with environment.

3.4.2 Preparation of Acrylic Acid Stock Solution

Acrylic acid solution with constant concentration was prepared. The fresh stock solution prepared is kept under ambient conditions. The initial concentration of acrylic acid, C_0 for each experiment is 40 000 ppm respectively.

Figure 3.2 shows the process water that got from BASF Petronas Chemical Sdn. Bhd.



Figure 3.2: BASF Petronas Chemical Sdn. Bhd. process water

3.4.3 Study on Effect of Activated Carbon Dosage

The method for this parameter process is as indicates below:

The powder activated carbon was weighted by using analytical balance with a difference amount which is 10 g, 20 g, 30 g, and 40 g. 100 mL of acrylic acid was put into eight of 250 mL Erlenmeyer flask respectively. The activated carbon based coconut shell in powder type is then added into the flask with different amount according to the label. All the sample are shakes by using orbital shaker with constant speed of 150 rpm at temperature $(30 \pm 1)^\circ\text{C}$. This batch process is let for 1 hour. After 60 minutes of batch process, all the samples are takes about 1 mL and filter by using 0.45 μm micro filter before put into vial. After that, all the samples are left about nine hours later for the adsorption process. After 9 hours, all the samples are takes about 1 mL and filter before put into vial.

3.4.4 Study on Effect of Contact Time

For this study, the adsorbent in size of powder was considered. The powder activated carbon based coconut shell was weighted by using analytical balance with amount required which is 10 g. 100 mL of acrylic acid is put into four 250 mL Erlenmeyer flask. The activated carbon is then added into the flask. This sample is shaking by using orbital shaker with constant speed of 150 rpm at temperature $(30 \pm 1)^\circ\text{C}$. This batch process is let for 5 hour. 1 mL of samples is taken for every 20, 40, 60, 90, 120, 150, and 180 minutes with rotation in taking the samples for four Erlenmeyer flask respectively. 1 mL of samples is takes and filter by using 0.45 μm micro filter and put into vial.

3.4.5 Study on Effect Particle Type of Activated Carbon

For this scope of study, particle type of the activated carbon based coconut shell is different which are granular size and powder size. The method of study for the granular activated carbon on amount of activated carbon added is as below:

The granular activated carbon is weighted by using analytical balance with a difference amount which is 10 g, 20 g, 30 g, and 40 g. 100 mL of acrylic acid is put into eight of 250 mL Erlenmeyer flask respectively. The coconut shell activated carbon in granular type is then added into the flask with different amount according to the label. All the sample are shakes by using orbital shaker with constant speed of 150 rpm at temperature $(30 \pm 1) ^\circ\text{C}$. This batch process is let for 1 hour. After 60 minutes of batch process, all the samples are takes about 1mL and filter by using $0.45 \mu\text{m}$ micro filter before put into vial. After that, all the samples are left about nine hours later for the adsorption process. After 9 hours, all the samples are takes about 1mL and filter before put into vial.

All the shaking condition for adsorption process of acrylic acid onto powder activated carbon based coconut shell has been done by using orbital shake as illustrate in figure 3.3



Figure 3.3: Orbital shaker

3.5 ANALYSIS MEASUREMENT

Residual concentration of an acrylic acid is determined by using HPLC. It is used because HPLC that can detect a solution with multi components. Before the analysis is doing, the solution is dilute first by using ultra pure water because the tendency of HPLC to detect solution is within the range of 25 ppm to 125 ppm. If the

AA solution's concentration is higher than maximum range of concentration, the result will be determined also but there will be error occurs. After that the samples will be filtered by using filter with a size 0.45 μm . The smaller size of filter's holes able to avoid the impurities flow together with the samples. This is because the impurities will influence the accuracy of analysis. Besides that, these impurities also might cause clogged on the HPLC's column.

In order to do the analysis by using HPLC, there are several things that need to be considered which are types of column used, types of mobile phase used, and preparation of stock solution in order to do calibration curve as well as the preparation of stock solution of each sample.

3.5.1 Condition on HPLC Analysis

In the HPLC analysis, the main thing needs to consider such as the types of mobile phase, types of column as well as the detection whether by using UV lamp or visible lamp. Table below shows the condition of HPLC analysis

Table 3.1: Condition for HPLC analysis

Parameter	Conditions
Types of Column	C ₈
Column Diameter	4.6 x 150 mm , ID = 5 μm
Column Pressure	67.5 bar
Column Length	15 cm
Column Flow	1.0 mL/min
Linear velocity	0.161 cm/s
Temperature	Ambient (normally 30 °C)
Injection volume	5 μL
Detection	UV at 220 nm, 16 (Ref: 360 nm, 100)
Mobile Phase	3 % methanol; 97 % water with 0.1 % trifluoroacetic acid (TFA)
Type of Signal	DAD 1

3.5.2 Overall Methodology for HPLC Analysis

In order to dilute the samples, there are several methods that need to be considered as indicates in chart below:

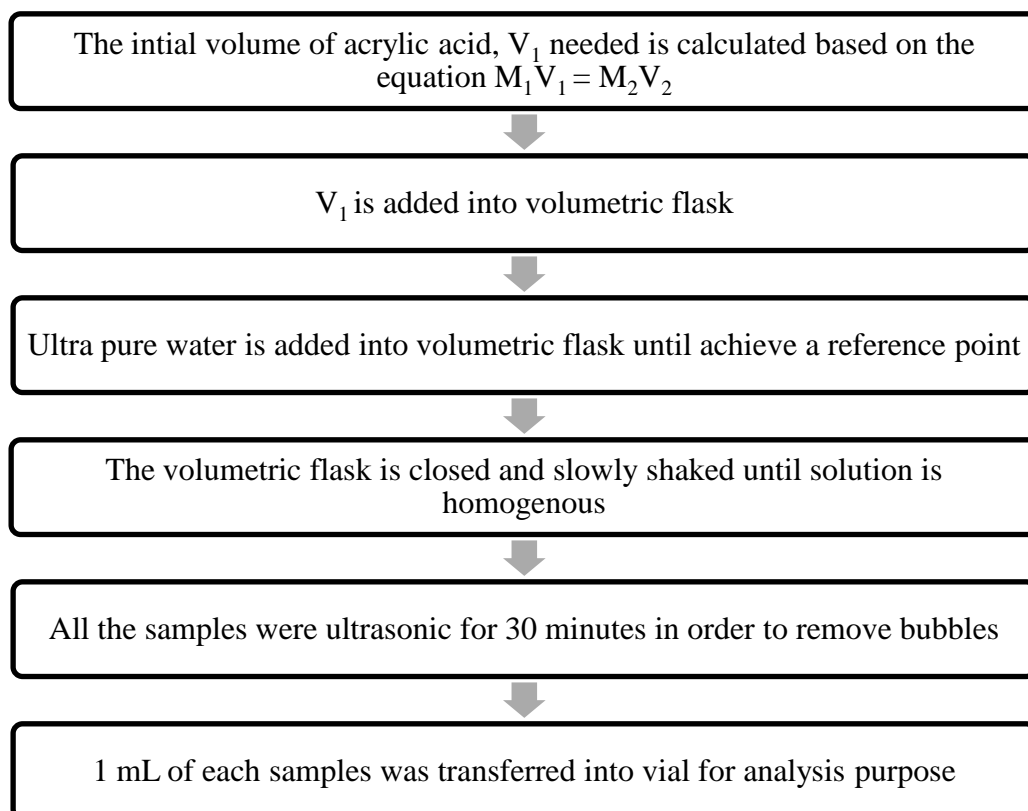


Figure 3.4: Methods for HPLC Analysis

3.5.3 Preparation of Stock Solution

The stock solution is prepared in order to do calibration curve as a reference for acrylic acid analysis. The stock solution is prepared for 1000ppm first and then, it was diluted to 25 ppm, 50 ppm, 100 ppm and 150 ppm.

