

REMOVAL OF ACRYLIC ACID (AA) FROM PROCESS WATER BY USING
ALUMINA

RAHIMAH BINTI SABTU

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering in Chemical Engineering

Faculty of the Chemical Engineering and Natural Resources
UNIVERSITI MALAYSIA PAHANG

JULY 2012

ABSTRACT

The presence of acrylic acid (AA) in process water is the major problem in many industries which are using acrylic acid. There is no proper method available to remove acrylic acid from process water and hence the industries incinerating the process water containing acrylic acid to remove it. But, this method consumes large amount of natural gas and in turn leads to high energy consumption and high costing. This research was attempted to remove acrylic acid via batch adsorption process by using alumina. The process water taken from BASF Petronas Chemicals Sdn Bhd containing 4% acrylic acid is used as sample water in this study. The adsorption capacity was tested by varying different temperature, amount of alumina and contact time. The initial and final concentration of acrylic acid was tested using High performance liquid chromatography (HPLC). The performance of adsorption process is modeled using two types of adsorption isotherms namely, Langmuir isotherms and Freundlich isotherm. From the experimental results it was found that the alumina was good in removing AA from process water and Freundlich isotherm describe the process well compared to Langmuir isotherms.

ABSTRAK

Kehadiran asid akrilik (AA) di dalam proses air merupakan masalah utama terhadap industri-industri yang menggunakan asid akrilik. Tiada kaedah yang betul untuk menyingkirkan asid akrilik dari proses air dan oleh sebab itu kebanyakan industri melakukan pembakaran hangus terhadap proses air mereka yang mengandungi asid akrilik untuk menyingkirkannya. Tetapi, kaedah ini memerlukan kandungan gas asli yang tinggi dan seterusnya membawa kepada penggunaan tenaga dan kos yang tinggi. Penyelidikan ini telah dilakukan untuk menyingkirkan asid akrilik melalui proses penjerapan dengan menggunakan alumina. Proses air yang diambil daripada BASF Petronas Chemicals Sdn Bhd yang mengandungi asid akrilik 4% telah digunakan sebagai sampel air di dalam kajian ini. Jumlah kapasiti penjerapan diuji dengan mengubah suhu, dos alumina dan masa yang berbeza. Kepekatan awal dan akhir asid akrilik telah diuji dengan menggunakan Kromatografi Cecair Prestasi Tinggi (HPLC). Prestasi proses penjerapan dimodelkan menggunakan dua jenis penjerapan isoterma iaitu, isoterma Langmuir dan Freundlich. Daripada keputusan uji kaji di dapati bahawa alumina merupakan agen penjerap yang bagus untuk menyingkirkan acrylic acid dari proses air dan Freundlich isoterma menunjukkan proses yang baik berbanding dengan isoterma Langmuir.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Water that used by industries to produce a product or affect a process is called process water (Watersmart Guidebook). For example process water from chemical and petrochemical, food and beverages, auto repair and service, paper manufacturing, metal finishing and etc. There are many contaminants and components that adsorb in the water and acrylic acid (AA) is one of it. So, the AA and the others compound need to remove before want to reused the water or for further treatment.

Acrylic acid (IUPAC: prop-2-enoic acid) is an organic compound with the formula $\text{CH}_2\text{CHCO}_2\text{H}$. It is the simplest unsaturated carboxylic acid, consisting of a vinyl group connected directly to a carboxylic acid terminus. This colorless liquid has a characteristic acrid or tart smell. It is miscible with water, alcohols, ethers, and chloroform. Annually, more than one billion kilograms are produced. Acrylic acid is produced from propene which is a byproduct of ethylene and gasoline production. Acrylic acid is used in a number of industrial applications.

To remove AA and the others components, there are many methods that can be used such as adsorption, separation, filtration, catalyst oxidation, extraction, electro coagulation that will form precipitate and etc quite same to the method that used to treat the wastewater. In this research, the adsorption method will be used because it is more simple process and it not required high cost. Adsorption process can be defined as a process where a solid is used

for removing a soluble substance from the water. There are several adsorbent can be used in adsorption process such as alumina that has been proved as an effective adsorbent in order to remove acrylic acid from aqueous solution or from gaseous environment.

