REMOVAL OF ACRYLIC ACID FROM PROCESS WATER USING CONTINUOUS ADSORPTION

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SUPERVISOR’S DECLARATION

I hereby declare that I have checked this thesis and in my opinion this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis entitled *"Removal of Acrylic Acid from Process Water using Continuous Adsorption"* is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
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To my beloved parents and siblings

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ABSTRACT

Adsorption processes have been widely applied in chemical industry for water treatment, valuable compound recovery and undesired compound removal. Continuous adsorption using fixed bed adsorption column has shown its big roles in the large scale of industry. This research aims to study the acrylic acid removal from industrial process water by using continuous adsorption system. Three series of adsorption columns using coconut shell based activated carbon as adsorbent are employed in this study. The process water containing 4% acrylic acid was fed to the column. The adsorption removal efficiency for different feed flow rate through the column and different amount of the adsorbent were studied. The result shows the composition profile concentration of acrylic acid in the outlet flow of each column as a function of time. Therefore, this concludes that continuous adsorption of acrylic acid waste is favorably influenced by a feed flow rate and the weight of adsorbent. The improvement research study was proposed which it should test with high number of continuous column also increase height of bed with regeneration facility because the concentration is too high and the economic analysis can be carried out.

ABSTRAK

Proses penjerapan telah digunakan secara meluas dalam industri kimia untuk rawatan air, pemulihan kompaun bernilai dan penyingkiran sebatian yang tidak diingini. Pnjerapan berterusan menggunakan katil kolum tetap telah menunjukkan skala besar dalam industri. Penyelidikan ini bertujuan untuk mengkaji penyingkiran asid akrilik daripada proses industri air dengan menggunakan sistem penjerapan berterusan. Tiga siri lajur penjerapan menggunakan tempurung kelapa berasaskan karbon yang diaktifkan sebagai adsorben untuk proses dalam kajian ini. Air proses yang mengandungi asid akrilik 4% dialirkan terus ke kolum. Kecekapan penyingkiran penjerapan untuk kadar suapan yang berbeza aliran melalui jumlah lajur dan berbeza daripada adsorben dikaji. Hasilnya menunjukkan kepekatan komposisi profil asid akrilik dalam aliran keluar setiap lajur berkadar dengan fungsi masa. Oleh itu, ini membuat kesimpulan yang berterusan penjerapan sisa asid akrilik menggalakkan dipengaruhi oleh kadar aliran suapan dan berat adsorben. Cadangan peningkatan dalam penyelidikan yang sepatutnya menguji dengan bilangan lajur yang berterusan dengan jumlah yang banyak dan juga meningkatkan ketinggian katil dengan kemudahan penjanaan semula kerana kepekatan asid akrilik yang terlalu tinggi dan analisis ekonomi boleh dijalankan.

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LIST OF SYMBOLS

Pb	Lead
H_2S	Hydrogen Sulfide
C_t	Concentration at times
C_0	Initial concentration
C_{eff}	Concentration Effluent
V_1	Volume 1
V_2	Volume 2
g	Gram
L	Liter
°C	Degree Celsius
ppm	Part per millions
µ	Micro
n	Nano
m	Meter
%	percent

LIST OF ABBREVIATIONS

AA	Acrylic Acid
AC	Activated Carbon
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
EBCT	Empty Bed Contact Time
GAC	Granular Activated Carbon
HPLC	High Performance Liquid Chromatography
NOM	Natural Organic Compound
TFA	Trifluoroacetic Acid
USA	United States of America
VOC	Volatile Organic Compound

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Adsorption process of a compound involves accumulation at the interface between two phases which are liquid-solid or a gas-solid. The molecule that accumulates, or adsorbs, at the interface is called an adsorbate, and the solid on which adsorption occurs is the adsorbent. Adsorbents of in water treatment include activated carbon; ion exchange resins; adsorbent resins; metal oxides, hydroxides, and carbonates; activated alumina; clays; and other solids that are suspended in or in contact with water.

Acrylic acid organic compound is generally not persistent in the environment because of its reactivity. In biochemical oxygen demand (BOD) studies, acrylic acid has been shown to degrade 81% in 22 days in water inoculated with sewage seed. Acrylic acid is also amenable to anaerobic treatment, degrading to about 75% of theoretical methane in acclimated cultures. Acrylic acid is moderately toxic to aquatic life, but not persistent in aquatic environments, due to rapid oxidation. Large releases can deplete dissolved oxygen.

Acrylic acid released to the atmosphere will react with ozone and photochemically produce hydroxyl radicals, resulting in a half-life of six to fourteen hours. Since acrylic acid is miscible with water, it would not be expected to absorb significantly on soil or sediment.

The activated carbons from artificial materials have high surface area and extensive chemistry for the continuous adsorption. Nowadays, activated carbons are widely used in a large range of applications, such as medical uses, removal of pollutants and odors and gas purification. Activated carbons are used worldwide in a great many industrial separation processes because of their ability to preferentially adsorb particular chemicals when introduced to solutions containing those chemicals (Mozammel *et.al*, 2002).

1.2 Problem Statement

Acrylic acid present in waste water 4% along with other components. Based on the data given on the BASF PETRONAS Chemicals process water, there are 23 others component that dilute in this water which this amount is not including acrylic acid. In this process water, the composition of water is approximately 87 weight percentage (wt %) and AA has the highest amount which is 4 wt%. Then, this amount is followed by acetic acid, formaldehyde, maleic acid anhydride with the value approximately about 3.3 wt%, 2.3 wt% and 1.8 wt% respectively. The current technology is incinerating the process water in the boiler and converts the organic components in to carbon-di-oxide and steam which consumes large amount of energy. So this research aims to remove acrylic acid from industrial process water by using continuous adsorption system because the concentration is too high.

1.3 Objectives

To develop continuous adsorption system to remove acrylic acid from process water

1.4 Scope of Research

The scope of this research is to identify the optimum conditions of the effluent concentration for continuous column of the removal of acrylic acid aqueous solution must be varied. The equilibrium between acrylic acid organic compound in the solution and the adsorbent surface is practically research using continuous adsorption.

1.5 Rationale & Significance

Rationale. The objective of the present study is to stimulate adsorption process for the organic compound using fixed-bed continuous adsorption column. Laboratory experiments have been proving that the granular activated carbon as adsorbent to remove organic compound. In this research, the results obtained from the experiments studies on continuous adsorption system can be used to replicate in wastewater treatment.

Significance. Adsorptive of acrylic acid (AA) has been found to be very efficient because exposure to AA can occur through all the three dermal, inhalation and ingestion routes. From the studies on the continuous adsorption, the results can be used to relate the adsorption organic compound with activated carbon using fixed-bed continuous adsorption column.

CHAPTER 2

LITERATURE REVIEW

2.1 Acrylic Acid Organic Compound

Acrylic acid (AA) is an unsaturated organic acid and is very toxic to living species. Exposure to AA can occur through all the three dermal, inhalation and ingestion routes. The fumes of AA have an acrid and unpleasant odor. AA imparts toxicity to water and is highly injurious to aquatic organisms. It severely irritates the skin, eyes, respiratory system and the gastro-intestinal tract of humans. The hazardous property of acrylic acid has been presented elsewhere.

AA is widely used in a variety of industrial processes, e.g., paints, synthetic fibers, adhesives, papers and detergents. It is released to environment during the manufacture of acrylic ester, water soluble resin and flocculants. In a typical acrylic manufacturing unit, the wastewater has AA concentration in the range of 10–20 g/l along with several other toxicants of AA family, namely, acrylonitrile, acetonitrile, etc. Such wastewaters also have very high concentration of dissolved solids, turbidity, very high chemical oxygen demand (COD), high alkalinity and many heavy metals. Therefore, adsorptive treatment of AA bearing wastewaters has been found to be very efficient (Kumar *et.al*, 2010).

Due to the breakdown of acrylic acid in the environment and its moderate acute toxicity, the chemical would not be expected to be toxic to aquatic or terrestrial animals at levels normally found in the environment. As a volatile organic compound (VOC), acrylic acid can contribute to the formation of photo-chemical smog in the presence of other precursors. Acute toxic effects may include the death of animals, birds, or fish, and death or low growth rate in plants. Acute (short term) effects are seen two to four days after animals or plants come in contact with a toxic chemical substance.

Acrylic acid has slight acute toxicity to aquatic life and high toxicity to birds. Insufficient data are available to evaluate or predict the short-term effects of acrylic acid to plants or land animals. Chronic toxic (long term) effects may include shortened lifespan, reproductive problems, lower fertility, and changes in appearance or behaviour. Chronic effects can be seen long after first exposures to a toxic chemical. Because of water solubility and vapour pressure most (about 90%) acrylic acid released to the environment is expected to end up in water.

The chemical can be removed from the atmosphere in rain. If released to soil the chemical leaches into groundwater or surface waters. Leaching into ground or surface waters is the major route of removal of acrylic acid from soils due to the chemical's high water solubility and low vapour pressure. Bioaccumulation of acrylic acid is not expected to be significant. Acrylic acid exists in the atmosphere in the gas phase. The dominant atmospheric loss process for acrylic acid is by reaction with the hydroxyl radical. Based on this reaction, the atmospheric life is only expected to be a few days. In the air acrylic acid reacts with ozone to produces glyoxylic acid and formic acid. Wet and dry deposition of gaseous acrylic acid may also be important. Acrylic Acid is biodegradable. It is also destroyed by sunlight in surface soils and water. It is slightly persistent in water but will degrade within a few weeks or months.

2.2 Applicability of Activated Carbon (AC)

AC is dominantly used for purposes of adsorption, a task for which it is well designed. Essentially, adsorption is restricted to working in one of two phases, from the gas/vapor phase (usually air) or from the liquid phase (usually water). Fortunately, there is only one gas/vapor phase, but for liquids, two distinct phases need to be considered, namely adsorption from aqueous systems and adsorption from non-aqueous systems. Adsorption from solution, in comparison, is relatively simple to do experimentally, as no volume changes are involved and modern analytical techniques can be easily adapted to measure concentration changes in solutions.

Competitive adsorption may occur between the solvent and the solute. Adsorption from solution may be further complicated because the solute may change chemically, or its concentration may change in the solution. Thus, concentration of an acidic molecule is a function of the pH of the solution and it is to be noted that both the non-dissociated molecule and an associated ion may be adsorbed. It is impossible to describe adequately the large number of liquid-phase applications allocated to AC. The following list below indicates the wide-ranging scenarios for AC (Marsh and Rodriguez-Reinoso, 2006):

a) Drinking water availability, to improve taste, smell and color including removal of chlorinated compounds and other Volatile Organic Compound (VOC).
b) Improvements to ground water purity, contaminants coming from disused sites of heavy industries.
c) Treatments of both industrial and municipal wastewater.
d) Mining operations require feed water treatment, metallic ion adsorption (gold and other metals), adsorption of excess flotation reagents and adsorption of Natural Organic Material (NOM).
e) Pharmaceutical processes, including purification of process water

f) The food, beverage and oil industries for removal of small, color and unacceptable tastes.
g) The electroplating industries require purification of wastewaters containing Pb, Cr, etc.

Figure 2.1: Granular Activated Carbon form

The application of AC in water treatment is mainly centered in the removal of pollutant organic compounds. These compounds can be classified in three different categories: (1) NOM, (2) synthetic organic compounds and (3) by-products of chemical water treatment. The removal of water contaminants by active carbon is the major market (55% in the USA) for liquid-phase applications which 80% of total AC demands in the USA. Of the total US water treatment market, about 50% is in drinking water, 40% in wastewater and the rest in ground water markets. Both powdered and GAC are used in the water treatment, the tendency being toward use of the granular type because of its regeneration capability (Marsh and Rodriguez-Reinoso, 2006).