The preparation of stock solution is prepared by using equation (3.1)

$$M_1V_1 = M_2V_2 \quad (3.1)$$

Where M_1 is initial acrylic acid concentration (40 000 ppm), M_2 is final concentration needed (1000 ppm), V_2 is final volume of solution (100 mL) and V_1 is initial volume acrylic acid needed from 40 000 ppm solution

Therefore, initial volume of acrylic acid needed to dilute the solution to 1000 ppm is

$$\begin{aligned} V_1 &= \frac{M_2 V_2}{M_1} \\ &= \frac{(1\,000\text{ ppm})(100\text{ mL})}{(40\,000\text{ ppm})} \\ &= 2.5\text{ mL} \\ &= 2\,500\text{ }\mu\text{L} \end{aligned}$$

After that, this stock solution is diluted to 5 difference concentrations which are 25 ppm, 50 ppm, 100 ppm, 150 ppm and 200 ppm. The diluted stock solution is prepared by using same equation (3.1) where M_1 is initial stock solution concentration (1 000 ppm), M_2 is final concentration needed and V_2 is final volume of solution (10 mL)

Therefore, initial volume of stock solution needed to dilute the solution to 20 ppm is 250 μL . The same procedure of calculation is done as above but with different value of M_2 which are 50 ppm, 100 ppm, 150 ppm and 200 ppm. Therefore, the initial volume of stock solution, V_1 needed are as shown in table 3.2 below:

Table 3.2: Value of initial volume for different concentration of stock solution

Concentration (ppm)	Initial Volume of Stock Solution, V_1 (μL)
25	250
50	500
100	1000
150	1500

3.5.4 Preparation of Sample Solution

In conjunction with the detection of acrylic acid by using HPLC, the concentration of samples must lower. This is happen because the lower concentration of samples, the accuracy of detection is increase. Therefore, a sample that has taken from the experiment is then dilute with ultra pure water.

The preparation of solution of each samples is by using equation same equation as (3.1) Final concentration needed is 50 ppm and the final volume, V_2 was kept constant for 10 mL for overall dilution process of acrylic acid.

Therefore, initial volume of acrylic acid needed to dilute the solution to 50 ppm is 12.5 μ L. Therefore, all the samples from the experiment is taken about 12.5 mL and put into 10 mL volumetric flask and then top up with ultrapure water until achieved reference point.

3.5.5 Preparation of Mobile Phase

In this experiment, there are two types of mobile phase used which are methanol HPLC grade and water with 0.1 % TFA. All these solutions were filtered first by using filter unit in order to remove impurities. After that, these samples were put into sonicated in order to remove bubbles for 30 minutes.

Figure 3.5 shows the condition of the sonication of the mobile phase.



Figure 3.5: Sonication condition of mobile phase

Figure 3.6 shows the instrument used in the determination of unknown concentration of acrylic acid.



Figure 3.6: High Performance Liquid Chromatography

CHAPTER 4

RESULT AND DISCUSSION

4.1 CALIBRATION CURVE OF ACRYLIC ACID

In order to determine the amount of acrylic acid in the solution, the determination of the acrylic acid's peak is needed by using High Performance Liquid Chromatography (HPLC) is necessary. In this study, four different concentration of acrylic acid solutions were used which are 25 ppm, 50 ppm, 100 ppm and 150 ppm. Based on these values, the calibration curve is determined as shown in figure 4.1

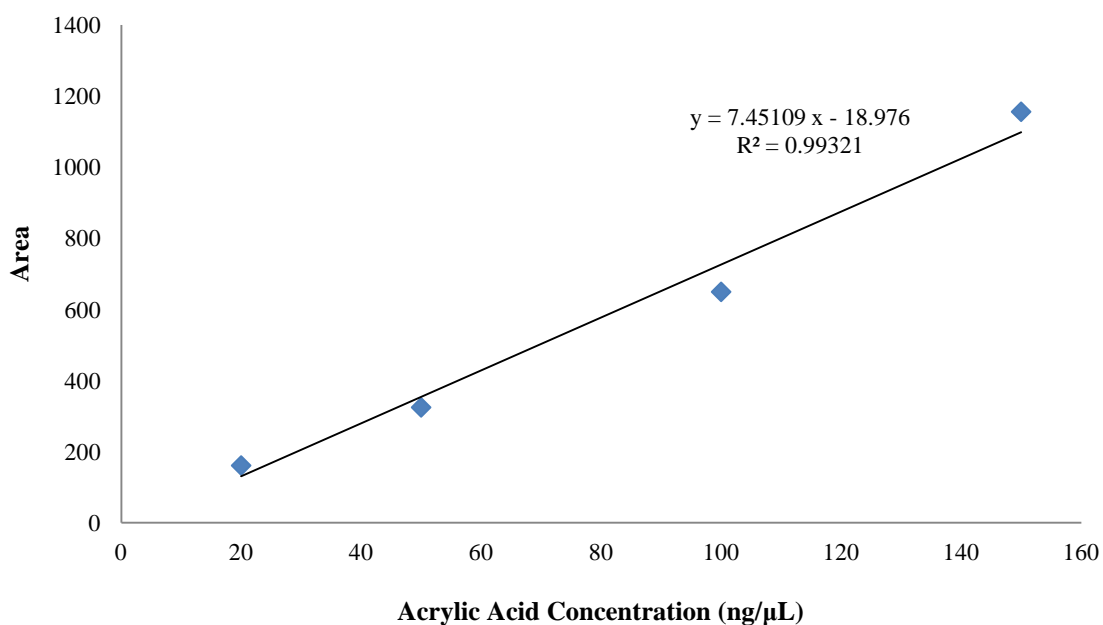


Figure 4.1: Calibration curve for acrylic acid

The value of slope and intercept which are 7.45109 and -18.976 respectively were used for all the experiments in order to find the remaining concentration of acrylic acid. Since the dilution was done for all samples, therefore the remaining concentration of acrylic acid got need to multiply with dilution factor which are 800.

4.2 BATCH ADSORPTION STUDY

The adsorption process in this study was conducted by using batch process. The parameters of adsorbent dosage, contact time as well size of adsorbent were evaluated on the efficiency of the in removing acrylic acid. For the overall process, the initial concentration of AA aqueous solution, C_0 , initial pH, volume of acrylic used and operating temperature were taken as constant with the value of 40 000 mg/L, 2.39, 100 mL and 30 °C respectively.

4.2.1 Effect on Adsorbent Dosage

The effect of amount adsorbent used on uptake on acrylic acid by using powder activated carbon (PAC) was conducted for 1 hour and analyzed. Based on this study, the removal process of acrylic acid is increase with the increasing of adsorbent dosage. The variations of efficiency of removal process based on the adsorbent dosage used are as illustrated in table 4.1 and figure 4.2 respectively.