In order to study the equilibrium isotherm of an adsorption process, there are several types of model can be used such as Langmuir isotherm and also Freundlich isotherm model.

1.2 PROBLEM STATEMENT

BASF Petronas Sdn. Bhd. is a large company that produce acrylic monomer such as detergent builders, pressure sensitive adhesive ,printing inks ,water treatment chemical ,acrylic latex paint and super absorbent products. BASF Company uses AA as their intermediate compound to produce this entire product.

In the process water, it consist of 24 component such as formaldehyde with 2.3 wt%, acetic acid (3.3 wt %), maleic acid anhydrated (1.8 wt %), including acrylic acid (AA) which has the higher weight percentage in the process water which is 4wt% . So, the AA and others component need to remove before the water can be used again. AA also can mix and found azeotrope with other component in the process water such as formaldehyde (2.3w %), acetic acid (3.3w %) and maleic acid anhydrated (1.8w %) and also will form azeotrope with water. Azeotrope means a mixture of two or more liquids in such a ratio that its composition cannot be changed by simple distillation.

Currently, to remove the acrylic acid and also the other components that present in the process water, BASF Petronas Chemical Sdn. Bhd. is incinerating their process water since there is no proper method available to remove it. 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 decrease the operation costing of the process.

1.3 RESEARCH OBJECTIVES

The proposed research was studied to achieve the following objectives:

1. To remove the acrylic acid from process water by using alumina.
2. To study the adsorption isotherms.

1.4 SCOPE OF STUDY

In order to achieve the objectives, the following scopes have been identified:

3. The effect on contact time between alumina and acrylic acid.
4. The effect on alumina dosage.
5. The effect on temperature.

1.5 RATIONALE/SIGNIFICANCE OF STUDY

Based on the research scopes mentioned above, the following rationale and significance that we could get have been outlined:

1. To remove or reduce the composition of hazardous material in the process water. AA is one of the hazardous material.
2. Simple process and operation. The Alumina is easy to prepared and get. It also less expensive, more economic and the adsorption process are easily to conduct rather than the other method. Besides, the adsorption of carboxylic acids on alumina is very strong, with adsorption energies much larger than those of other organic compounds (Mao & Fung, 1997).
3. To reused the water.
4. To lower the operating cost because the incineration process can be substitute with other process which is more saving in cost.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

In this chapter, the adsorbate and adsorbent will be further discussed based on its general information, properties, method of production, application and also the toxicology. Other than that, the adsorption process and its isotherm also will be further explained based on the research that has been done by others researcher before so that the trend and factor towards adsorption process can be studied.

2.2 ACRYLIC ACID

In this research acrylic acid will be used as the adsorbate or the material and chemical that wants to remove by using adsorption process. AA will be act as the substance get adsorbed or attached on the surface of adsorbent (Readcast.TM, 2010).



Figure 2.1: Acrylic acid

2.2.1 Name and General Information

Acrylic acid (CAS no.79-10-7; IUPAC: prop-2-enoic acid) is an organic compound with the formula $\text{CH}_2 = \text{CH}-\text{COOH}$. It is the simplest unsaturated carboxylic acid, consisting of a vinyl group connected directly to a carboxylic acid terminus. The other names for AA are acroleic acid, ethylene carboxylic acid, vinylformic acid, propene acid, glacial acrylic acid and acrylate (NIST Chemistry WebBook, 2011).

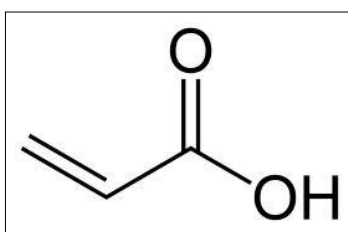


Figure 2.2: Chemical structure of acrylic acid

Nexants, 2009 stated that commercially, there are two grades of acrylic acid that available: technical and glacial grade. Usually the technical grade acrylic acid has about 94% acrylic acid content and it is more suitable for the production of commodity acrylate esters for example surface coating, adhesives and sealants, textiles, plastic additives, and paper treatment. While glacial grade acrylic acid is generally has about 98-99.7% acrylic acid content. This glacial grade is suitable for the production of super adsorbent polymers, detergents, water treatment, and dispersants.