When the powdered form of AC is used, it is added to the slurry with automatic feeders. Dosage rates of AC in taste and odor control depend on the type of carbon and the level of impurities in the water, but in general terms the dosage is low, and the carbon can last for up to one year. As a result, it is not usually economic to regenerate the carbon, and spent carbon is generally discarded. Granular Activated Carbon (GAC) is preferred when there is a persistent problem with taste and odor control, and it is also used in special filters and disposable cartridges in industrial, commercial and residential installations.

GAC is used in gravity columns, through which water flows continuously for a set contact time. Contacting systems can be of the up-flow or down-flow type, the former adsorbing organic compounds, whereas the latter filters suspended solids in addition. In an up-flow system, replacement of the spent carbon is carried out from the bottom of the column, with addition of new carbon at the top, while the unit remains in operation. In a down-flow system that does not have pre-filtration, suspended solids may accumulate at the top of bed, requiring periodic back-washing of the bed to relieve the pressure drop caused by the accumulated solids. This type of bed is operated in series or in parallel. As the carbon will be exhausted first at the top of the bed, it is necessary to remove the entire bed in order to replace the carbon. The world’s largest municipal GAC potable water treatment system was installed in Cincinnati, Ohio 1989 with a potential capacity of over 830 million liters per day (Marsh and Rodriguez-Reinoso, 2006).

Wastewater is treated involves the removal of inorganic and organic compounds by adsorption. It results in an extremely high-purity effluent, where the BOD can be reduced by over 99%, to 1 mg/L. AC is used in the treatment of industrial wastewater to upgrade the water for reuse or to pre-treat effluents prior to discharge into municipal treatment plants, rivers and streams. Adsorption by an AC may be used as the only treatment before biological treatment or as a tertiary process after biological treatment (Marsh and Rodriguez-Reinoso, 2006)

AC is used to purify industrial wastewater, as it removes not only biodegradable organic compounds, but also chemicals that are not responsive to, or are toxic to, conventional biological treatments. These include pesticides, phenols, organic dyes and polyols. AC is used to treat effluent wastes from chemical factories, rubber tread factories, fabric dyeing, fertilizer plants, pulp, and paper mills, etc. AC systems are more flexible than biological ones as they can handle sudden fluctuations in the concentration of impurities, and the water purity can be controlled to meet specific requirements (Marsh and Rodriguez-Reinoso, 2006).

The selection of the AC for a given application (solutes to be retained, concentration, stream flow, etc.) is made by dynamic tests in pilot adsorption units. The determination of the adsorption isotherm of a given solute over a wide range of concentration is the method to obtain the equilibrium capacity of the adsorbent. In this way, the amount of solute it can remove from the solution can be estimated and consequently the suitability of the AC for achieving the required removal of the solute (Marsh and Rodriguez-Reinoso, 2006).

The analysis of the adsorption isotherm gives the adsorption capacity at equilibrium, but it says nothing about the time required reaching equilibrium, and this is a very important parameter in the design of an adsorbed bed. Once a group of carbons has been selected, it is necessary to carry out dynamic tests to determine the breakthrough curve to determine the volume of water that can be treated by the carbon bed before it become saturated, or before the concentration of the solute in the effluent (at the exit of the adsorbent bed) become higher than that required (breakthrough point). The breakthrough curve in an adsorption system depends on several parameters. It depends on the space velocity of the stream (the ratio between the volumetric flow and the volume of the bed); it is clear that the adsorbent bed can be used for a larger period of time with low space velocities.

But, the breakthrough curve also depends on the characteristics of the stream to be treated (composition, concentration of impurities, temperature, pH) and on the adsorbent (surface characteristics, particle size). After the AC becomes saturated, it is sometimes necessary to regenerate it in order to recover its adsorption capacity. Physical adsorption is a reversible process, and desorption can be more or less easily achieved. Regeneration is usually carried out by means of a thermal process. The exhausted carbon is taken off the adsorption column as slurry. It is dewatered and passed to a rotary kiln, where it is heat treated under controlled conditions and with a limited oxygen content to avoid carbon combustion. This treatment removes residual water and volatilizes organic compounds, which are also oxidized. Then the carbon is quenched with water, washed and recycled. The carbon is regenerated either on or off site. Some carbon losses (2-10wt %) is unavoidable during the regeneration step, and fresh carbon has to be supplied. The regeneration process takes about 30min (Marsh and Rodriguez-Reinoso, 2006).

2.3 Coconut Shell Based Activated Carbon

A coconut shell-based activated carbon was studied as hydrogen sulfide adsorbent in four subsequent adsorption/ regeneration cycles. The regeneration of exhausted carbon was done using washing with cold and hot water with a defined ratio of water volume to the unit weight of carbon. The observed changes in the capacity were linked to such surface features of activated carbons as pH and porosity. The cold and hot water washing result in the similar capacity for H_2S adsorption. After the first adsorption run, the capacity of carbon for hydrogen sulfide adsorption significantly decreased (around 60%). The subsequent runs revealed more or less constant capacity with similar efficiency for the removal of sulfur species (Bagreev *et.al*, 2000).

The results indicate that after the first run the most active adsorption cites located in small pores are exhausted irreversibly. The sulfur adsorbed on those sites is strongly bound as elemental sulfur and sulfuric acid. Despite this, the carbon surface was found to have other adsorption/oxidation sites which can be regenerated using cold or hot water washing. Besides sulfuric acid being removed from the pore volume of activated carbon a significant percentage of elemental sulfur was also removed (Bagreev *et.al*, 2000).

Activated carbon can be produced from different raw carbon resources like lignite, peat, coal, and biomass resources such as wood, sawdust, bagasse, and coconut shells (Ioannidou and Zabaniotou, 2006). However, the abundant supply of coconut shell as a waste-product from the coconut oil and desiccated coconut industry makes production of activated carbon from this material more financially viable since using grain or coal as raw materials for activated carbon will require manufacturers extra amount of money for procurement. Furthermore, besides being an amorphous form of carbon that can absorb many gases, vapors, and colloidal solids, coconut shell activated carbons are advantageous over carbons made from other materials because of its high density, high purity, and virtually dust-free nature. These carbons are harder and more resistant to attrition (Gratuito *et.al*, 2008).

Figure 2.2: Coconut Shell Activated Carbon

2.4 Fixed-Bed Adsorption Column Studies

In the studies of fixed-bed adsorption processes, breakthrough and number of bed volumes are normally used in the description and comparison. The breakthrough is usually defined as the phenomenon when the effluent concentration from the column is about 3–5% of the influent concentration (Chen *et.al*, 2003).

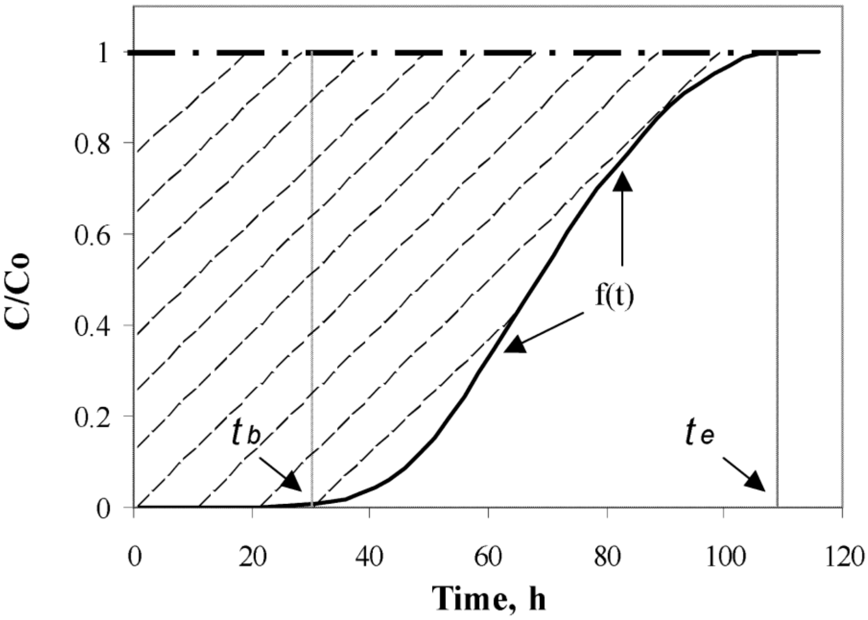


Figure 2.3: Typical Breakthrough Curve of Carbon Fixed-Bed Column (Chen *et.al*, 2003)

Fixed-bed adsorption process has been widely used to remove many organic pollutants from industrial wastewater, and the relevant breakthrough curves for a specific adsorption process are essential when determining the operating parameters such as feed flow rate. Although many models were developed to predict the breakthrough curve, most of them are sophisticated and need many parameters determined by serial independent batch kinetic tests or estimated by suitable correlations (Pan *et.al*, 2005).

The performance of a fixed-bed column is described through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The loading behavior of the adsorbed solution in a fixed-bed is usually expressed in term of C_t /C_0 as a function of time or volume of the effluent for a given bed height, giving a breakthrough curve (Han *et.al*, 2009).

Fixed bed adsorber columns have been widely used for treatment of textile industry effluents. In this regard, one important aspect to consider will be the analysis of the columns performance subjected to different operating conditions. Also, the design of the adsorption columns usually requires information from pilot-plant experiments. However, a mathematical model, once it has been validated, can minimize the number of experiments associated with new operating conditions, and therefore decrease additional costs. A valid model can predict the system dynamics expressed through breakthrough curves with respect to adsorption equilibrium isotherms (Goshadrou and Moheb, 2011).

2.5 Continuous Adsorption Systems

The adsorption systems related to granular activated carbon (GAC) contactors. It can be classified by the following characteristics: (1) driving force-gravity versus pressure; (2) flow direction-downflow versus upflow; (3) configuration-parallel versus series; and (4) position-filter-adsorber versus postfilter-adsorber. GAC may be used in pressure or gravity contactors. Pressure filters enclose the GAC and can be operated over a wide range of flow rates because of the wide variations in pressure drop that can be used. Gravity contactors are better suited for use when wide variations in flow rate are not desirable because of the need to remove turbidity, when large pressure drops are undesirable because of their impact on operation costs, and when visual observation is needed to monitor the condition of the GAC.

For many systems the decision between pressure or gravity contactors is made on the basis of cost. Medium-size and large systems normally use gravity contactors. Water may be applied to GAC either upflow or downflow, and upflow columns may be either packed bed or expanded bed. Downflow columns are the most common and seem best suited for drinking water treatment. The pulsed-bed contactor can also be used to decrease carbon usage rate from that of a single contactor. The flow is applied upward through the column; the spent GAC, a fraction of the total amount present, is periodically removed from the bottom of the column and an equal amount of fresh GAC is applied to the top.

Single-stage contactors are often used for small groundwater systems, but if more than one contactor is required, lower activated carbon usage rates can be achieved by arranging the contactors either in series or in parallel as shown in Figure 2.4, possibly yielding a lower-cost system. At this point only a portion of the activated carbon is saturated at the influent concentration, so the activated carbon usage rate may be relatively high. Alternatively, columns may be arranged in series so that the mass transfer zone (MTZ) is entirely contained within the downstream columns after the column has been saturated with the influent concentration.

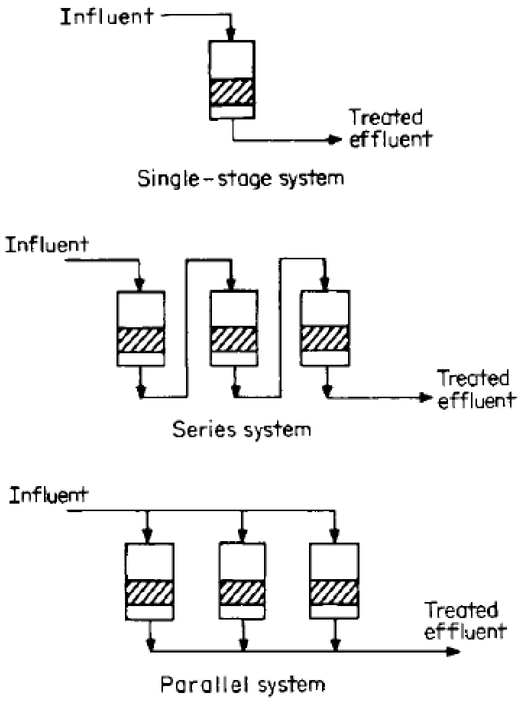


FIGURE 13.13 Adsorber systems.