Table 4.1: Percentage removal of acrylic acid with different weight of adsorbent

Adsorbent Weight (g/100 mL)	Percentage of Removal (%)	Correlation Coefficient (R^2)
10	21.3	0.9950
20	36.0	
30	55.9	
40	69.7	

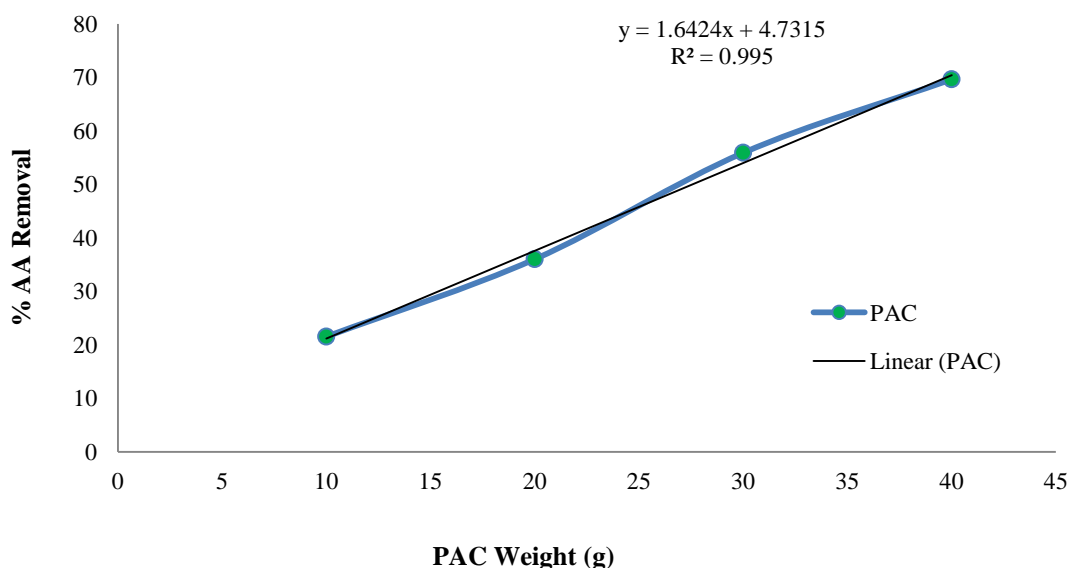


Figure 4.2: Graph of percentage removal of acrylic acid against adsorbent dosage

The graph of 4.2 shows the percentage removal of acrylic acid for condition of 30 °C, and variation of amount of adsorbent weight of 10 g, 20 g, 30 g and 40 g. The lowest adsorbent amount of 100 g/L has shown the efficiency of removal about 21.5 %. Meanwhile, with the highest adsorbent dosage of 400 g/L, the removal efficiency is about 69.7 %. This is shown that the percentage removal of acrylic acid is directly proportional to the amount of activated carbon used.

The efficiency in removal of acrylic acid is increase with the increasing of adsorbent dosage. This condition is occurs because by increasing the adsorbent dosage, it will produce higher surface area. Therefore, there is more capability of larger surface area to do adsorption process. Meanwhile, by using the lower amount of adsorbent, the surface area of adsorbent may become saturated with acrylic acid as well the other compounds. This means, when the adsorbent having the condition of saturated, there is no more acrylic acid is adsorbed. Hence, there are large amount of acrylic acid that residue in the solution. This condition also has stated by Kumar *et al.* (2008) and Kumar *et al.* (2010) in the removal of acrylic acid as well removal of acrylonitrile.

Besides that, the removal of acrylic acid do not achieve higher percentage of removal just approximately 69.7 % by using highest amount of adsorbent compared to removal that has been done by Kumar *et al.* (2010) which removal efficiency was achieved about 93 %. This condition is occurring because this process water aqueous solution not only contains acrylic acid, but also 23 other components. This activated carbon may also adsorb the other components. In addition to that, when compared on the type of the water used also different where Kumar *et al.* (2010) was used is synthetic water, but this study used real process water from industry with higher value of concentration.

4.2.2 Effect on Contact Time

Effects of contact time on the adsorption process occur when the adsorbent is added into the acrylic acid solution. For this study, the initial concentration of acrylic acid, C_0 , pH of solution, volume acrylic acid used are remaining constant with value of 40 000 mg/L, 2.39 and 100 mL respectively. This acrylic acid solution was kept in contact with 100 g/L of activated carbon within time of 3 hours. Table 4.2 and figure 4.3 indicates the removal efficiency of acrylic acid with the variation of contact time respectively.

Table 4.2: Percentage removal of acrylic acid with different contact time

Contact Time (min)	Percentage of Removal (%)
20	26.3
40	27.3
60	30.6
90	39.5
120	39.3
150	39.3
180	38.8

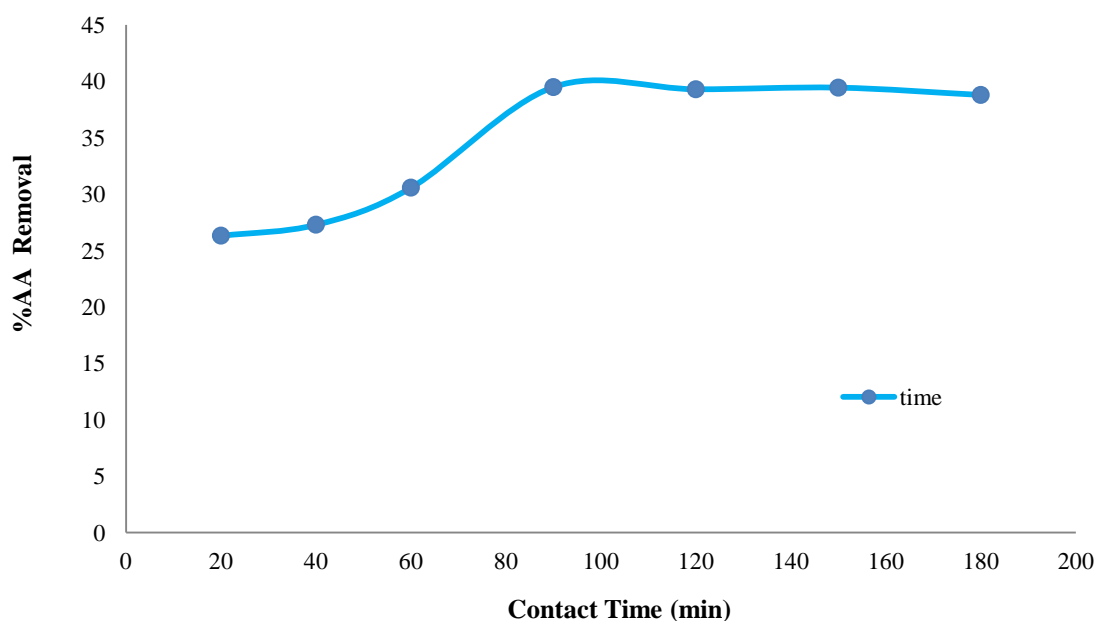


Figure 4.3: Graph of percentage removal of acrylic acid against contact time

From the figure above, it can be shown that the adsorption of acrylic acid onto powder activated carbon occur like simultaneously change at the first 20 minutes of the contact time where approximately about 26.3 % acrylic acid . After that, it has shown only a little increase on the removal process. Based on this trend also, it indicates that the system able to achieve equilibrium condition at the time of 90 minutes with the highest removal percentage of 39.5 %. In addition to that, the optimum value of acrylic acid removal identified is lower and this condition occurs because of the saturated condition facing by using small amount of adsorbate.