2.2.2 Physical Properties & Characteristic

Table 2.1: Properties and characteristics of acrylic acid

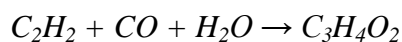
Properties	Information
Formula weight	72.06
Physical state	Liquid above 13°C

Table 2.1: Continued

Color	Clear and colorless
Odor	Acrid
Density	1.04 g/mL at 30°C
Solubility	Freely soluble in most solvents
Flash point	50°C
Boiling point	141-142°C
Melting point	12°C
Critical Pressure	56 atm
Critical Temperature	342°C
Heat of Combustion at 25°C	1376 kJ/g mol
Heat of Fusion	11.1 kJ/g mol
Heat of Polymerization	77.5 kJ/g mol
Heat of Neutralization	58.2 kJ/mol
Heat of Vaporization at 27°C	27.8 kJ/mol
Specific Heat at 25°C	2.09 kJ/ kg. K

2.2.3 Method of Production

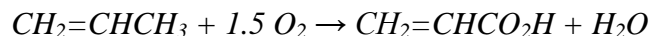
There are two methods to produce acrylic acid which is via hydrocarboxylation of acetylene and the second method is vapor phase oxidation of propylene. The hydrocarboxylation of acetylene was the early method:



But the disadvantage of this method is it requires nickel carbonyl and high pressures of carbon monoxide. But this method has been abandoned for economic or environmental reasons. It was once manufactured by the hydrolysis of acrylonitrile which is derived from

propene by ammoxidation, was abandoned because the method cogenerates ammonium derivatives (AbsoluteAstronomy, 2011).

The most widely process that applied by many company for making acrylic acid is the vapor phase oxidation of propylene (Laskowski et al., 1998).



Normally, this method involving two reactors in series and utilizing two separate catalysts. The first reactor was used to convert the propylene to acrolein while the second reactor completes the conversion from acrolein to acrylic acid. Even though the standard process involves two series reactors with separate catalysts, the system can be modified as a single reactor with one catalyst. This will make the system easier and can lower the operating cost.

2.2.4 Uses and Application

From Chemlink (1997) and Chemicaland21, acrylates that derivatives of acrylic acid can be used as emulsion and solution polymers. These products may be used as coatings, finishes and binders leading to applications in paints, adhesives, and polishes with solutions used for industrial coatings as emulsions. While homopolymers and copolymers used in a variety of industrial applications including plastics, textiles, thickening agents, dispersing agents, surfactants, chelating agents, adhesives, water-based coatings, water treatment.

EPA (2011) also stated that acrylic acid is also used as a chemical intermediate. Acrylic acid also can be used in superabsorbent polymers. This product is lightly crosslinked polyacrylic acid salts. They are used for fluid retention, largely in baby diapers, but also in products for feminine hygiene, adult incontinence and agriculture (acrylic acid glacial, 2001).

2.2.5 Toxicology and Exposure

Vapor that released from acrylic acid has a very strong acrid odor. The table below indicated a list of current standards for levels to which the standard-setting bodies consider that most workers can be exposed during an 8-hour workday without harmful effects, the results of tests used to determine the levels at which acrylic acid usually will be smelled, and also the rating of acrylic acid based on health, flammability, reactivity and contact. Smelling acrylic acid vapor while unpleasant is not necessarily indicative that such levels have been exceeded.

Table 2.2: Toxicology and exposure to acrylic acid

ACGIH Threshold Limit Value (TLV) (ppm)	2 (TWA), skin
Odor Threshold (ppm)	1.04
Health	4 (extreme)
Flammability	2 (moderate)
Reactivity	2 (moderate)
Contact	4 (extreme)
Storage code color	Red (flammable)

Because consumer products contain only trace levels of acrylic acid as a result of the polymerization process, consumers are not generally exposed to these compounds in finished products. Although potential for exposure does exist during acrylic acid manufacture, transportation, and use, enclosed systems limit the exposure to worker populations and nearby communities. Employees and contractors should wear appropriate safety equipment and undergo special training while do any work that involved in acrylic acid manufacturing.