Figure 2.4: Adsorber Systems

When the activated carbon is replaced in the lead column, the flow is redirected so that it goes through the freshest activated carbon last. Thus, the activated carbon “moves” countercurrent to the flow of water, and lower activated carbon usage rates are achieved than with single-stage contactors. Series configuration is best utilized when the effluent criterion is very low compared to the influent concentration (Wiesner *et.al*, 1987). The increased cost of plumbing counters the cost benefit of reduced activated carbon usage rate, however, especially when more than two columns must be used in series.

Other flow arrangements can be used to produce lower activated carbon usage rates. Each of the two layers can be backwashed and replaced independently, and the order of flow through the layers can be reversed. 35% lower activated carbon usage rate for this system for removing halogenated hydrocarbons from groundwater was reported compared to a single-stage system. GAC contactors can also be classified by their position in the treatment train. The filter-adsorber employs GAC to remove particles as well as dissolved organic compounds.

The GAC influent should be representative of that anticipated for the future full scale system. If this influent is not available, the pilot plant should include the necessary pretreatment processes. For postfilter-adsorbers, three or four GAC columns in series, such as shown in Figure 2.5, provide maximum operating flexibility. Alternatively, one or two long columns with several taps can be used so that samples can be taken at different depths. For filter-adsorbers, the GAC and other media, including underdrain media, would be contained in one column. The concentrations of all substances that might have a significant effect on the primary contaminant should be monitored. The data obtained can be used to calculate total annual costs (capital plus operating costs) for alternative designs to determine the most economical design.

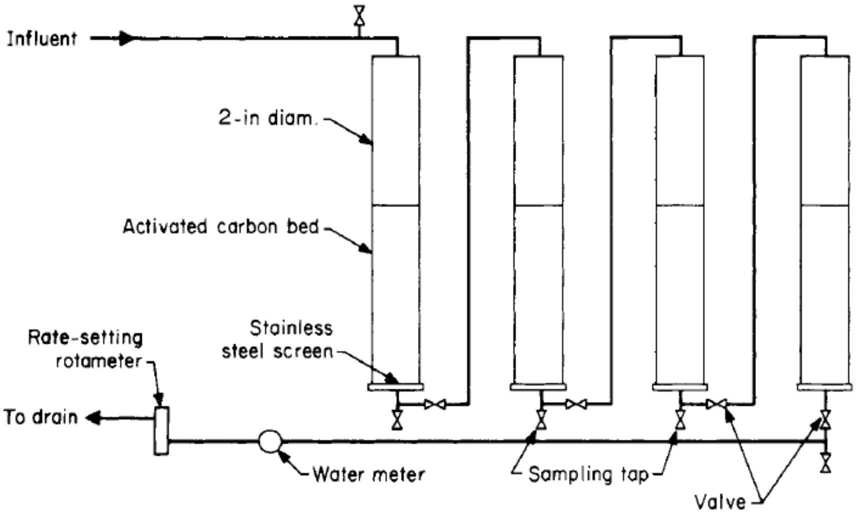


FIGURE 13.31 Downflow pilot carbon columns.

Figure 2.5: Downflow of Pilot Columns

2.6 Series Column Analysis

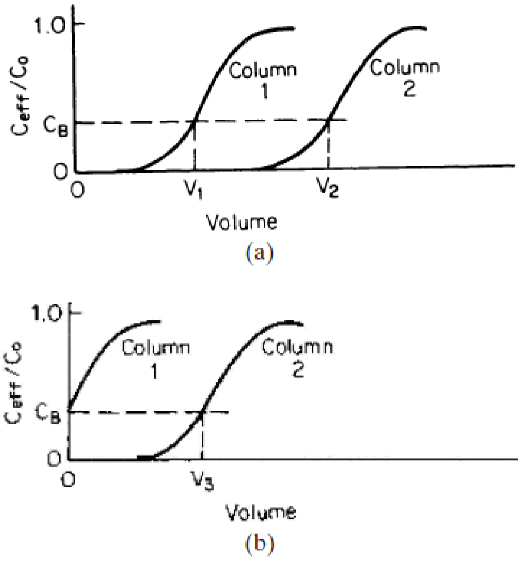


FIGURE 13.38 Breakthrough curves for two columns in series. (*a*) Fresh GAC in each column at start of test. (*b*) Column 1 was in the second position until CB was reached and then moved to the first position. Fresh GAC was in column 2 at start of test.

Figure 2.6: The Breakthrough Curve for Column in Series

The advantage of series operation of columns was discussed. The pilot test should be carefully designed to show the reduction in activated carbon usage rate that can be achieved by such operation. The simplest case is experienced if only a single compound with no competing adsorbates is present in the water to be treated. The breakthrough curves for each column in a two-column series are shown in Figure 2.6. Each column is equal in size and thus has the same Empty Bed Contact Time (EBCT).

The run can be terminated when the effluent concentration in the second column reaches C_B, because moving column 2 to position 1 and placing a fresh GAC column in position 2 should give the same breakthrough curves shown in Figure 2.6 between V_1 and V_2. The activated carbon usage rate (g/L) is then the mass of GAC in one column (g) divided by the total volume of water processed between replacements $V_2 - V_1$ (L). The number of bed volumes processed is ($V_2 - V_1$) divided by the volume of GAC in one column.

The situation is more complex if competing organics are present with the contaminant, or if a mixture of compounds is to be removed. The run must begin with fresh GAC in each position, and then operated until the C_{eff} in the second column reaches C_B. The data should be plotted as shown in Figure 2.6(a). Column 2 then must be moved to position 1, a fresh GAC column must be placed in position 2 and operation must continue until C_{eff} for the second column again reaches the breakthrough concentration. These data should be plotted as shown in Figure 2.6(b).

However, volume V_3 probably will not be the same as volume $V_2 - V_1$ because of the effects of competition. The activated carbon usage rate (g/L) for this case now becomes the mass of GAC in one column (g) divided by V_3(L). The plots in Figure 2.6 show that column 1 is completely saturated when column 2 reaches C_B (point A). If this does not happen, a lower activated carbon usage rate can probably be achieved with more than two columns in series. The pilot test to determine this carbon usage rate, assuming competing organics are present, must be run until the column initially in the last position rotates into the first position, followed by continued operation until this sequence of columns reaches breakthrough.

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter discussed methodology for this project in general, with a specific focus on the experiment for the organic compound removal in wastewater using continuous fixed-bed adsorption column. The available activated carbon used in this project obtained in granular form. The organic compound used in this study is from BASF Petronas Acrylic Acid process waste.

3.2 Experimental Set up

Fixed-bed adsorption column were carried out in a continuous three series adsorption column. Continuous adsorption process system using acrylic acid waste as the compound is then to be adsorbed by activated carbon. Figure 3.1 illustrates the schematic of the unit operation for the study.

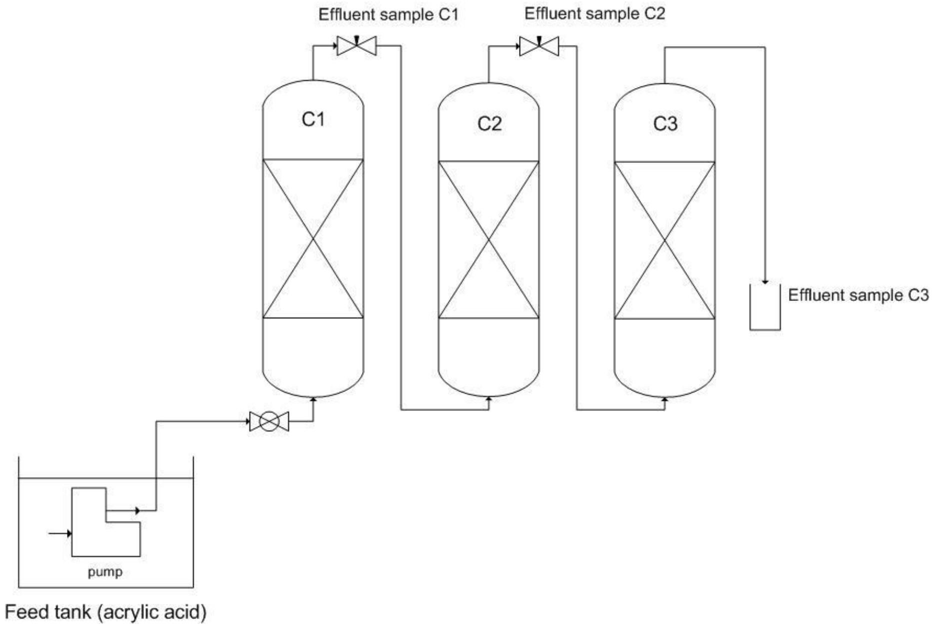
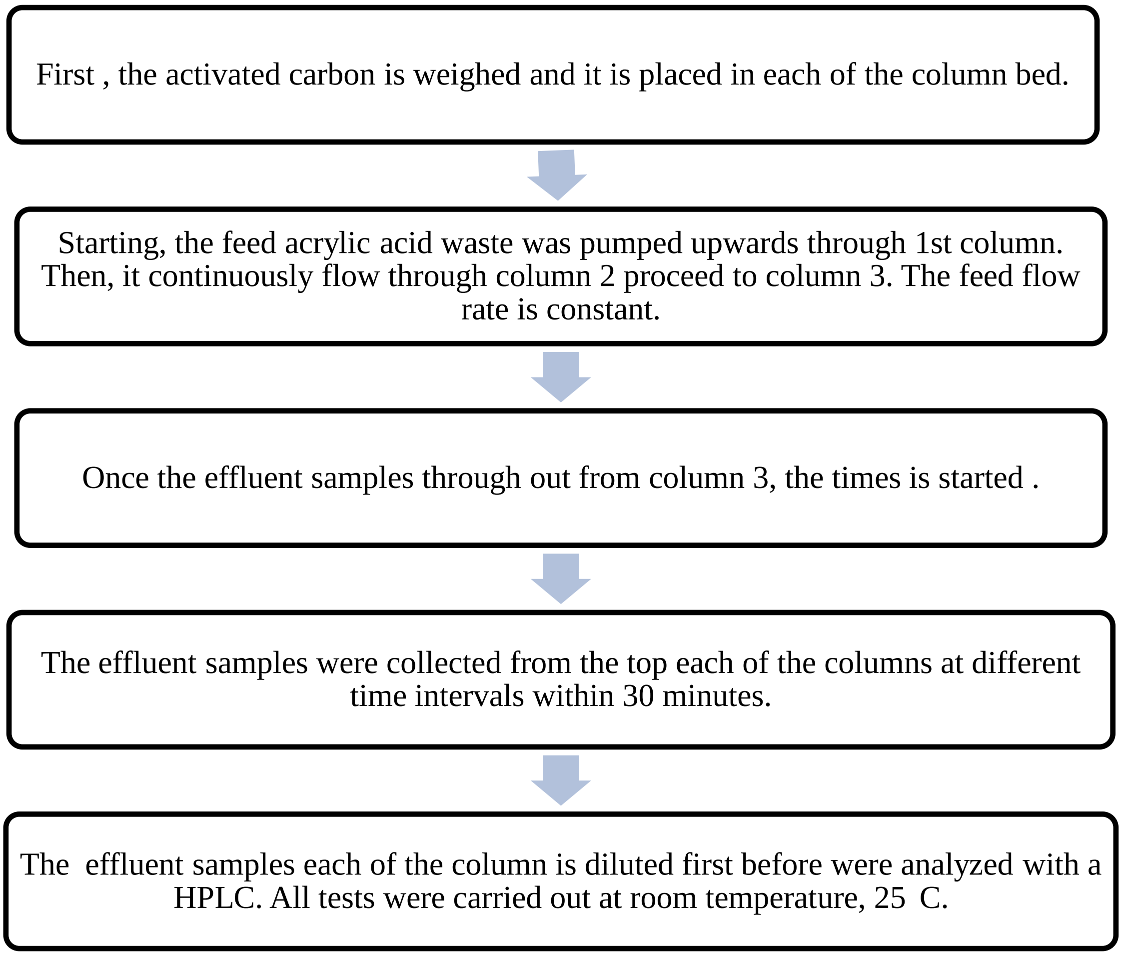


Figure 3.1: Schematic of Continuous Adsorption Experimental (pilot scale)

Figure 3.2: Overview of Continuous Fixed-Bed Adsorption System

3.3 Experiment of Continuous Adsorption for Column Studies

The experimental flow chart is used as the guidelines and the sequences to make it run smoothly. As illustrated in Fig. 3.3, the flow of three series of continuous fixed-bed adsorption column.