The simultaneous adsorption process occur at the initial step of the contact time onto activated carbon occur because of there are large number of vacant site that are available for adsorption process. After the several times, the amount of vacant site having by activated were decrease. According to Kumar *et al.* (2010), after the several times, the remaining vacant site that not occupied by acrylic acid are too difficult to penetrate. This condition is occur due to the repulsive force that happen between acrylic acid molecules on the solid phase and therefore, the driving force of the acrylic acid molecules to reach the vacant site of activated carbon become weaken.

4.2.3 Effect on Particle Type of Adsorbent

The effect of the adsorbent dosage on the removal of acrylic acid in the solution by using powder activated carbon (PAC) was compared with granular activated carbon (GAC) was studied for the initial concentration, C_0 of 40000 mg/l. By taking the experiment with different dosage for each particle and by conducting the removal process occur along 1 hour, the differences in the effectiveness of acrylic acid removal by using powder size and granular size are as shown in table and graph below respectively.

Table 4.3 below show the percentage removal of acrylic acid based on the type of activated carbon used which are granular and powder activated carbon.

Table 4.3: Percentage removal of acrylic acid with different particle type of adsorbent

Types of Adsorbent Particle	Adsorbent Weight (g/100 mL)	Percentage Removal (%)	Correlation Coefficient (R^2)
Powder Activated Carbon (PAC)	10	21.5	0.9950
	20	36.0	
	30	55.9	
	40	69.7	
Granular Activated Carbon (GAC)	10	11.3	0.9441
	20	25.3	
	30	38.4	
	40	39.5	

Figure 4.4 shows the relationship between removals of acrylic acid towards type of particle used.

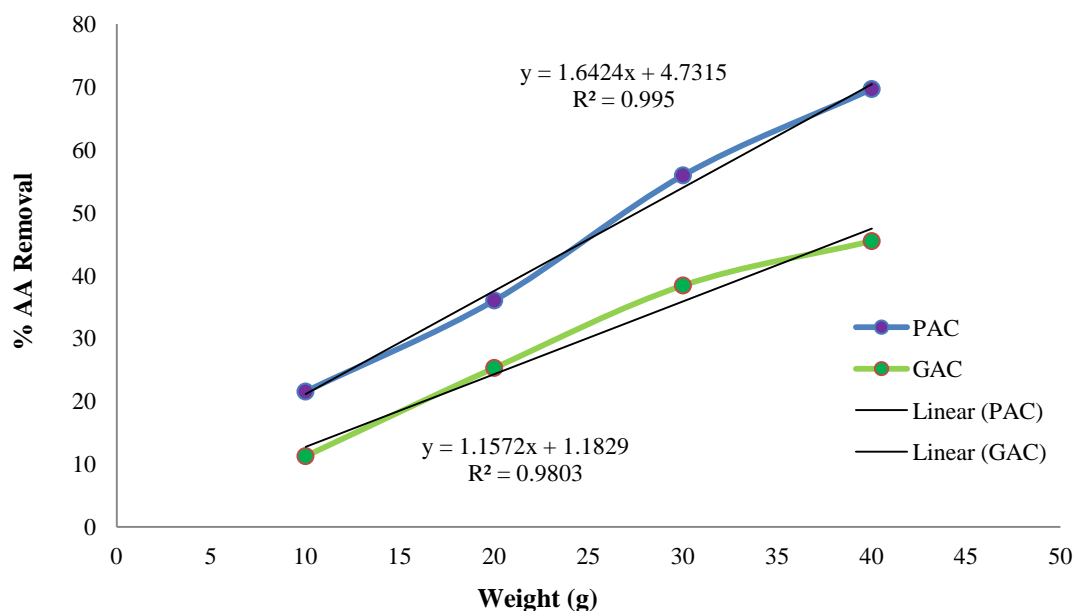


Figure 4.4: Graph of percentage removal of acrylic acid against weight of adsorbent for different type of particle

By looking on the figure 4.4 which is represent the efficiency of the removal process by using different size of activated carbon which are powder size and granular size. From this figure, it indicates that the efficiency on the removal of acrylic acid for the powder size is higher compared to the granular size. This is exhibit that by decreasing the particle size, it will increase the capacity of the removal process. This condition could occur because by decreasing the particle size, there is more surface area that available in the adsorption process (Acharya *et al.*, 2009).

According to Matthews in El Qada *et al.* (2006) which stated that the adsorption process is limited to the external surface area of the adsorbent. The different size of particles posses different size of external surface area where the smaller particles having larger external surface area when compared to large particle size of adsorbent. By this condition, it proved that the limited adsorption process occur to the granular size of adsorbent where this condition will increase the tendency of residual concentration of acrylic acid is higher.

From this study also, it shows that the powder size of adsorbent has higher efficiency from granular size of adsorbent. This condition also has been proved by previous study like removal of acrylonitrile (Kumar *et al.*, 2008), removal of methylene blue (El Qada *et al.*, 2006) that the removal of acrylic acid by using powder activated carbon having higher percentage of removal compared to granular activated carbon.

4.2.4 Effect of Contact Time and Adsorbent Dosage

The effect of contact time as well effect of amount adsorbent used was conducted together where with different amount of 100 g/L, 200 g/L, 300 g/L and 400 g/L for powder activated carbon. The residual concentration of acrylic acid was evaluated for the 1 hour and for 10 hours of contact time respectively. The data of the removal efficiency are as shown in table 4.4 below.

Table 4.4: Percentage removal of acrylic acid with different amount of adsorbent and different contact time

Time (Hr)	Adsorbent Weight (g/100 mL)	Percentage Removal (%)	Correlation Coefficient (R^2)
1	10	21.5	0.9950
	20	36.0	
	30	55.9	
	40	69.7	
10	10	22.2	0.9557
	20	41.8	
	30	59.0	
	40	72.4	

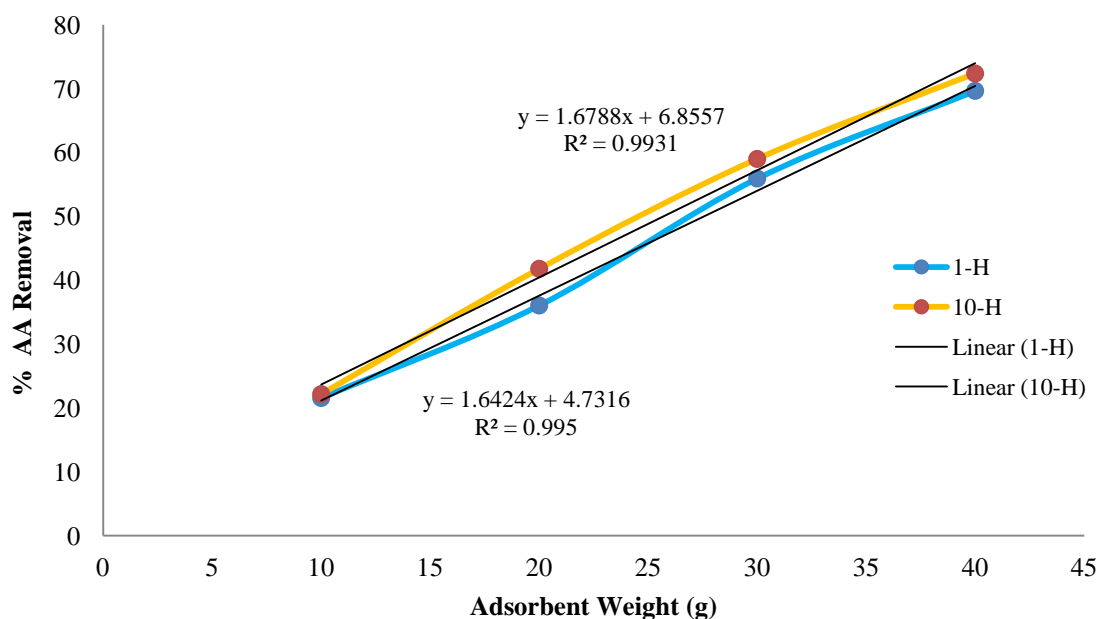


Figure 4.5: Graph of percentage removal of acrylic acid against adsorbent weight for 1 hour and 10 hours