Acrylic acid vapors can potentially escape from leaks in the piping system, during repair or replacement of the piping system, or during removal of samples for quality control

purposes in spite of the manufacturer's efforts to contain the manufacturing process. In manufacturing facilities, worker exposure should monitor with specialized monitoring systems. Leaks should be detected and repaired because odors will be detected at such low levels before a product can cause adverse health effects (BASIC ACRYLIC MONOMER, 2011).

During loading, unloading, transportation of tank trucks, railroad tankers, barges, and drums exposure could occur and it will give bad and huge effect. However, to handle acrylic acid a dedicated systems was designed and it are typically used for loading and unloading purposes and procedures should be in place to minimize spills or leaks during transportation.

2.3 ALUMINA POWDER

In this research, alumina will be use as the adsorbent in the adsorption process. Alumina powder will provide the surface upon which adsorption occur.



Figure 2.3: Alumina powder

2.3.1 Name and General Information

Alumina (Al_2O_3) with CAS number 1344-28-1 is a white powder produced from bauxite ores (iron alumino silicate). The others names for alumina is aluminum oxide, activated alumina, calcined alumina, dispersing alumina infiltrating alumina, reactive alumina, tabular alumina (Reade, 2011). Calcined, tabular, hydrated, and synthetic boehmite are the four types of alumina that generally utilized. Usually, there are two grades of alumina that available: industrial grade with purities 98% and high purity grade with purity 99.999%. But in pure alumina, it only contains 52.9 per cent aluminium (Chemlink, 1997).

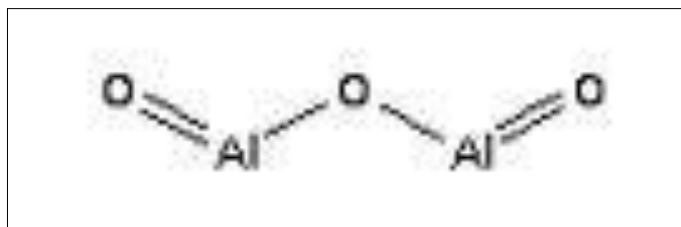


Figure 2.4: Chemical structure of alumina

2.3.2 Physical Properties & Characteristic

Tabel 2.3: Properties and Characteristics of Alumina powder

Molecular Weight (g/mol.)	101.94
Appearance	White solid and very hygroscopic
Odor	Odorless
Density (g/cm ³)	3.95-4.1
Melting point (°C)	2072
Boiling point (°C)	2977
Solubility	insoluble in diethyl ether and water practically insoluble in ethanol

Tabel 2.3: Continued

Hardness	Hard, wear-resistant
Electricity	Excellent dielectric properties from DC to GHz frequencies (Adams, 2002)
pH	Resists strong acid and alkali attack at elevated temperatures
Conductivity	Good thermal conductivity
Shape capability	Excellent size and shape capability
Strength and stiffness	High strength and stiffness

2.3.3 Method of Production

In early 20th century alumina is still produced by melting bauxite in an electric furnace and this method was applied in a process devised for the abrasives industry (Alumina, 2011). But now, most companies was produced alumina by extracted it from bauxite through the Bayer process. In this process, bauxite is crushed then it was mixed in a solution of sodium hydroxide. After that, bauxite will seeded with crystals to precipitate aluminium hydroxide. Finally, in order to drive off the water and produce several grades of granular or powder alumina, including activated alumina, smelter-grade alumina, and calcined alumina the hydroxide was heated in a kiln.

2.3.4 Uses and Application

Alumina was applied in refractory, abrasives, cement, slag adjusters, traditional & advanced ceramics, aluminum chemicals, flame retardants, fillers, welding fluxes, adsorbents, adhesives, coatings, and detergent zeolites (Reade, 2011). It also used in gas laser tubes, wear pads, seal rings, high temperature electrical insulators, high voltage insulators, furnace liner tubes, thread and wire guides, electronic substrates, ballistic armor, abrasion resistant tube and elbow liners, thermometry sensors, laboratory instrument tubes

and sample holders, instrumentation parts for thermal property test machines, and grinding media (Adams 2002).

