CERTIFICATION OF APPROVAL

Adsorption Isotherm Measurement and Correlation of Toluene and n-Hexane on Activated Carbon in an Aqueous Solution

by

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

The number of hazardous waste disposals reported has increased in recent years due to improper management of chemical generated by chemical and petrochemical industries. Volatile organic compounds are one of the major pollutants to the environment. Two of the volatile organics compounds selected for this study are toluene and n-hexane are The adsorption measurement in aqueous solutions has been carried out by using batch system at 35°C, 55°C and 65°C with the range of initial concentration between 10 to 200ppm. There are three types of activated carbon that have been used, which are Granular Activated Carbon (GAC) 2.5mm, Granular Activated Carbon 0.25mm, and Powder Activated Carbon.

The objectives of this study are to determine the adsorption isotherms of toluene and n-hexane on activated carbon through the adsorption process, to investigate the effect of temperature on the adsorption capacity of toluene and n-hexane, and to model the experimental adsorption isotherm data by using the established adsorption isotherm equations on activated carbon.

The equilibrium concentrations have been analyzed using UV-Vis Spectrophotometer and Gas Chromatography with Purge and Trap after the solutions were adsorbed for 24 hours.

The toluene adsorption isotherm has the S-shaped form and of type V isotherm based on the classification of Brunaeur, Deming, Deming and Teller (BDDT). Among the three temperature conditions, it is found that the adsorption favors the lowest temperature (35°C). This indicates that adsorption process is exothermic, lower the temperature will shift the adsorption equilibrium to adsorption rather than desorption. GAC 2.5 mm is found to have the highest adsorption capacity among the others. It is impossible to carry out the experiment with n-hexane due to its high volatility. The amount of n-hexane is considered negligible in aqueous solution and adsorption process does not require.

Freundlich isotherm is the most popular model which is widely used in the correlation of liquid adsorption. Sips isotherm which is the combination between Langmuir and Freundlich equation is an alternative model. However, the techniques were not successful with toluene isotherm measurement.

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INTRODUCTION

1.1 BACKGROUND OF STUDY

Water is needed for all life on earth. It may seem that we have it in abundance with two thirds of the planet covered by oceans, but unfortunately, it is not the quantity but quality that counts. Especially in densely populated or industrial areas the quality of water can become a problem. These areas have a high demand and produce large amounts of wastewater. Beyond a certain point the natural occurring purification processes are no longer sufficient and ground water quality will start to deteriorate, causing both environmental and economical problems. With an ever-increasing world population and industrialization, these problems will get bigger in the future. One technological solution is the utilization of adsorption process using activated carbon in the wastewater treatment facilities. This is where adsorption comes into play.

Public has raised a significant concern about the severe damage to the environment which is caused by improper management of chemical generated by the chemical and petrochemical industry. The water source and many other natural resources have been polluted, causing the imbalance to the living organisms and ecosystems. Toluene and n-hexane are two components classified as hazardous waste. There is a public concern that these two components may also be released as the effluent from the chemical industries which pollutes the river and other water sources.

Toluene can enter the environment through paints, paints thinner, adhesives, finger nails polish and gasoline. Toluene enters surface water and groundwater (wells) from spills of solvents and petroleum products as well as from leaking underground storage tanks at gasoline stations and other facilities. Leaking underground storage tanks also contaminate the soil with toluene and other petroleum-product components.

n-Hexane is the product from crude oil. Because n-hexane is a volatile compound, it is not stored or concentrated in plants or animals. However, if n-hexane spills or it is discharged to the ground, it will evaporate into the air and pollute the environment. (http://www.osha.gov/SLTC/healthguidelines/n-hexane)

Various methods have been applied in removing volatile organic compounds (VOCs), including adsorption process, membrane process, and biological process. However, adsorption has gained favor recently due to their efficiency in removing aromatics compound and hydrocarbon. It also produces high quality products and economically feasible. (Choy et. al. 1997)

Among the adsorbents, activated carbon has been proved to be one of the most effective adsorbent used in adsorption process. The application of activated carbon in adsorption has been suggested as a promising technique in controlling the organic pollutants. This method with efficiency up to 95% is effective for solvent recovery requires a relatively low capital investment (Chiang et al., 2001). Activated carbons are carbonaceous materials of highly developed porous structure and high specific surface area. Properties of activated carbon such as their surface area, microporous structure and surface chemistry can be tailored, making them versatile materials for a range of separation applications (Banasal et al., 1988). These applications include the removal of contaminants from water and gas streams, and as catalyst support (Banasal et al., 1988)

In liquid phase adsorption, it established that the adsorption capacity of an activated carbon depends on the following factors. Based on Nouri et al., 2004, the adsorption capacity depends on the nature of the adsorbent such as its pore structure ash content and functional groups. Secondly, it depends on the nature of the adsorbate (its pK_a, functionality, polarity, molecular weight, and size) and finally on the solution conditions, referring to its pH, ionic strength and the adsorbate concentration.

1.1.1 General definitions of adsorption

Based on Geankoplis (1993), adsorption is the process in which one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished.

There are two types of adsorption. Physical Adsorption is caused mainly by Van Der Waals and electrostatic force between the adsorbate molecules and the atoms which compose the adsorbent surface. In effect, the resulting adsorption is like condensation, which is exothermic and thus is accompanied by a release of heat. In contrast, chemical adsorption is adsorption which results from a chemical bond formation between the adsorbent and adsorbate in a monolayer on the surface.