According to the table and graph that exhibit above, when comparing on the amount of activated carbon used, it shows that the efficiency of the removal process is increase with the increasing of activated carbon used. The efficiency of the removal process by using 400 g/L activated carbon is highest for both different contact time of 1 hour and 10 hours where percentage of removal about 69.7 % and 72.4 % respectively. The same condition also occurs for the activated carbon used for 300 g/L which are 55.9 % and 59.0 % for 1 hour and 10 hours respectively. This condition may occur because are as explained in section 4.2.3.

Meanwhile, the condition occurs for the amount activated carbon used which 100 g/L and 200 g/L shows are also increasing on the efficiency on the removal process. Based on the result, by using 100 g/L of activated carbon, amount of removal is about 21.5 % and 22.2 % for 1 hour and 10 hours respectively. The usage of 200 g/L of activated carbon also shows the same condition where removal efficiency is about 36.0 % and 41.9 % for 1 hour and 10 hours respectively.

This condition is occur may cause of the usage of small amount of adsorbent, where at the interval time between 1 hour and 10 hours of operating process, the activated carbon become saturated and there is no more space of area that available for the adsorption process. Therefore, as the nature of adsorption process, desorption occur naturally during the process when there is saturated condition is occur. Hence, the residual concentration of acrylic acid in the solution is increase.

As the overall result, the percentage removal for each adsorbent dosage shows only a little difference between 1 hours and 10 hours of operating process in the uptake of acrylic acid onto powder activated carbon. Therefore, this can be said that for each amount of adsorbent used in the removal of acrylic acid can be considered achieve the equilibrium at the time of 1 hour. This condition has been proved by study on the contact time, where the equilibrium condition is achieved for the time of 90 minutes (1 hour and 30 minutes). This is because, although by considering the operation of 10 hours, the effectiveness of the removal is only occurring a little bit. In addition to that, this will increase the power consumption in the treatment process as well will increase the cost of the process. Besides that, by considering the long time, this is required energy consumption of the process as well the recycling of process water occurs. This will increase the cost of treatment.

4.2.5 Changes in pH

The acrylic acid solution with the concentration of 40 000 mg/L is in acid condition which is cation. At the initial condition where there is no adsorbent is added, the initial pH value, pH_0 is found about 2.39. This value too differs when compared to the pH_0 value of acrylic acid obtained by Kumar *et al.* (2010). This condition occurs because there are a lot of the other components in this solution that also may affect the pH value of the solution.

By adding 100 g/L of powder activated carbon into 40 000 mg/L of acrylic acid solution, the pH of the solution was changes. The changing in pH value is occurring due to the adsorption process that takes pace onto powder activated carbon.

The trend of the changing of pH value on the contact time is as indicates in table 4.5 below.

Table 4.5: pH values for different contact time

Contact Time (min)	pH
0	2.39
20	3.08
40	3.09
60	3.14
90	3.17
120	3.17
150	3.17
180	3.17

Figure 4.6 exhibits the trend of changes in pH towards contact time between acrylic acid and powder activated carbon based coconut shell

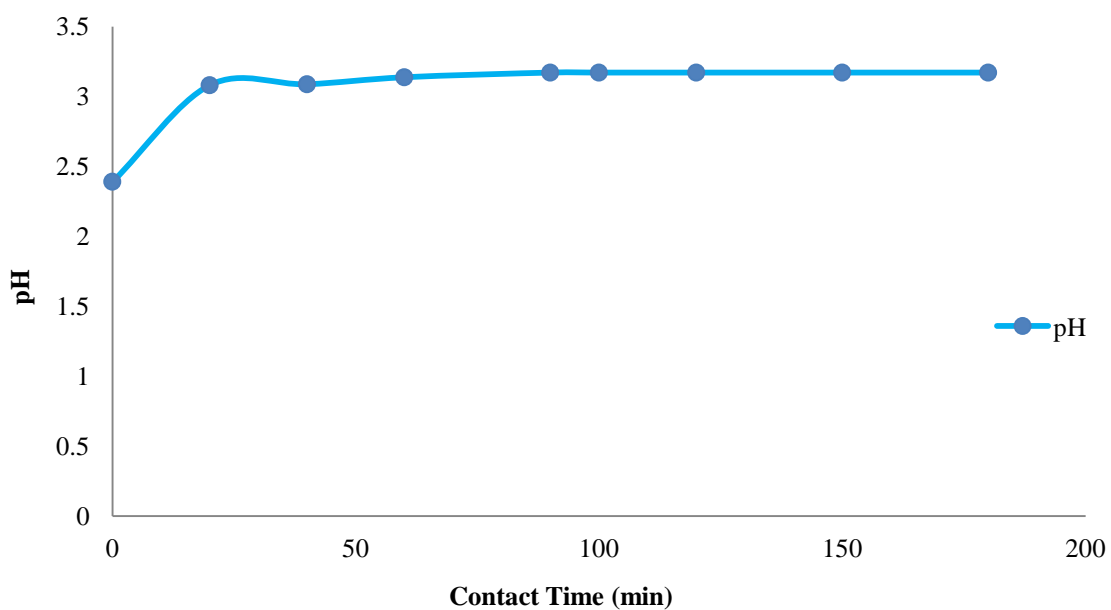


Figure 4.6: pH pattern against contact time

Based on the result and table below, the pH value of the aqueous acrylic acid solution is changing and increase with the function of contact time. The condition of pH is usually changing from the acidic towards to neutral condition. By adding 10g/ml of

powder activated carbon, the spontaneous change occurs on the pH value where from 2.39 to 3.08 at time 0 min to time 20 minutes respectively. After that, it can be see that there is a little increasing value in pH which is 3.09 and 3.14 for 40 minutes and 60 minutes respectively until it become constant at the time of 90 minutes and above.

4.3 ISOTHERM STUDY

In conjunction with the adsorption process, this is important in determining the most suitable and appropriate correlation for the equilibrium curves. There are a lot of types of isotherms equation model that has been developed in order to describe the equilibrium nature of adsorption process. For instance, there are Langmuir isotherms, Freundlich isotherm as well Redlich-peterson isotherm. All of isotherm model having different non-linear equation. With this non-linear equation, it is difficult to determine as well to compare the best fit model these three types isotherm model. Therefore, all these models need to do linearization of each single isotherm models and determine the error for each of models (Wong *et al.*, 2004).

4.3.1 Langmuir Isotherm

Langmuir model isotherm is used and by assuming that the monolayer sorption occur on the adsorbent surface. From final equation of $C_e/q_e = C_e/q_m + 1/q_m K_L$, the graph of C_e/q_m against C_e was plotted. The value of C_e and C_e/q_e are as exhibit in table 4.6 below.