2.4 ADSORPTION

2.4.1 Theory and Process

A process where a solid is used for removing a soluble substance from the water is called adsorption. Uhrikova (2011) state that adsorption also can be defined as a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Adsorption also happens when one or more components of gas and liquid stream adsorbs onto a solid surface. Normally, it is occur at low temperature and the separation process usually due to relative solubility of components solutes in sorbate.

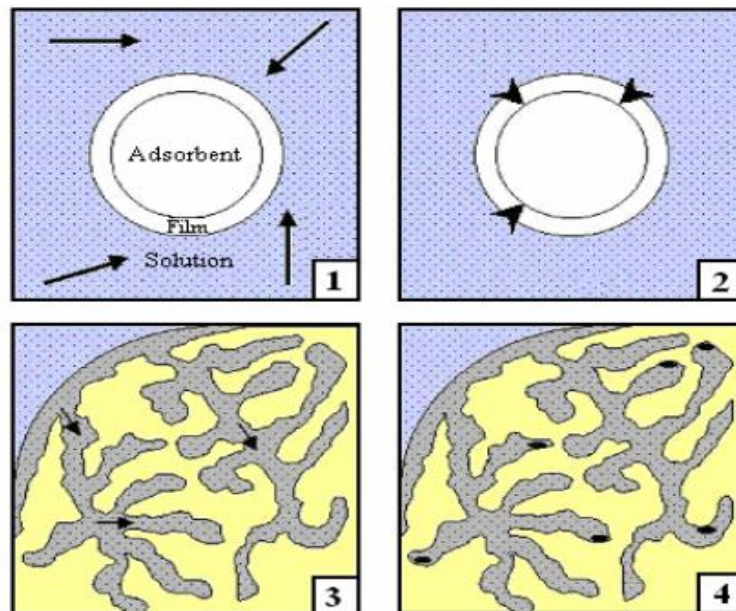


Figure 2.5: Schematic illustration of adsorption steps

Source: Kelesoglu, 2007

Based on Figure 2.5 that shows below, there are four steps in the adsorption process which is bulk solution transport, film diffusion transport, pore transport and adsorption. Bulk solution transport involves the movement of the material to be adsorbed through the bulk liquid to the boundary layer of fixed film of liquid surrounding adsorbent. In the film diffusion transport, it involves the transport by diffusion of the material through the stagnant liquid film to the entrance of the pores of the adsorbent. The transport of the material will be adsorbed through the pores. This process called pore transport. Last but not least, the adsorption process occur which involve the attachment of adsorbate to adsorbent at an available adsorption site (Kelesoglu, 2007).

2.4.2 Classification of Adsorption

Adsorption can be classified into two types: physisorption and chemisorptions (Kelesoglu, 2007). Physisorption is the most common form of adsorption. Physical adsorption is a type of adsorption in which the molecules are attracted by van der Waals forces, and attach themselves to the surface of the solid. The molecules remain intact, can be freed easily and also responsible for the non-ideal behaviour of real gases. For example, adsorption of various gases by charcoal.

While in chemisorptions, the adsorbed molecules are held by chemical bonds. The molecules undergo a chemical bonding with the molecules of the solid, and this attraction may be stronger than the forces holding the solid together. If the molecules are removed, they may form different compounds. The example of this type of adsorption is the adsorption is the adsorption of oxygen on tungsten, and on charcoal.

2.4.3 Adsorption Method using Alumina

Mao & Fung (1997) stated that removal of AA from process water by using alumina obeys the Langmuir isotherms and the adsorption process depends on pH. The pH that most

suitable for AA in this adsorption process in 4.5 and the maximum amount of acid adsorbed is 727 $\mu\text{mol/g}$. As the pH increase, the adsorption process also will increase and finally it will increase the percentage on removal of AA. Based on their study, they found 80% removal of AA at pH 2.5 after 24h. They also state that the adsorption isotherm will depend on specific surface area and surface chemistry of adsorbents, the nature of adsorbates and the pH medium of the solution. This finding was similar with Wu et.al (2010). They also observe that adsorption depends on pH of the solution and follow the Langmuir isotherm which is the rules of adsorption.