First , the activated carbon is weighed and it is placed in each of the column bed.

Starting, the feed acrylic acid waste was pumped upwards through 1st column. Then, it continuously flow through column 2 proceed to column 3. The feed flow rate is constant.

Once the effluent samples through out from column 3, the times is started .

The effluent samples were collected from the top each of the columns at different time intervals within 30 minutes.

The effluent samples each of the column is diluted first before were analyzed with a HPLC. All tests were carried out at room temperature, 25 C.

Figure 3.3: Overall flow of the Methodology

3.3.1 Effect of Outlet Concentration of Continuous Column

1. All the equipment is prepared.
2. The activated carbon is weighed and is added into each of the column.
3. The liquid feed waste is filled in the tank up to half of the tank.
4. The feed pump to column 1 is opened.
5. After the sample is start throughout from column 3, the times is started.
6. For the first, the samples are collected each 2 minutes using syringe for each column.
7. After 10, 15 and 30 minutes, the samples are collected each column.
8. An experiment was finish at 30 minutes of operation. The pump is turned off.

3.3.2 Preparation of Standard Solution

1. Ensure wear the personal protection equipment, such as mask and rubber glove during the experiment.
2. An acrylic acid standard solution with concentration of 20ppm, 50ppm, 100ppm, 150ppm is prepared.
3. For AA stock solution (1000ppm):
   a) The liquid sample of AA is prepared in a 100 ml beaker.
   b) The AA sample is put into vial by using syringe and micro filter.
   c) The AA sample is pipette 2.5 mL or 2500 µL by using micropipette from the vial and it is put into the 100 ml volumetric flask.
   d) The volumetric flask is top up with ultrapure water until the graduated level then shakes it until dilute.
   e) The stock solution is put in ultrasonicator for 30 minute to break the bubbles in the solution.
4. 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) The entire volumetric flask is top up with ultrapure water until the graduated level and shakes it until dilute.
f) All the standard solution is put in ultrasonicator for 30 minute to break the bubbles in the solution.
g) By using syringe and needle (0.2 um) for inject the entire standard into vial and label every vial for each of four standard.

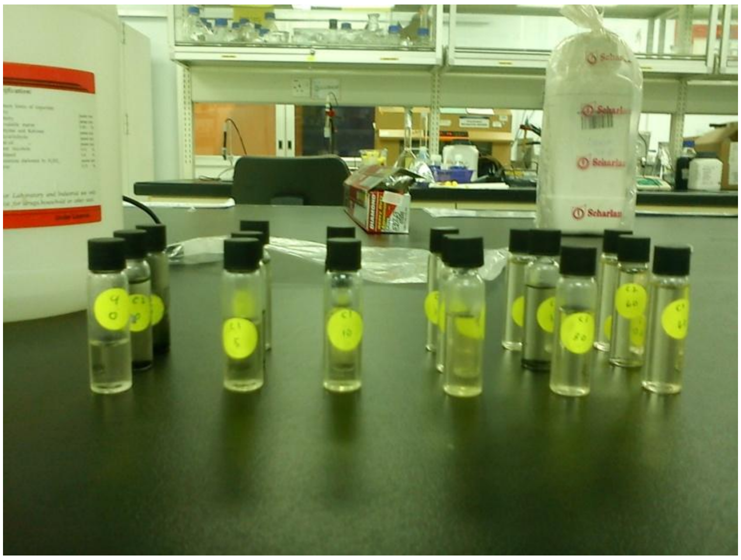


Figure 3.4: Preparation for AA Standard Solution

3.3.3 Sample Preparation for HPLC Analysis

1. The samples are prepared for HPLC analysis with concentration 100ppm.
2. The samples are pipette 0.0125 mL or 12.5μL of the entire parameters sample into the 10 mL volumetric flask.
3. The volumetric flask is top up with ultrapure water until the graduated level and shakes it until dilute.
4. The sample is sonicated for 30 minutes until no gas bubble is observed.
5. The sample is filtered before put in into vial.
6. Every vial is labeled.
7. The sample analysis procedure for HPLC is followed.

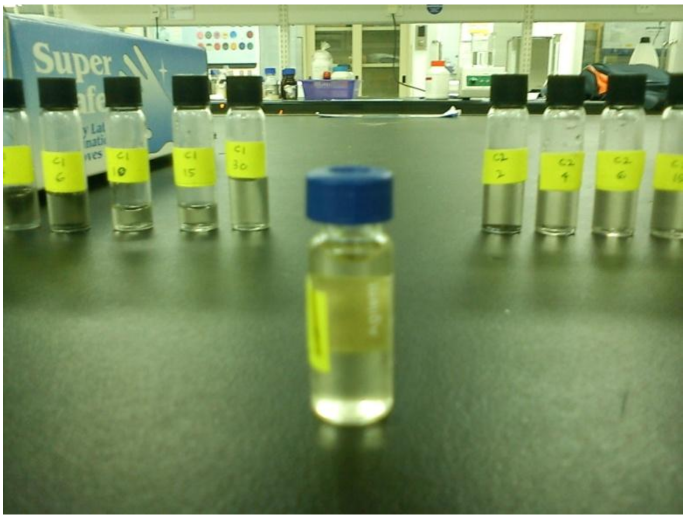


Figure 3.5: Vial fill-up with AA sample for HPLC Analysis

3.3.4 Preparation of Mobile Phase

1. Preparation of mobile phase (Mix water & trifluoroacetic acid 200 mL)
    a) 0.1% trifluoroacetic acid (TFA) with 1 mL of TFA is diluted with ultrapure water in the 1000 mL volumetric flask until the graduated level and shakes it until dilute.
    b) The filtration kits (0.45 um) and vacuum pump system is assembled.

   c) The mobile phase mixture is filtered using vacuum filtration unit.
   d) The flask containing after filtrate is put into ultrasonicator.

2. Preparation of mobile phase (HPLC Grade Methanol)
   a) 1000 mL of pure HPLC grade methanol is poured into a volumetric flask.
   b) Mobile phase & vial need to be sonicated for degassing purposes.

3.3.5 Condition of HPLC Analysis

Table 3.1: Condition for HPLC Analysis

Column	8
Diameter	4.6 cm with ID =5µm
Length	15 cm
Flowrate	1 ml/min
Temperature	35 ^{0}C
Detection	UV at 220nm,16 (Ref:360nm,100)
Injections	10µL
Mobile Phase	3:97 Methanol: water with 0.1% TFA

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 Introduction

The purpose of this chapter is to show the objective presentation of results. Tables and figures show the results with sufficient supporting description. The results section is illustrate the end-result based on the parameters mentioned in the objectives section in graphical format. The parameters include feed flow rate and weight of adsorbent in the column have been studied through the continuous adsorption system. The results are showed in the composition profile of acrylic acid in the outlet flow of each column as a function of time. The outlet concentration each column has been studied.

4.2 Adsorption in Each Column

From the table 4.1 to 4.3, we can observe area values of each column after comparing with the standard graph calibration shows the outlet concentration within certain times. The results indicated from table 4.4 that the concentration gives a significant effect to the adsorption process of acrylic acid onto the activated carbon.

However, the others factors which are feed flow rate and weight of adsorbent may influence the result obtained.

Table 4.1: The Values Area of Column 1

Time (min)	**RT (min)**	**Column 1 AREA (mAU*s)**
2	3.158	584.00574
4	3.156	541.07788
6	3.152	553.9585
10	3.15	594.9231
15	3.146	621.86176
30	3.145	616.22894

Table 4.2: The Values Area of Column 2

Time (min)	**RT (min)**	**Column 2 AREA (mAU*s)**
2	3.145	655.04828
4	3.145	603.32336
6	3.148	567.86829
10	3.15	583.40082
15	3.143	565.59534
30	3.145	553.84296

Table 4.3: The Values Area of Column 3

Time (min)	**RT (min)**	**Column 3 AREA (mAU*s)**
2	3.147	566.24554
4	3.144	513.6275
6	3.144	498.97189
10	3.139	550.43036
15	3.137	564.92322
30	3.142	673.49615

Table 4.4: The Values of Outlet Concentration Each Column

Time (min)	**Concentration C1(ppm)**	**Concentration C2 (ppm)**	**Concentration C3 (ppm)**
0	0	0	0
2	80.9252942	90.45981058	78.541723
4	75.1640082	83.51788396	71.479932
6	76.8926976	78.75951035	69.513024
10	82.3904972	80.84410871	76.419191
15	86.0058958	78.45446103	78.364257
30	85.2499232	76.87719112	92.935672

Figure 4.1 to 4.3 below shows the effluent concentration of acrylic acid in each column. For the figure 4.1 and 4.2, it shows for column 1 and column 2 after 2 minutes the concentration is decreased then slowly increased to reach equilibrium state. It showed within 10 minutes the changes of the concentration and the total capacity of the bed is practically constant regardless of the composition of the solution being treated. For figure 4.3 of continuous column 3, after 2 minutes the concentration gradually increases. As compare with column 1 & 2, it is not reached equilibrium state. For column 3, the amount of adsorbent is higher than other 2 columns. Therefore, the maximum adsorption capacity of the column is not reached yet within 30 minutes earlier.