Table 4.6: Value of C_e , q_e and C_e/q_e

Adsorbent Weight (g/100 mL)	C_e (mg/L)	q_e (mg/g)	C_e/q_e (g/l)	Correlation Coefficient (R^2)
10	31382.6	86.2	364.2	0.9427
20	25585.9	72.1	355.0	
30	17629.2	74.6	236.4	
40	12136.2	69.7	174.2	

Figure 4.7 below shows the graph of the Langmuir isotherm model.

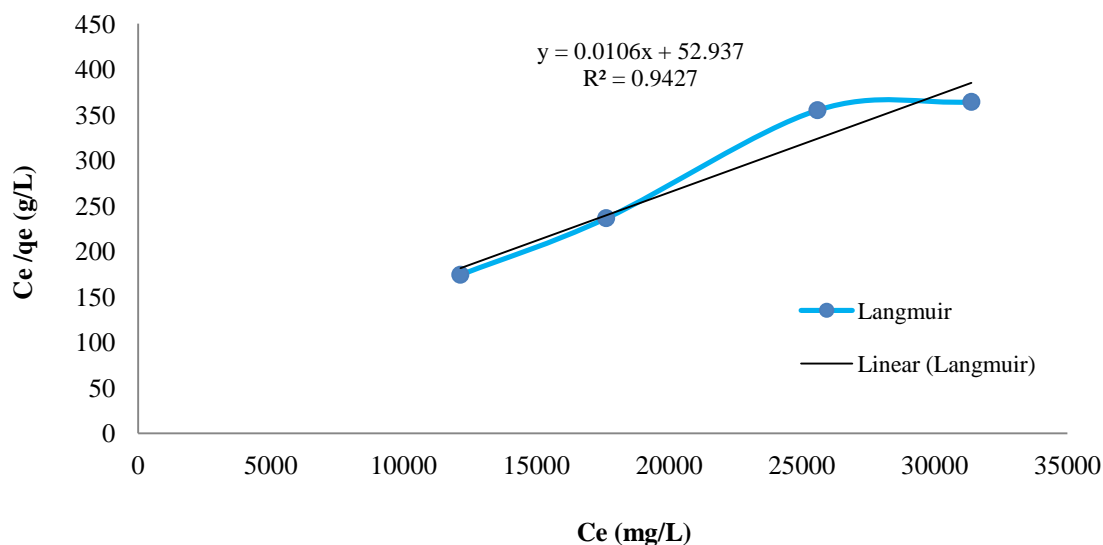


Figure 4.7: Graph of C_e/q_e against C_e

Based on the graph of Langmuir model isotherm which is the graph of C_e/q_e against C_e , the value of maximum adsorption capacity, q_m was got from the slope with the value of 94.3396 mg/g. On the other value which is Langmuir constant that got from the intercept of the graph shown the value of 0.00020 L/mg.

According to the value of the R that get from the equation of $R = 1/(1+bC_0)$, it shows that value of R is about 0.125 which is in the range of $0 < R < 1$. Therefore, this value of R shows that favorable adsorption process of acrylic acid onto powder activated carbon (El Qada *et al.*, 2006; Amuda *et al.*, 2007 and Hameed *et al.*, 2008).

Table 4.7 below show difference in maximum of adsorption, q_m based on the different concentration of solution used.

Table 4.7: Differences q_m value in removal acrylic acid

Types of Adsorbent	C_0 (mg/L)	W (G/L)	q_m (mg/G)	References
Commercial activated carbon	100	20.00	36.2300	Kumar <i>et al.</i> (2010)
Alumina	7 200	66.66	52.2300	Mao and Fung (1997)
Activated carbon based coconut shell ^a	40000	400.00	94.3396	

a- Present Study

For the previous study in the removal of acrylic acid by using activated carbon which is commercial activated carbon, the result obtained that the maximum capacity of adsorption, q_m is 36.23 mg/g with the optimum activated carbon, w of 20 g/L and initial concentration, C_0 of 100 mg/L (Kumar *et al.*, 2010). Meanwhile, for the other type of adsorbent used like alumina (Mao and Fung, 1997), the result reported that with the higher value of Alumina used and initial concentration of acrylic acid which are 66.66 g/L and 7200 mg/L respectively, the q_m value is about 52.23 mg/g. In this present study, the maximum capacity of adsorption for acrylic acid solution, q_m shown the value of 94.3396 mg/g with higher adsorbent dosage of 400 g/L and C_0 of 40000 mg/L. Based all these three result, it indicates that the value of maximum adsorption, q_m is increasing with the increasing of initial concentration of acrylic acid. This condition also has been proved by Kumar *et al.* (2010).

4.3.2 Freundlich Isotherm

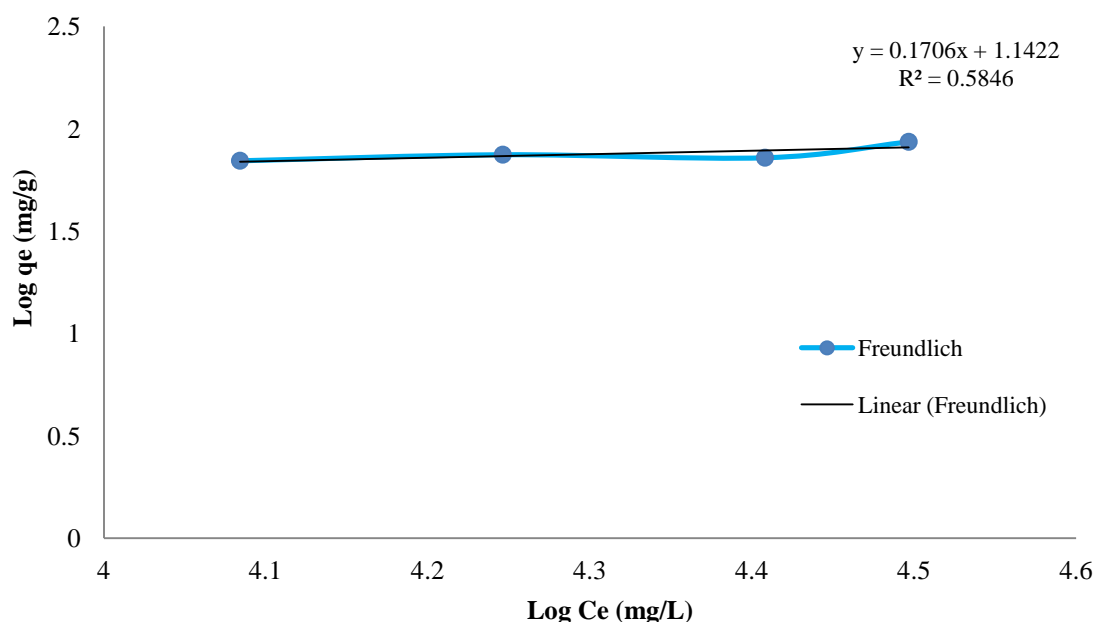
The Freundlich isotherm model is able to fit the experimental data where the concentration of the adsorbate used is in the range of the 300 mg/dm³ (0.3 mg/L) to 700 mg/dm³ (0.7 mg/L) (El Qada *et al.*, 2006)

Freundlich isotherm model is determined from final equation of $q_e = 1/n \log C_e + \log K_F$. Therefore, in conjunction of determination of K_F as well intensity of adsorption, n , graph of $\log q_e$ against $\log C_e$ was plotted. The value of $\log C_e$ and $\log q_e$ are as shown in table 4.8 below.