In 1997, While Ishiduki & Esumi conducted an experiment and discovered that the adsorption of poly AA alone shows a strong affinity with a large adsorbed amount for alumina surface. While Karamanan et.al (2001) discovered that the hydrocarbon carboxylic acids were found to adsorb strongly onto alumina due to the pH effect and its follow the Langmuir isotherm.

Bournel et.al (1996) also demonstrates an experiment and they found new parameter that will give effect on the adsorption process which is temperature. From the experiment, they get result when the temperature decrease, the adsorption will increase but when the temperature increase, the adsorption will decrease.

2.4.4 Adsorption Isotherm

Usually adsorption was described through isotherms. Isotherm represent the functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). Basically, there are two main isotherms that will be studied in this research: Langmuir isotherm and Freundlich isotherm.

2.4.4.1 Langmuir Isotherm

Basically, Langmuir isotherm is used to determine the amount of a contaminant which can be removed from water using adsorbent because adsorption will never remove

every molecule of a contaminant from the water. Instead, once a certain amount of contaminant molecules have been adsorbed on the surface of the adsorbent, the process reaches equilibrium. At this point, a longer contact time will not result in more adsorption. The adsorbent will tend to release contaminant molecules from its surface at the same rate that other molecules become stuck to the surface.

There are some limitations in the Langmuir isotherm which is it is not valid at high pressure. Even only in a small amount fraction of the area of the adsorbent is covered, the apparent saturation of a surface will be observed also. In this isotherm, the adsorption maximum is also variable on temperature and pressure and this equation also does not explain the multimolecular layer formation.

The Langmuir adsorption was developed assuming that the number of sites that available on the adsorbent surface are fix and all have same energy. The monolayer adsorption process can occur reversible and there are no lateral interactions among the adsorbates (Kelesoglu, 2007).

Based on some quite reasonable assumptions, Langmuir derived a relationship for weight adsorbed per unit wt of adsorbent (q) and concentration in fluid (C). The assumptions are: a uniform surface, a single layer of adsorbed material, and constant temperature. The equation for adsorption based on Langmuir isotherm is (Bungah, 2000):

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2.1)$$

Where C_e = equilibrium concentration of adsorbate in solution after adsorption in mg/L.

q_e = amount adsorbed per unit weight of adsorbent at equilibrium in mg/g

q_m = maximum adsorption capacity in mg/L

K_a = Langmuir constant in L/mg

Taking reciprocals and rearranging:

$$q_e (1 + K_a C_e) = q_m K_a C_e \quad (2.2)$$

$$\frac{C_e}{q_e} = \frac{1 + K_a C_e}{q_m K_a} \quad (2.3)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{K_a C_e}{q_m K_a} \quad (2.4)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_a} \quad (2.5)$$

A plot of $\frac{C_e}{q_e}$ versus C_e should indicate a straight line of slope $\frac{1}{q_m}$ and an intercept of $\frac{1}{q_m K_a}$.

2.4.4.2 Freudlich Isotherm

The Freudlich adsorption isotherm is an adsorption isotherm, which is a curve relating the concentration of solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact.

For this isotherm, it also has limitations which are: purely empirical basis, valid up to certain pressure and invalid at high pressure, fails when concentration of adsorbate is very high and K and n are temperature dependents, vary with temperature.

Freundlich equation:

$$q_e = K_f C_e^{1/n} \quad (2.6)$$

where: K_f = Freundlich constant in mg/g

$\frac{1}{n}$ = Freundlich exponent

q_e = amount adsorbed per unit weight of adsorbent at equilibrium in mg/g

C_e = equilibrium concentration of adsorbate in solution after adsorption in mg/L.

The adsorption system almost has no limit to the amount adsorbed and there is a multilayer adsorption if the good fit of Freundlich isotherm was obtained. The linearization equation for Freundlich isotherm is shown below so that the best fit can be obtained.