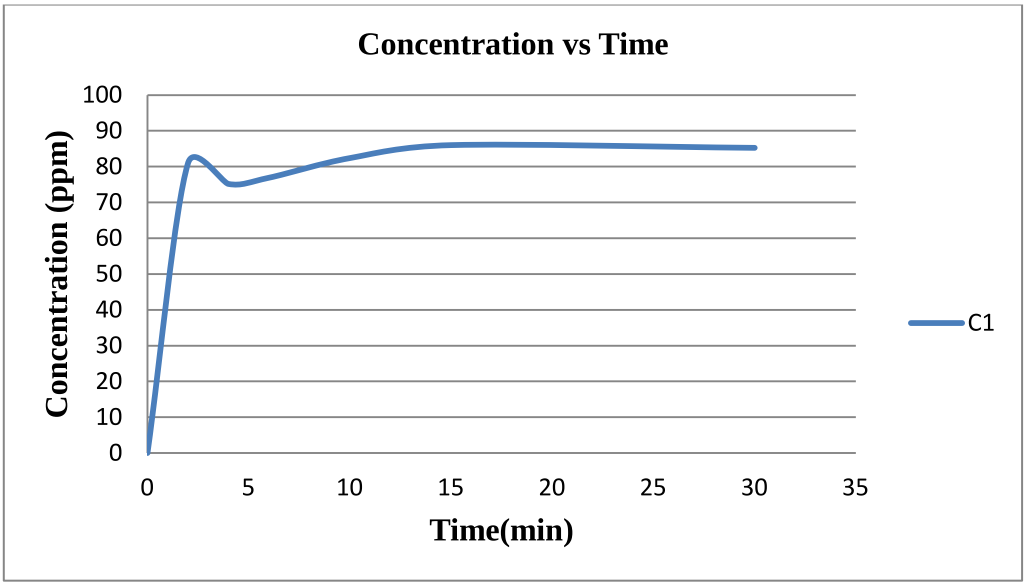


Figure 4.1: The Graph of Outlet Concentration Column 1 against Time

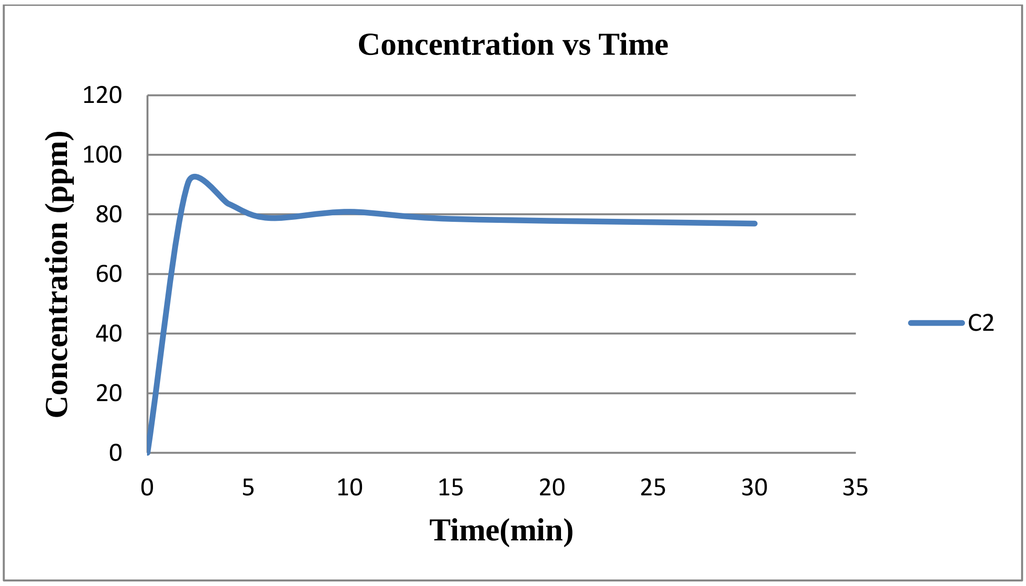


Figure 4.2: The Graph of Outlet Concentration Column 2 against Time

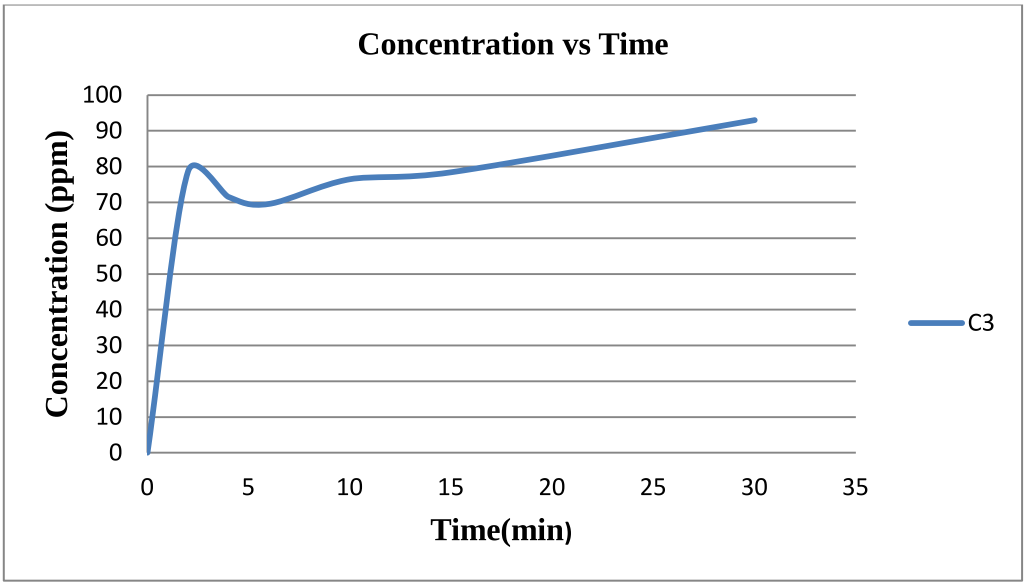


Figure 4.3: The Graph of Outlet Concentration Column 3 against Time

4.3 Effect of Feed Flow Rate

The determination of maximum column adsorption capacity is depending on the feed flow rate. For this experimental, the feed flow rate is constant. The amount of acrylic acid waste to be adsorbed on the granular activated carbon for these three series of column around 2L.

4.4 Effect of Weight of Adsorbent

The effect of adsorbent weight on the uptake of acrylic acid by granular activated carbon was studied. It was found the total maximum continuous three series of column adsorption capacity is within 10 minutes. Because of the size continuous fixed-bed adsorption is small the weight of adsorbent is not varying. The weight of adsorbent for the three continuous columns is already reached maximum about 900g within 10 minutes of adsorption process. Therefore, if we change the amount of weight adsorbent it will not so affect the removal of AA efficiency. Adsorption of AA gets enhanced with an increase in the adsorbent dosage because of the greater surface area and the availability of larger number of adsorption sites (Kumar *et.al*, 2010).

4.5 Effect of Outlet Concentration in Continuous Column

Column type continuous flow operations depend on the concentration of solute in the solution being treated. For continuous column operation the carbon is continuously in contact with a fresh solution. Consequently, the concentration in the solution in contact with a given layer of carbon in a column changes very slowly. For batch treatment, the concentration of solute in contact with a specific quantity of carbon decreases much more rapidly as adsorption proceeds, thereby decreasing the effectiveness of the adsorbent for removing the solute. Thus a fixed-bed adsorption continuous column is generally preferred.

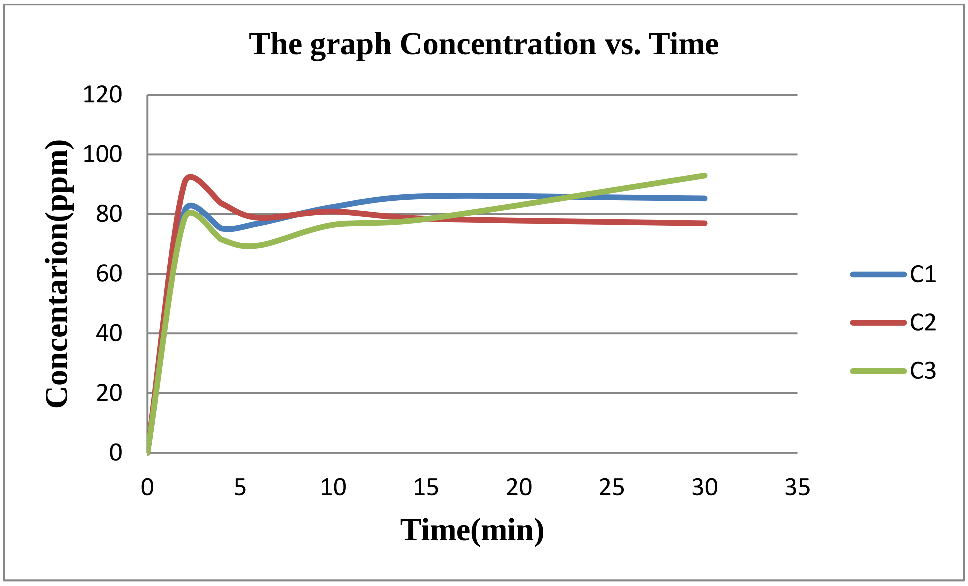


Figure 4.4: The Graph Concentration against Time for Continuous Column 1, Column 2 and Column 3

Figure 4.4 above shows the overall view graph from column 1 to column 3. For the continuous adsorption process discussed, the impurity is adsorbed most rapidly and effectively by the first few layers of fresh activated carbon during the initial stage of operation. The acrylic acid (AA) waste enter the bed, it first encounters the saturated zone in which the carbon is already saturated with the pollutants. In fixed-bed adsorption column, the bed can be divided into three approximate zones, i.e., the saturated zone (containing carbon nearly saturated with the pollutants), followed by the adsorption zone (were adsorption actually takes place), followed by a zone in which the carbon contains little or no adsorbed pollutant. As the acrylic acid waste enters the bed it first encounters the saturated zone in which the carbon is already nearly saturated with the pollutant. Practically no adsorption occurs in the saturated zone.

As more AA waste travels the bed the saturated zone expands progressively through the bed eventually including it completely. Pollutant adsorption occurs nearly exclusively over a portion of the bed called the adsorption zone, downstream of the saturated zone. The concentration of AA in the carbon varies from near saturation (at the beginning of the adsorption zone) to near zone (toward the end of the adsorption zone). At any given time the portion of the bed downstream of the adsorption zone contains very little adsorbed pollutant since the AA waste it is in contact with has already been nearly completely depleted of the pollutants. As time goes by a greater portion of the bed becomes saturated with the pollutant and the adsorption zone moves downstream forming an adsorptive wave. It is shown from the figure 4.4 above after 2 minutes the outlet concentration is decreasing for each of the column.

Then, the forward part of the adsorption wave reaches the end of the bed. Therefore, the bed begins to release acrylic acid waste having a concentration higher than the desired value. The figure 4.4 shows after 10 minutes the concentration is slowly increase for the continuous adsorption column system. This point is called breakpoint. The corresponding curve of pollutant concentration in the effluent vs. time is called breakthrough curve. The pollutant concentration in the effluent rises rapidly (i.e., the breakthrough curve is typically steep), until it reaches an arbitrarily defined exhaustion point where the column approaches saturation.

Nonsteady-state conditions prevail in that the carbon continues to remove increasing amounts of impurities from solution over the entire period of useful operation. The breakpoint on this curve represents that point in operation where for all practical purposes the column is in equilibrium with the influent wastewater, and beyond which little additional removal of solute will occur. At this point it is desirable to reactivate or replace the carbon. The method chosen for operation of a fixed-bed adsorber depends to a large extent on the shape of the curve given by plotting C/C_0 versus time or volume. As noted previously, this curve is referred to as a breakthrough curve.

For most adsorption operations in water and wastewater treatment, breakthrough curves exhibit a characteristic S shape but with varying degrees of steepness and position of breakpoint. Factors which affect the actual shape of the curve include all of the parameters discussed earlier (shape of the adsorption isotherm, solute concentration, and pH. For this continuous adsorption experiment, because of the concentration acrylic acid waste is too high the effluent concentration will affect the characteristics of the curve.

As a general rule, the time to breakpoint is decreased by: (1) increased particle size of the carbon; (2) increased concentration of solute in the influent; (3) increased pH of the water; (4) increased flowrate; and (5) decreased bed depth. If the total bed depth is smaller than the length of the primary adsorption zone required for effective removal of solute from solution, then the concentration of solute in the effluent will rise sharply from the time the effluent is first discharged from the adsorption column. Thus, for each type of adsorption operation there exists a critical minimum carbon depth.

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

From the experimental data achieved, it can be concluded that acrylic acid from process waste can be removed using continuous fixed-bed adsorption column and concluding the achievement of the objectives to study the composition profile of acrylic acid in the outlet flow of each column as a function of time.

From Chapter 4, Results and Discussions, the experimental has been run and the study of the outlet concentration in each column has been carried out. The results show the activated carbon of granular form as adsorbent affect the changes of the outlet concentration each of the column. Meanwhile, the adsorbent dosage does not play any important role in continuous adsorption for organic compound removal. The results for effluent concentration between acrylic acid in the solution and the adsorbent surface were practically achieved in 30 minutes. Therefore, this concludes that first objectives adsorption of acrylic acid waste is favorably influenced by a feed flow rate and the weight of adsorbent.