Table 4.8: Value of $\log C_e$ and $\log q_e$

Adsorbent Weight (g/100 mL)	Log C_e (mg/L)	Log q_e (mg/G)	Correlation Coefficient (R^2)
10	4.4967	1.9354	0.5846
20	4.4080	1.8578	
30	4.2462	1.8726	
40	4.0841	1.8430	

Figure 4.8 shows the graph for Freundlich isotherm model

**Figure 4.8:** Graph of $\log q_e$ against $\log C_e$

Based on the graph of Freundlich model isotherm which is the graph of $\log q_e$ against $\log C_e$, the value of intensity of adsorption, n was got from the slope with the value of $1/n$ is 0.1706 and therefore value of n is 5.8610. In addition to that, when n value is interval of $2 - 1$ -, it means that the process represent a good adsorption process. Besides that, the value of Freundlich constant was got from the intercept of the graph which shown the value of $5.6702 \text{ (mg/g)/(mg/L)}^{1/n}$.

The constant value of Freundlich, K_F represent the easiness of the acrylic acid to be adsorbed by activated carbon. Meanwhile, the heterogeneity factor for the Freundlich isotherm model shows that the activated carbon has the heterogeneous structure. Higher value of $1/n$ will affect the higher bonding or connection between adsorbate and adsorbent and this value is depending on the nature as well strength of the adsorbent site (Kumar *et al.*, 2010). In order to fit the Freundlich model, the value of heterogeneity factor, n must in the range of 1 to 10. With this high value of n and value of $1/n$ is less than 1, it indicates that the acrylic acid is favorable adsorbed by using activated carbon (El Qada *et al.*, 2006 and Kumar *et al.*, 2010).

With this favorable condition for adsorption process for the Freundlich model, when comparing to the value of R for the Langmuir isotherm model, this is shows that this condition is related and same with the conditions of R . Therefore, this is become the strengthens in proving that activated carbon is favorable and suitable used as an adsorbent in the process of adsorption of acrylic acid.

4.3.3 Redlich-Peterson Isotherm (R-P isotherm)

From the equation of $q_e = (K_R C_e) / (1 + \alpha_R C_e^\beta)$, where the value of K_R , α_R are the Redlich-Peterson isotherm. Meanwhile β is the exponent which is value of the β is $0 \leq \beta \leq 1$. Based on this model, there are three parameters that unknown which are K_R , β and lastly α_R . Because of there are three parameters unknown, therefore, the value of K_R is assume with various value which that can maximize value of correlation coefficient, R^2 as well the exponent value is still in the range of $0 \leq \beta \leq 1$.

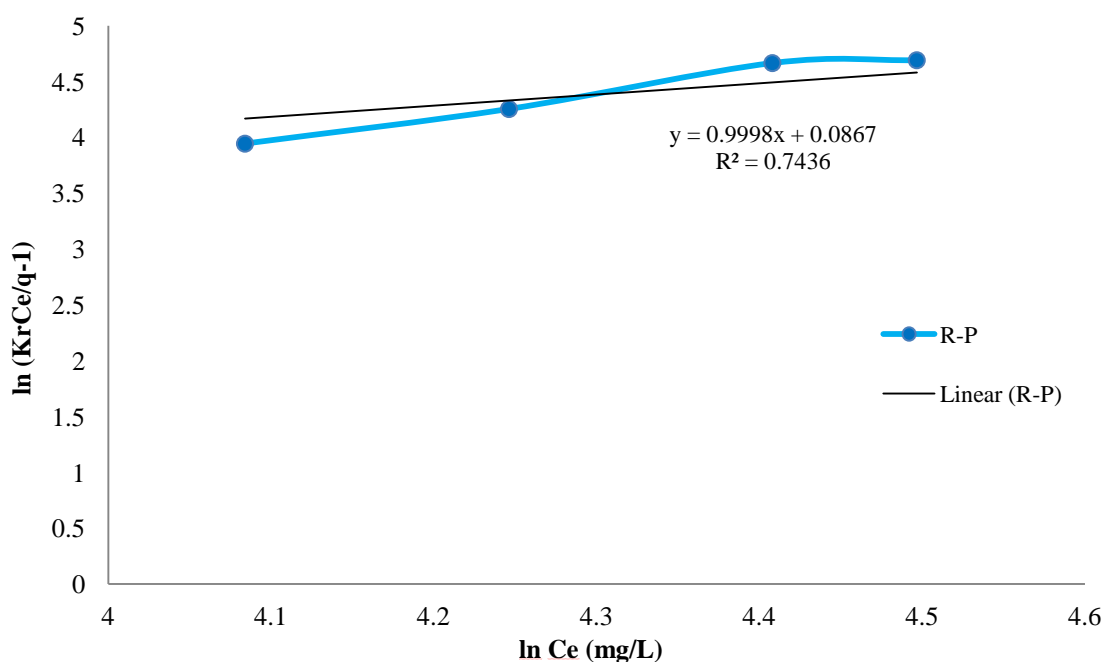
Therefore, in conjunction of determination of β as well α_R , the graph of $\ln ((K_R C_e / q_e) - 1)$ against $\ln C_e$ was plotted. The value of $\ln ((K_R C_e / q_e) - 1)$ and $\ln C_e$ are as shown in table 4.8 below

The value of K_R is modified Langmuir constant by assuming 0.3021 L/mg at 30°C which is at ambient temperature.

Table 4.9: Value of $\ln ((K_R C_e/q_e)-1)$ and $\ln C_e$

Adsorbent Weight (g/100 mL)	$\ln ((K_R C_e/q_e)-1)$	$\ln C_e$	Correlation Coefficient (R^2)
10	4.6868	10.3540	0.7436
20	4.6636	10.1498	
30	4.2566	9.7773	
40	3.9523	9.40400	

Figure 4.9 below shows the relationship for the Redlich-Peterson isotherm model

**Figure 4.9:** Graph of $\ln ((K_R C_e/q_e)-1)$ against $\ln C_e$

Based on the graph of Redlich-Peterson model isotherm which is the value of exponent, β was got from the slope with the value of 0.9999. Meanwhile, the α_R is the Redlich-Peterson isotherm constant is about $1.090 (L/mg)^\beta$.

For this type of isotherm model, when the exponent value, $\beta = 1$, this means it will results the Langmuir equation. On the other side, when the $\beta = 0$, the Redlich-

Peterson equation will transforms to Henry's law equation (Hameed *et al.*, 2008). Therefore, for this study, the value of $\beta = 0.9999$ and it approximately to 1, it means that the Langmuir equation will results.

4.4 CHOOSING THE BEST ISOTHERM MODEL

In this study, there are 3 isotherm equation models that used which are Langmuir isotherm, Freundlich isotherm as well Redlich-Peterson isotherm. Table below shows the summary of the isotherm constant, as well correlation coefficient, R^2 of each isotherm model.