Taking logs and rearranging:

$$\log q = \log K_f C^{1/n} \quad (2.7)$$

$$\log q = \log K_f + \frac{1}{n} \log C \quad (2.8)$$

$$\log q = \frac{1}{n} \log C + \log K_f \quad (2.9)$$

By plotting $\log q$ versus $\log C$, the slope is $\frac{1}{n}$ and the intercept is $\log K_f$.

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

In this chapter, the method and process of experiment on how to remove acrylic acid from process water by using alumina will be discussed. The effect of adsorbent dosage, temperature and time contact will be done to see the effect of all these parameters on removal of AA.

3.2 ADSORBENT

In this research, will be use alumina powder (Al_2O_3) as the adsorbent. The commercial grade alumina powder with CAS NO 1344-28-1 was obtained from supplier that used for tested for laboratory use only. The purity is 99% extra pure. While handle this chemical make sure avoid it from skin and eyes contact.

3.3 ADSORBATE

AA sample was supplied by BASF PETRONAS, Gebeng. It's taken from their process water with concentration of 4wt% or 4000 ppm. It is considered as hazardous material so need to remove in order to reuse the water. Make sure that you always wear personal protection equipment, such as mask and rubber glove during the experiment.



Figure 3.1: Acrylic acid from BASF process water

3.4 OVERALL METHODOLOGY

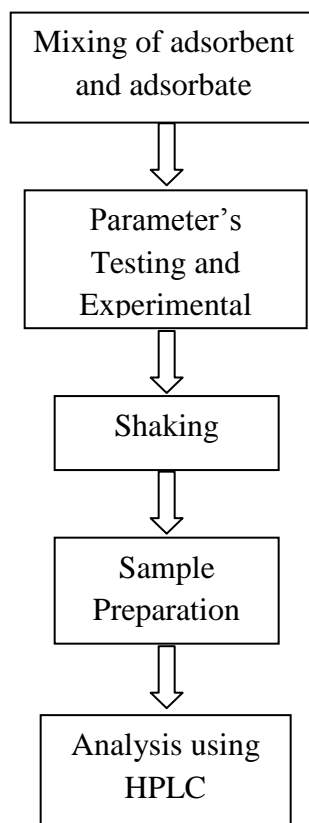


Figure 3.2: Experimental flow chart

3.4.1 Preparation of Standard Solution

$$\text{ppm} = \text{mg/l} = \mu\text{g/ml}$$

1. Liquid sample contains 4wt% acrylic acid that is considered as hazardous material.
2. Make sure that you always wear personal protection equipment, such as mask and rubber glove during the experiment.
3. Prepare an acrylic acid standard solution with concentration of 20ppm, 50ppm, 100ppm, 150ppm and 200ppm.
4. For AA stock solution (1000ppm):
 - a) Accurately put liquid sample of AA in a 100 ml beaker.
 - b) Put the AA sample into vial by using syringe and micro filter.
 - c) Pipette 2.5 mL or 2500 μL of AA sample by using micropipette from the vial and put it into the 100 ml volumetric flask.
 - d) Top up the volumetric flask with ultrapure water until the graduated level and shake it until dilute.
 - e) Put the stock solution in ultrasonicator for 30 minute to break the bubbles in the solution.
5. For AA standard solution for analysis:
 - a) Standard 20ppm: 0.2 ml or 200 μl stock solution into 10 ml volumetric flask.
 - b) Standard 50ppm: 0.50 ml or 500 μl stock solution into 10 ml volumetric flask.
 - c) Standard 100ppm: 1 ml or 1000 μl stock solution into 10 ml volumetric flask.
 - d) Standard 150ppm: 1.5 ml or 1500 μl stock solution into 10 ml volumetric flask.
 - e) Standard 200ppm: 2 ml or 2000 μL stock solution into 10 ml volumetric flask.

- f) Top up the entire volumetric flask with ultrapure water until the graduated level and shake it until dilute.
- g) Put all the standard solution in ultrasonicator for 30 minute to break the bubbles in the solution.
- h) By using syringe and needle (0.45 μm) for inject the entire standard into vial and label every vial for each of five standard.