5.2 Recommendations

There is always improvement in every research work or projects. The adsorption study for the removal of organic compound using continuous fixed-bed adsorption column is one of the comprehensive study to treat the wastewater from industries which can impact the environment.

Therefore, the improvement proposed for the research study is as follows:

- The effluent samples, it should has the applicable taken samples same time for the three of the continuous adsorption column.
- It should test with high number of continuous column also increase height of bed with regeneration facility because the concentration is too high.
- Economic analysis can be carried out.

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APPENDIX A

EXPERIMENT HPLC RESULT

Table A.1: The Values of Standard Calibration Graph Plot

Concentration (ppm)	**Area (mAU*s)**
0	0
20	160.47668
50	324.08389
100	649.07373
150	1155.83374

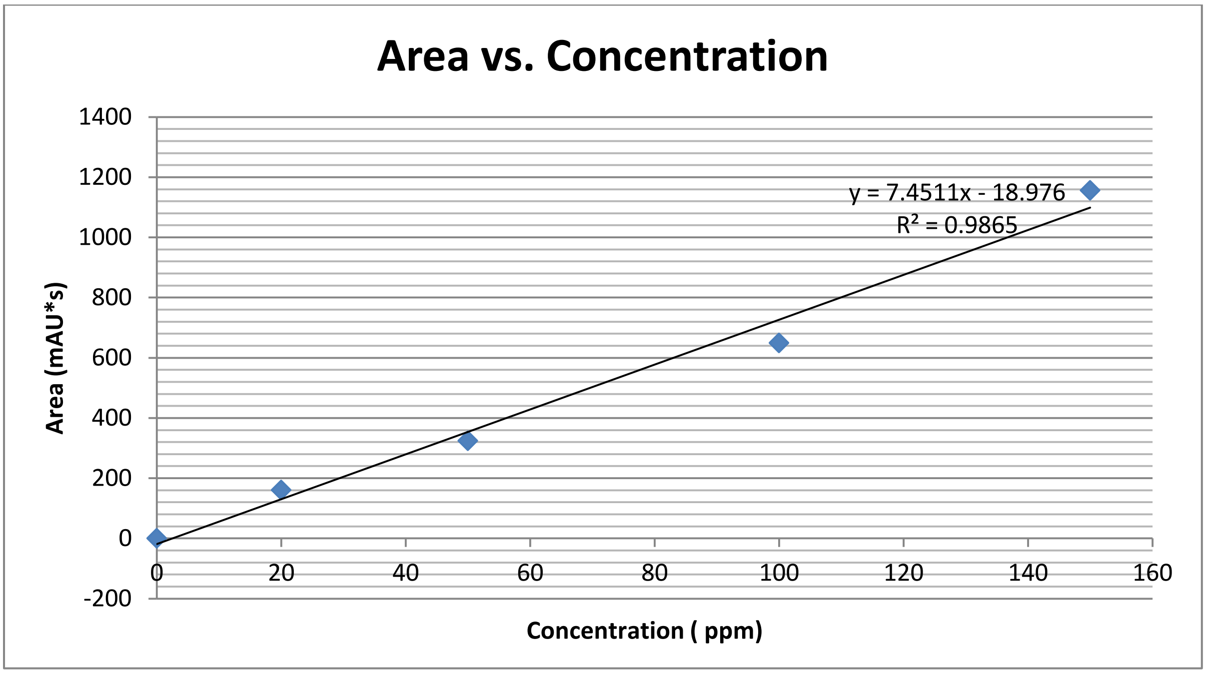

Figure A.1: The Standard Calibration Graph

APPENDIX B

HPLC REFERENCE REPORT

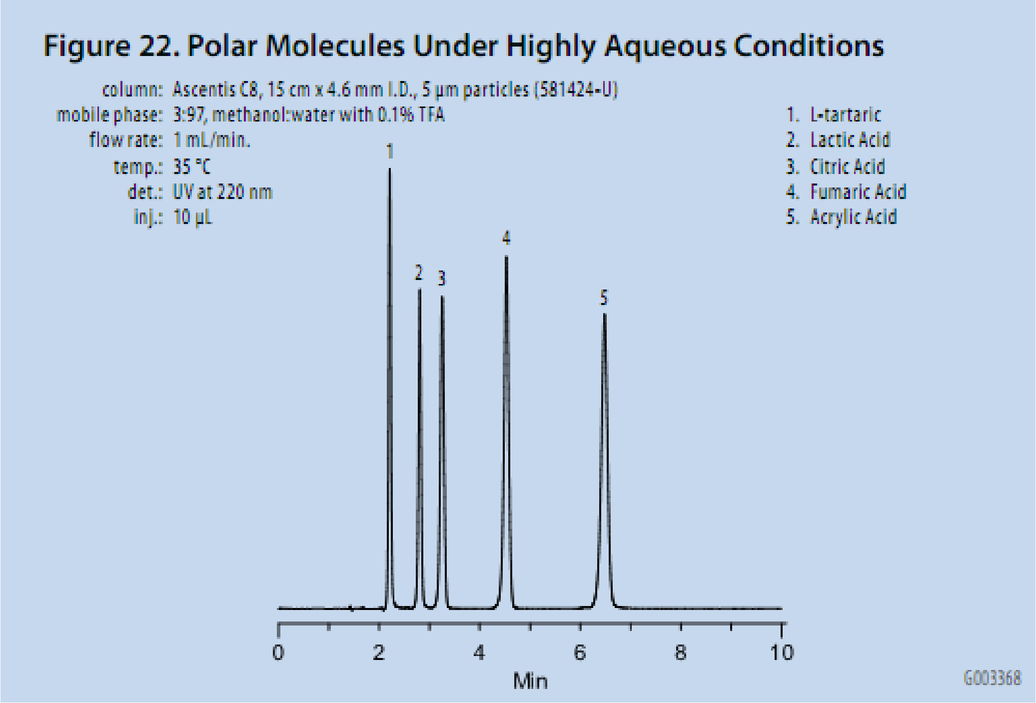

Figure B.1: The peak graph for HPLC

Figure B.2: HPLC Agilent 1200 Series

APPENDIX C

HPLC REPORT

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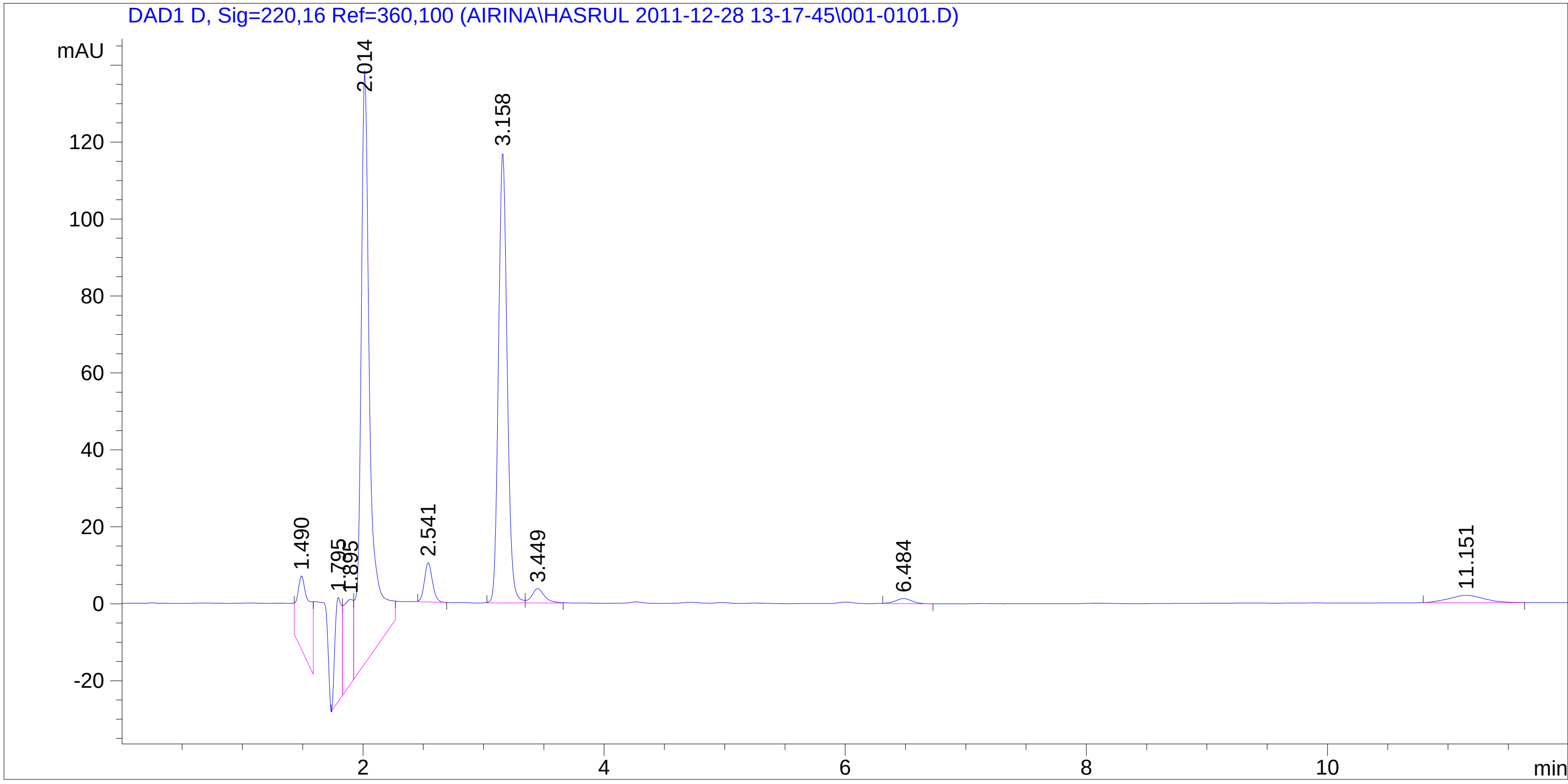

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       2   1.795 BV    0.0581  102.05463   27.00717   5.2783
       3   1.895 VV    0.0799  124.38078   22.03568   6.4330
       4   2.014 VB    0.0782  847.66223  154.06096  43.8411
       5   2.541 BB    0.0718   47.31152   10.25157   2.4470
       6   3.158 BV    0.0781  584.00574  117.25047  30.2048
       7   3.449 VB    0.1070   27.37671    3.75963   1.4159
       8   6.484 BB    0.1468   12.41618    1.30760   0.6422
       9  11.151 BB    0.2923   38.22965    1.90362   1.9772