Table 4.10: Summary of Data for Langmuir, Freundlich and Redlich-Peterson Isotherm

Constant	Parameter/Value
Langmuir Isotherm	
$b(l/mg)$	0.00020
$q_m(mg/g)$	94.3396
R^2	0.9427
Freundlich Isotherm	
K_F	13.8739
$1/n$	0.2713
R^2	0.5846
Redilich-Peterson Isotherm	
$K_R(l/g)$	0.2945
$\alpha_R(l/mg)$	1.0900
R^2	0.7508

Based on the summary of the correlation coefficient of the Freundlich isotherm is lower than Langmuir isotherm. Meanwhile, there is significant different value of correlation coefficient between Freundlich isotherms with Redlich-Peterson isotherm. In conjunction of choosing the best fit, the value of correlation coefficient, R^2 for each model determined must higher which means the lower value of error (Arslanoğlu *et al.*, 2005). In addition to that, Gan *et al.* (2010) also has been state that the best fitting model could have the R^2 value to be at least 80%.

As the overall, for the entire model fitted has shown the R^2 value more than 50 % with 0.9427, 0.5846, and 0.7508 for Langmuir, Freundlich and Redlich-Peterson isotherms model. Based on this, the Freundlich and Redlich-Peterson has shown that these two models do not have a good fit model because both of these models has the correlation coefficient less than 80 %. Therefore, for this experiment study, it shows that the Langmuir model isotherm has higher correlation of coefficient, R^2 with the value of 0.9427. This means that the error between predicted data and experimental data are too lower. Since the condition of choosing the best fit model is depending on the correlation coefficient, R^2 of the linearised isotherm plot, it shows that Langmuir model has been fit the adsorption of acrylic acid solution in the high concentration of solution.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

As the encapsulation, the liquid phase adsorption process was conducted as well the adsorption isotherm was identified in order to see the performances and ability of the adsorbent especially activated carbon based coconut shell in removal of acrylic acid from process water solution. The effect of the different parameters like types of adsorbent (granular and powder), adsorbent dosage and contact time were evaluated on the efficiency of removal of acrylic acid. In addition to that, the performance of adsorption process is modeled using three types of adsorption isotherms namely, Langmuir isotherms, Freundlich isotherm and Redlich-Peterson isotherm.

From this study, it shows that the powder activated carbon able to act as an effective adsorbent for the removal of acrylic acid from process water. The optimum adsorption process occurs at the weight of 400 g/L. Meanwhile, the equilibrium time found for the removal process for acrylic acid is 90 minutes. As the effectiveness is compared with particles size, powder activated carbon which has large surface area is having high removal efficiency compared to the granular activated carbon.

The best model of equilibrium adsorption data for acrylic acid removal onto powder activated carbon based coconut shell were presented by Langmuir isotherm model with the value of correlation coefficient, R^2 of 0.9427. From the overall adsorption system that studied, it was found that adsorption process of acrylic acid is favorable adsorbed by activated carbon with the value of R is 0.125 ($0 < R < 1$) and $1/n$ is less than 1.

5.2 RECOMMENDATION

As the recommendation for improvement for future analysis on the adsorption process by using various parameter like take consideration on the effect of initial concentration and initial pH of adsorbate as well effect of temperature.

Besides that, the improvement can be done looking the effect of the adsorption process on the different type of activated carbon with different raw material such as peat, sawdust and the other type of raw material. In addition to that, for each type of activated carbon may conducted also with different size of particles. The study on the life time of the activated carbon also may conduct in order to avoid wasting the treatment cost.

Last but not least, the experiment can be done by using Design Expert Software, where the experimental parameter can be conducted either by using response surface methodology, Box-Benkhen, 3-Level Factorial and others in other the get more accurate optimum value as well minimizing the number of experiment.

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APPENDIX

List of Compounds Exist in BASF Petronas Chemical Sdn. Bhd. Process Water

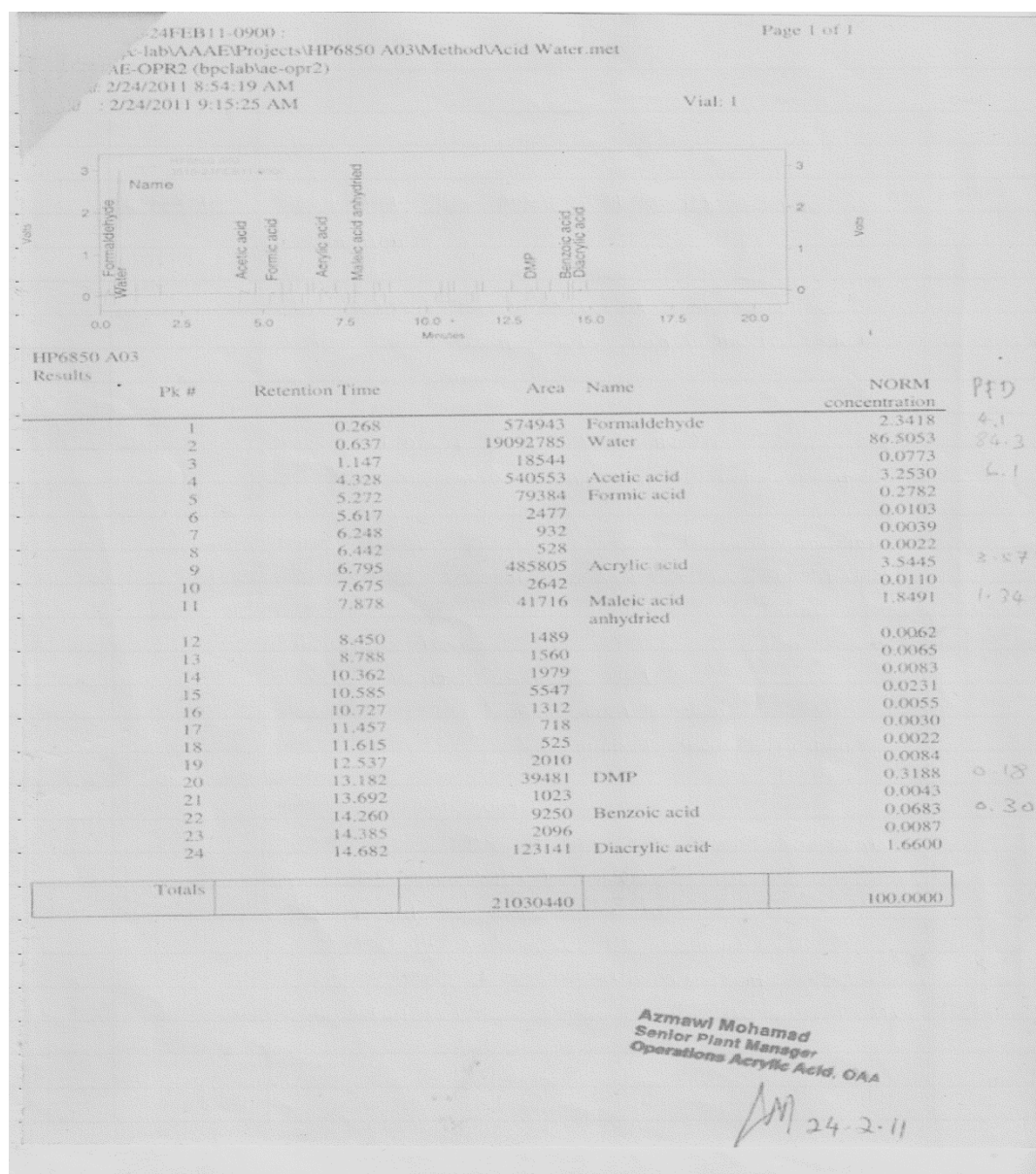


Figure: List of compounds exist in BASF Petronas Chemical Sdn. Bhd process water