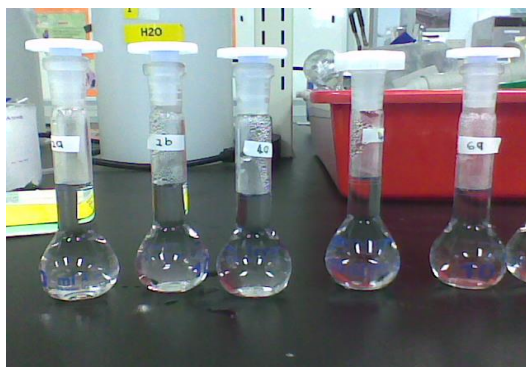


Figure 3.3: Preparation for AA standard solution

3.4.2 Effect of Time Contact between Adsorbate and Adsorbent

1. Prepare all the equipment required.
2. Fill up Erlenmeyer with liquid sample up to 100 ml each.
3. Add 10 gram powder alumina into each 100 ml Erlenmeyer.
4. Put the Erlenmeyer on the shaker.
5. Set temperature at ambient T.
6. Run the shaker at about 150 rpm.
7. For the first, collect sample for 10 minutes using syringe.
8. After 10 minutes, collect sample every 20 minutes.
9. After 60 minutes, collect sample every 30 minutes.
10. Experiments finish at 180 minutes of operation. Turn off the shaker.



Figure 3.4: Orbital shaker that use to shake the solution

3.4.3 Effect of Adsorbent Dosage

1. Prepare all the equipment required.
2. Fill up 9 Erlenmeyer with liquid sample up to 100 ml each.
3. Add powder alumina into each Erlenmeyer with variation of weight: 10, 20, 30, 40, 50, and 60.
4. Put all the Erlenmeyer on the shaker.
5. Set temperature at ambient temperature, T.
6. Run the shaker at about 150rpm for 60 minutes.
7. After 60 minutes of operation, turn off the shaker.
8. Collect sample for analysis from each Erlenmeyer.
9. Turn on again the shaker; continue the experiment up to 10 hours.
10. After 10 hours, turn off the shaker and collect sample.

3.4.4 Effect of Temperature

1. Prepare all the equipment required.
2. Fill up Erlenmeyer with liquid sample up to 100 ml each.
3. Set the shaker at 40⁰C and turn on, wait until T= 40⁰C.
4. Add 100 gram powder alumina into each Erlenmeyer.

5. When T has reach 40⁰C, put all the Erlenmeyer on the shaker and turn on.
6. After 60 minutes, turn off the shaker and collect sample.
7. Do the experiment by varying T: 30, 40, 50, 60, 70 and 80⁰C.

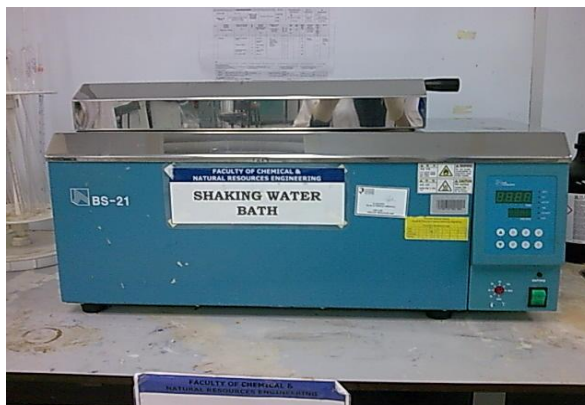


Figure 3.5: Shaking water bath used in temperature parameter test

3.4.5 Sample Preparation for HPLC Analysis

1. Prepare the sample for HPLC analysis with concentration 50ppm.
2. Pipette 0.0125 mL or 12.5 μ L of the entire parameters sample into the 10 mL volumetric flask.
3. Top up the entire volumetric flask with ultrapure water until the graduated level and shake it until dilute.
4. Sonicate the sample for 30 minutes until no gas bubble is observed.
5. The supernatant (top layer) is taken using syringe.
6. Filter the sample and put it into vial.
7. Label every vial for the entire parameters sample.
8. Follow the sample analysis procedure for HPLC.