    Totals :                  1933.48623  356.71618
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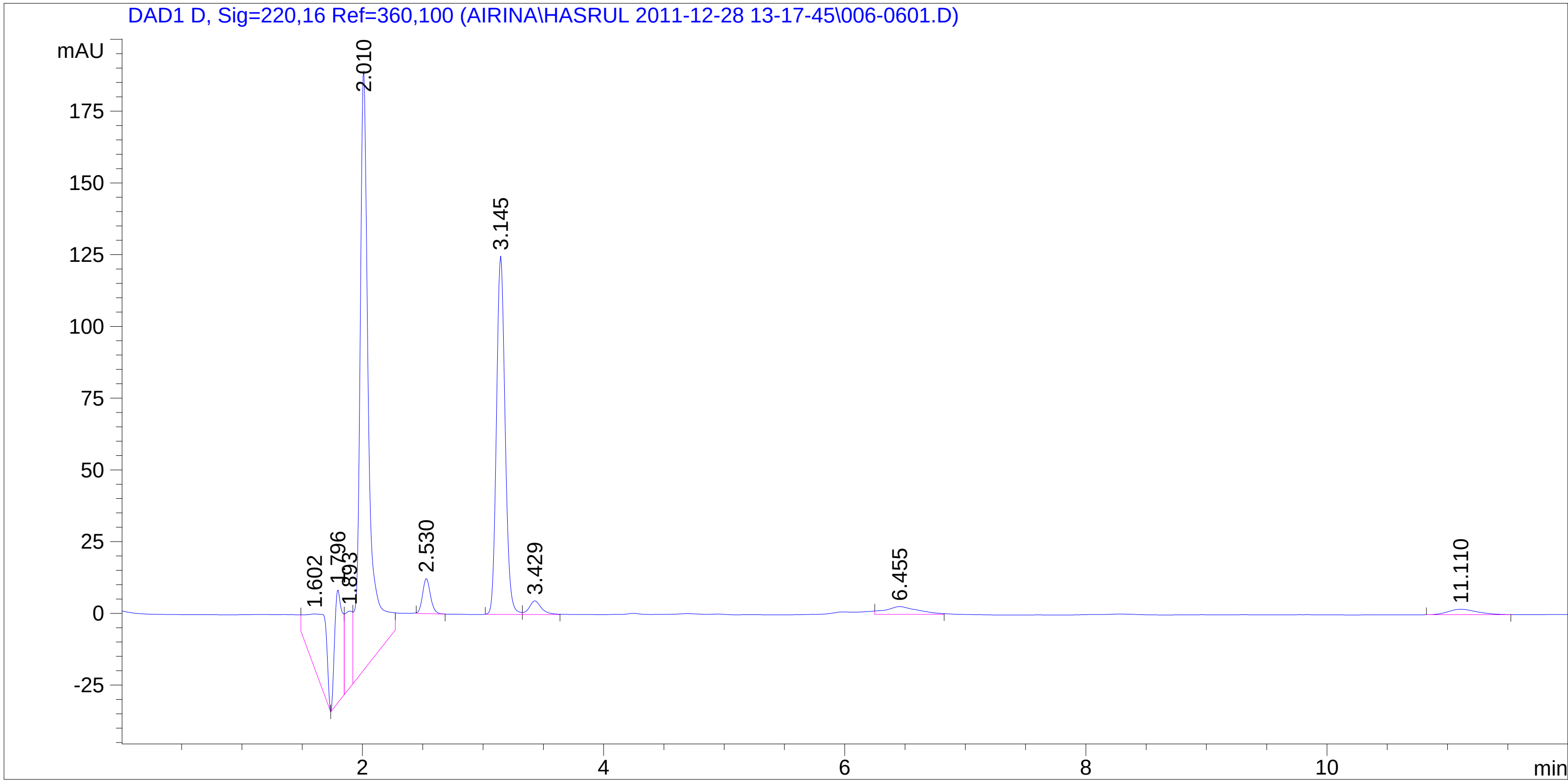

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       2   1.796 VV    0.0664  176.64053   39.35476   7.2710
       3   1.893 VV    0.0620  114.83765   26.79150   4.7270
       4   2.010 VB    0.0777 1108.58618  209.57993  45.6322
       5   2.530 BB    0.0691   55.79216   12.25105   2.2965
       6   3.145 BV    0.0756  616.22894  124.86571  25.3655
       7   3.429 VB    0.1061   33.44257    4.75115   1.3766
       8   6.455 BB    0.2558   51.18501    2.69221   2.1069
       9  11.110 BB    0.2592   31.91848    1.88797   1.3138

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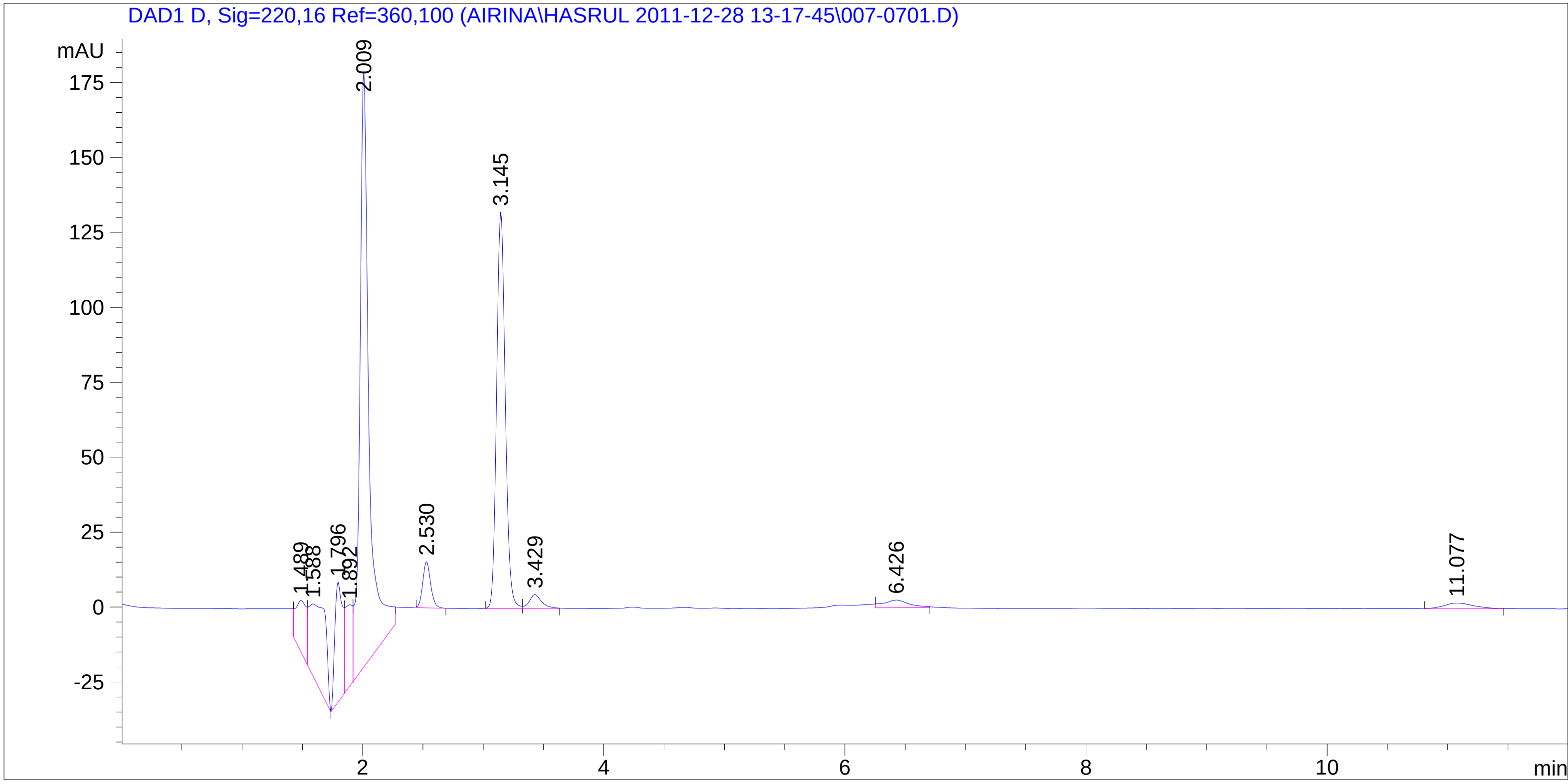

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       2   1.588 VV    0.1407  261.42526   24.06922  10.2095
       3   1.796 VV    0.0667  180.66946   39.96015   7.0557
       4   1.892 VV    0.0619  116.22923   27.18210   4.5391
       5   2.009 VB    0.0785 1067.16846  199.17368  41.6765
       6   2.530 BB    0.0713   70.25663   15.39049   2.7438
       7   3.145 BV    0.0757  655.04828  132.34563  25.5818
       8   3.429 VB    0.1089   33.80396    4.64625   1.3202
       9   6.426 BB    0.2094   38.57164    2.56618   1.5064
      10  11.077 BB    0.2471   31.18639    1.86526   1.2179

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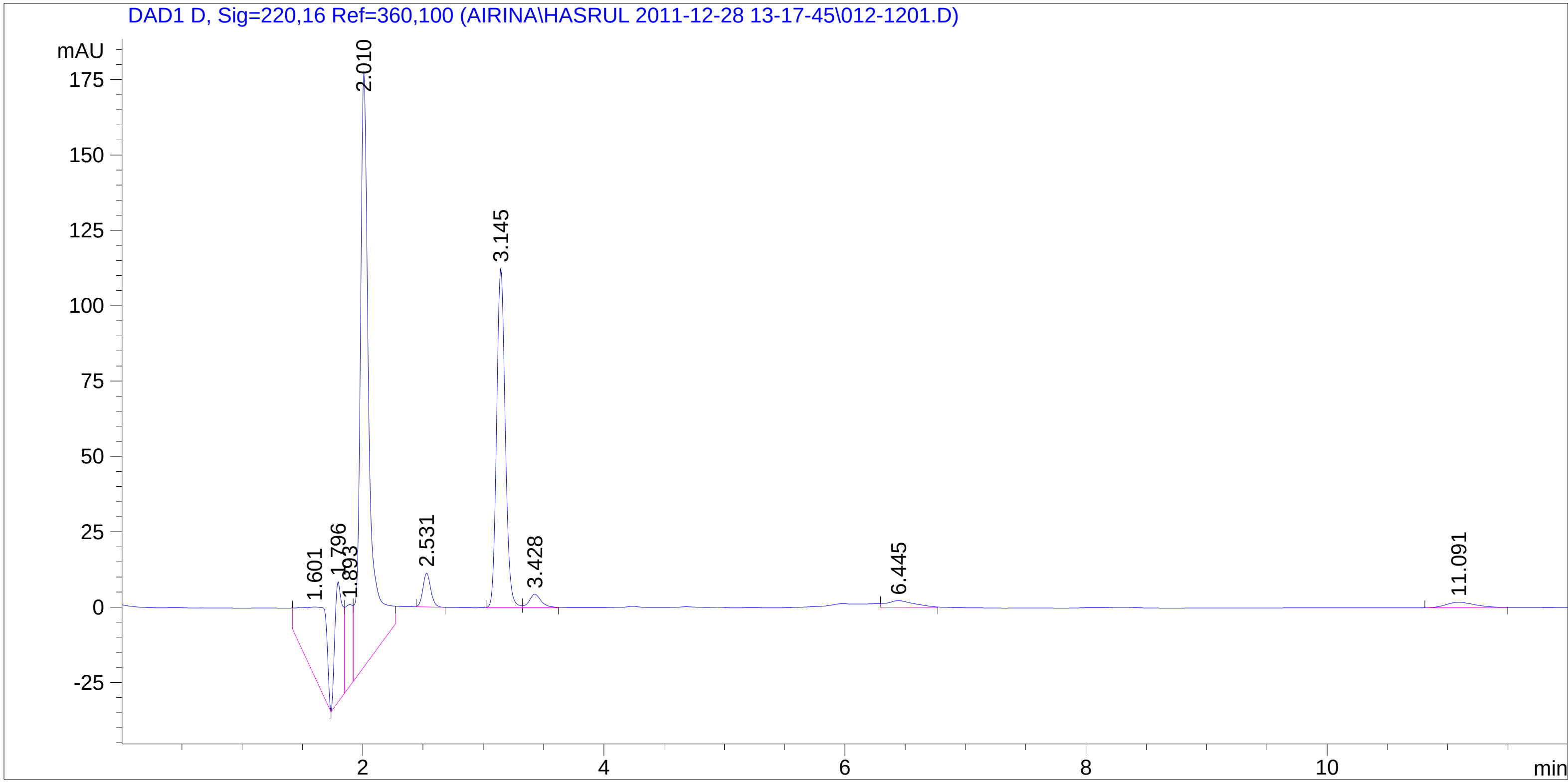

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Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 D, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
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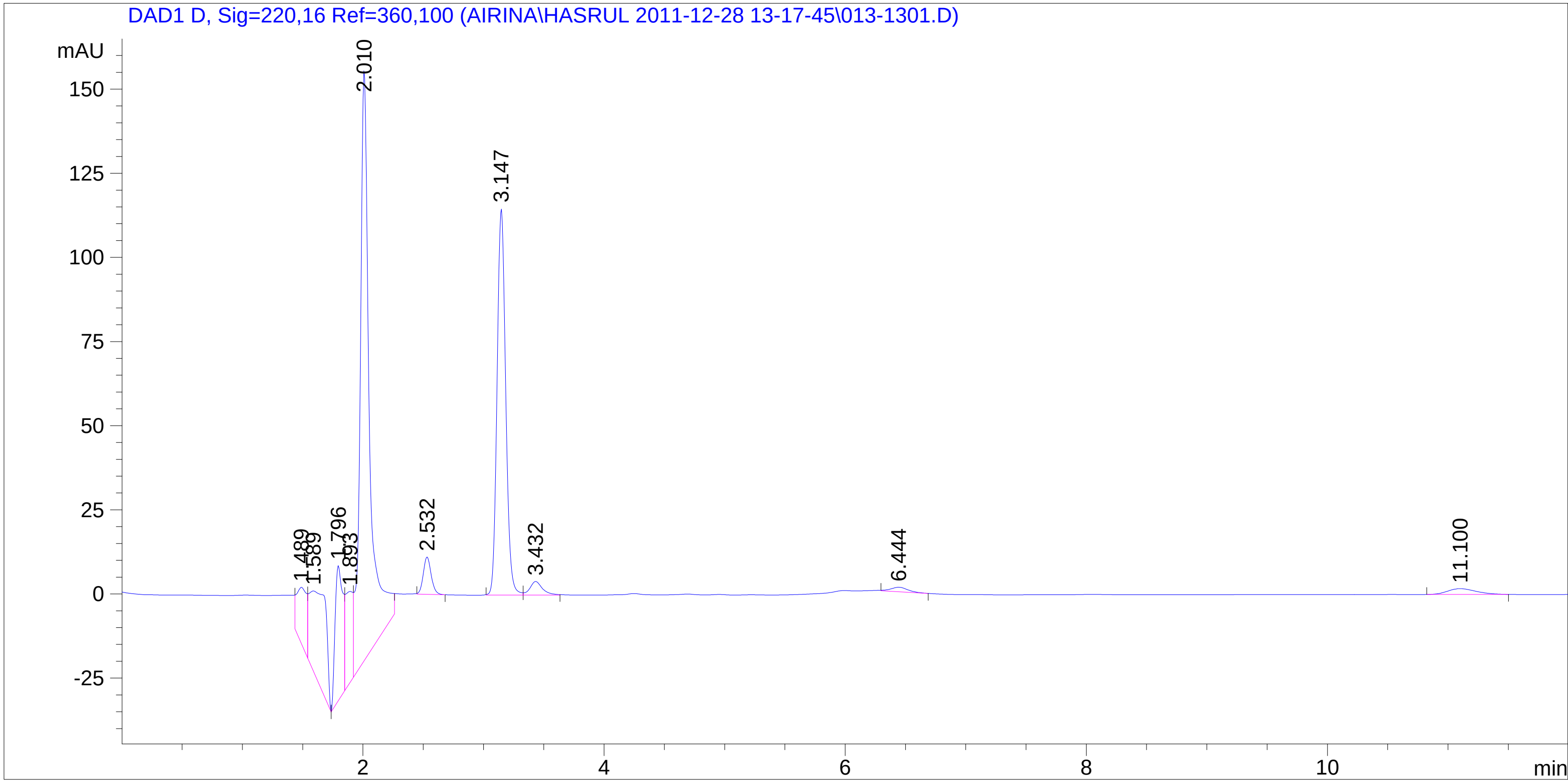
   1   1.601 BV    0.1895  343.54822   23.10408 14.3328
   2   1.796 VV    0.0667  180.13252   39.88065  7.5151
   3   1.893 VV    0.0600  116.10133   27.07423  4.8437
   4   2.010 VB    0.0762 1055.00061  197.73952 44.0145
   5   2.531 BB    0.0710   51.10244   11.25797  2.1320
   6   3.145 BV    0.0754  553.84296  112.61318 23.1063
   7   3.428 VB    0.1054   30.97811    4.44126  1.2924
   8   6.445 BB    0.2216   35.86739    2.20732  1.4964
   9  11.091 BB    0.2527   30.36371    1.78313  1.2668

Totals :                  2396.93729  420.10135
```

```
    =====================================================================
    Acq. Operator   : airina                          Seq. Line :  13
    Acq. Instrument : Instrument 1                     Location : Vial 13
    Injection Date  : 12/28/2011 4:11:43 PM                 Inj :   1
                                                     Inj Volume : 10 µl
    Acq. Method     : C:\CHEM32\1\DATA\AIRINA\HASRUL 2011-12-28 13-17-45\AIRINA.M
    Last changed    : 12/28/2011 11:57:31 AM by AEDLAN
    Analysis Method : C:\CHEM32\1\METHODS\AIRINA.M
    Last changed    : 12/28/2011 11:57:31 AM by AEDLAN
```



```
    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier:                  :      1.0000
    Dilution:                    :      1.0000
    Use Multiplier & Dilution Factor with ISTDs

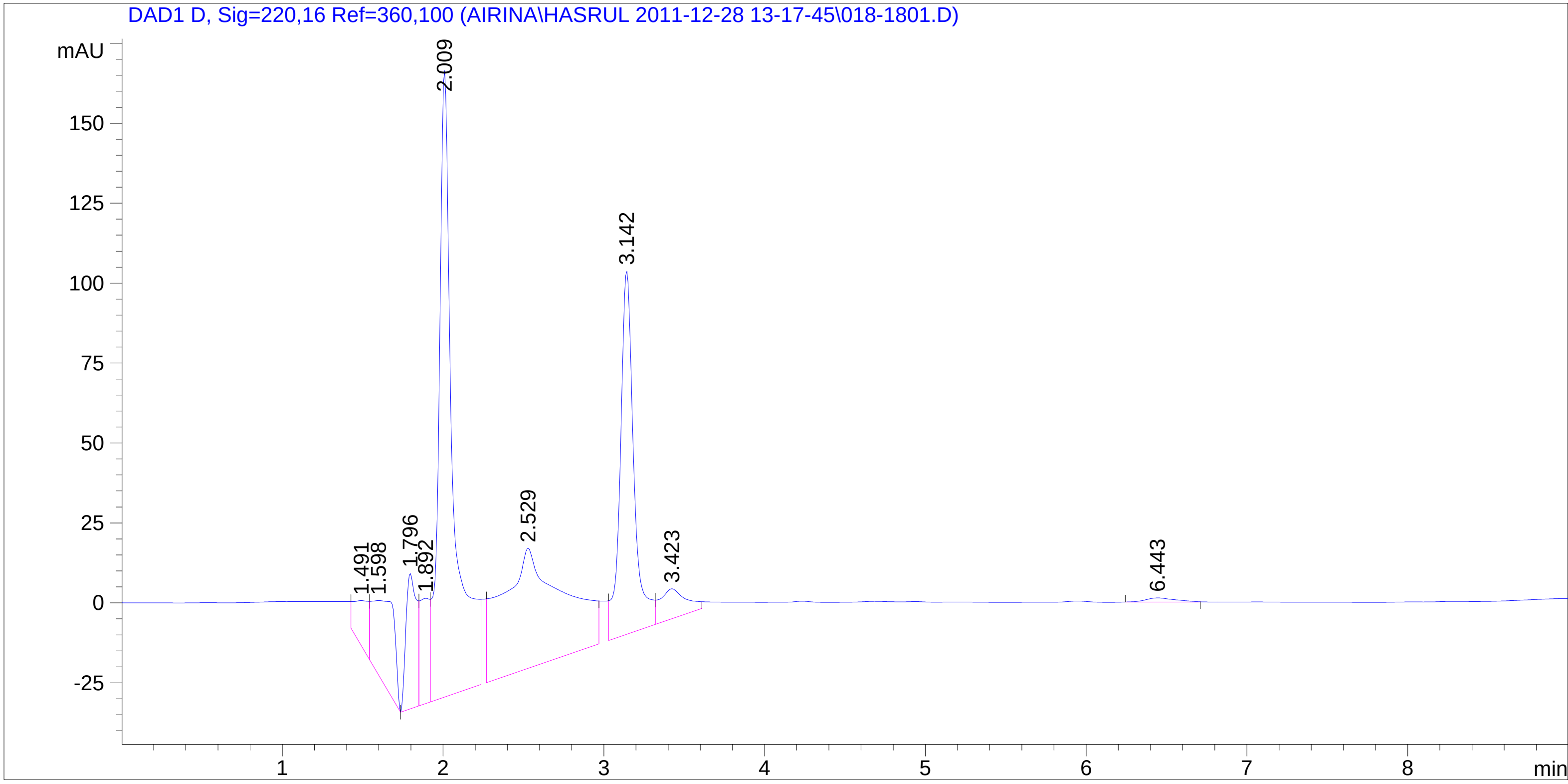

    Signal 1: DAD1 D, Sig=220,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1   1.489 BV    0.0833   99.16698   16.69921   4.3035
       2   1.589 VV    0.1416  260.21692   23.79832  11.2924
       3   1.796 VV    0.0668  181.78181   40.14032   7.8886
       4   1.893 VV    0.0600  116.24287   27.10043   5.0445
       5   2.010 VB    0.0777  958.85223  175.71098  41.6105
       6   2.532 BB    0.0691   50.64273   11.12875   2.1977
       7   3.147 BV    0.0755  566.24554  114.88152  24.5729
       8   3.432 VB    0.1083   29.22865    4.04587   1.2684
       9   6.444 BB    0.1498   13.13719    1.32304   0.5701
      10  11.100 BB    0.2544   28.83922    1.73077   1.2515

    Totals :                  2304.35415  416.55922
```

```
Data File C:\CHEM32\1\DATA\AIRINA\HASRUL 2011-12-28 13-17-45\018-1801.D
Sample Name: C330

    =====================================================================
    Acq. Operator   : airina                          Seq. Line :  18
    Acq. Instrument : Instrument 1                     Location : Vial 18
    Injection Date  : 12/28/2011 5:20:20 PM                 Inj :   1
                                                     Inj Volume : 10 µl
    Acq. Method     : C:\CHEM32\1\DATA\AIRINA\HASRUL 2011-12-28 13-17-45\AIRINA.M
    Last changed    : 12/28/2011 5:08:23 PM by airina
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\AIRINA.M
    Last changed    : 12/28/2011 11:57:31 AM by AEDLAN
```



```
    =====================================================================
                             Area Percent Report
    =====================================================================

    Sorted By             :      Signal
    Multiplier:                   :      1.0000
    Dilution:                     :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 D, Sig=220,16 Ref=360,100

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1   1.491 BV    0.0907   92.41653   14.06520   2.4981
       2   1.598 VV    0.1430  251.84293   23.12757   6.8074
       3   1.796 VV    0.0680  196.18462   42.36884   5.3030
       4   1.892 VV    0.0611  138.36644   32.90869   3.7401
       5   2.009 VB    0.0892 1230.14453  196.01761  33.2513
       6   2.529 BB    0.3267  993.30493   37.53702  26.8494
       7   3.142 BV    0.0872  673.49615  113.59489  18.2049
       8   3.423 VB    0.1553  106.75388    9.34479   2.8856
       9   6.443 BB    0.1860   17.02565    1.30704   0.4602

    Totals :                  3699.53566  470.27165
```