Adsorption from liquid is a more difficult phenomenon to measure experimentally or describe (Seader, 1998).When the fluid is a liquid, no simple procedure for determining the extent of adsorption from a pure liquid exists. As a result, experiments are usually conducted using liquid mixtures, including dilute solutions.

1.1.2 Absorbent characteristics

Many adsorbents have been developed for a wide range of separations. Normally, adsorbent has various shapes, including small pellets, beads, or granules. A particle of adsorbent has a very porous structure with many fine pores and pore volume up to 50% of the total volume. The adsorption often occurs as a monolayer on the surface of the fine pores.

Based on Yang (2003), among a various types of adsorbent, activated carbon is the universal standard for purification and removal of trace organic contaminants from liquid and vapor streams. Activated carbon is non-polar adsorbent. Its "hydrophobic" property makes activated carbon have more affinity with oil than water. The raw material for activated carbon are carbonaceous matters such as wood, peat, coals, petroleum coke, bones, coconut shell, and fruit nuts. Through a complex process of devolatization and activation, these materials develop a unique internal pore structure which makes them suitable for a variety of filtration applications.

In water treatment, activated carbon has been widely used because of large surface area, from 300 up to 2500 m^2/g as measured by the BET method, which is the largest among all adsorbents. A majority of the pore volume is from pores near or larger than 30Å in diameter in liquid-phase carbon whereas the pores for gas-phase carbon are mostly from 10Å to 25Å. The need for larger pores in liquid-phase carbons is due to the large size of many dissolved adsorbate, and the slower diffusion in liquid than in gas for molecules of the same size. Activated carbons used in this project are granular activated carbon (GAC) and powder activated carbon (PAC).

Table 1.1: Pore sizes in typical activated carbons (Adapted from Ruthven, 1984, p.8)

	Micropores	Mesopores or transitional pores	Macropores
Diameter (nm)	<2	2-50	>50
Pore volume (cm^3/g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area (m^2/g)	100-1000	10-100	0.5-2
(Particle density 0.6-0.9 g/cm^3;porosity 0.4-0.6)			

Granular activated carbon (GAC) is either in the form of crushed granules (coal or shell) or in the palletized form prepared by granulation of pulverized powders using binders such as coal tar pitch. GAC is widely used in water treatment for example to remove pesticides from potable water. Size of the granules differs depending on the application. In the case of liquid adsorption, intraparticle diffusion becomes the rate determining step.

Powder activated carbons (PAC) in most cases are produced from wood in the form of sawdust. The average size of PAC is in the range of 15 to 25 μm which assures that intraparticle diffusion is not the rate limiting step. In the use of PAC in water phase, surface charge of the carbon powder becomes an important factor since it affects the ease of separation of PAC from the bulk fluid after adsorption. When PAC is used, not only is its adsorbability utilized but its surface charge may also cooperate as a coagulant for colloidal fractions in the liquid phase. Therefore, regeneration of PAC is difficult.

1.1.3 Factors affecting adsorption process

There are many factors which affect the adsorption process (http://www-ec.njit.edu/~hsieh/ene670/adsorptn.html). Understanding the factors that affect the adsorption process is important in determining the optimum requirements for the process.

Nature of the adsorbate is an important factor which affects the adsorption process. Adsorption of a solute is inversely proportional to its solubility in the solvent. The greater the solubility is, the stronger the solute-solvent bond and the smaller the extent of adsorption (Lundelius's rule). In general, the solubility of any organic compound in water decreases with increasing chain length, because the compound becomes more hydrocarbon-like as the number of carbon atoms becomes greater (Traube's rule)

Molecular sizes -If the rate is controlled by intraparticle transport, the reaction generally will proceed more rapidly to the smaller adsorbate molecule, within a given class of compound.

Charge (Ionic species) -As long as the compounds are structurally simple, adsorption is at minimum for the charged species and at a maximum for the neutral species. As compounds become more complex, the effect of ionization becomes less important. Decreasing adsorption with increasing ionization has been observed for many organic acids. Adsorption of propionic acid on carbon decreases markedly with increasing pH to a minimum in the range pH 3.5 to 5.5 (succinic acid to a min. in the range pH 4.0 and 7.0, caproic acid between pH 4.8 and 7.5).

pH - Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influence by the pH of the solution. In general, adsorption of typical organic pollutant from water is increased with decreasing pH.

Temperature -Adsorption reaction are normally exothermic, thus the extent of adsorption generally increases with decreasing temperature.

Adsorption of mixed solutes -The degree of mutual inhibition of competing adsorbates should be related to the relative sizes of the molecules being adsorbed, to the relative adsorptive affinities, and to the relative concentrations of solutes.

Nature of the adsorbent -The physicochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption. Commercial carbons can be prepared from a variety of raw materials, including wood, lignite, coal, petroleum residues, and nut shells. The raw material is generally activated in an atmosphere of CO_2, CO, O_2, H_2O, vapor, air, or other selected gases, at a temperature between 300 and 100°C often followed by quenching in air or water. The most characteristic physical property of activated carbon is its extremely large surface area, which is composed mainly or surfaces bordering inner pore spaces.

1.2 PROBLEM STATEMENT

Toluene and n-hexane can affect central nervous system including headache, dizziness, loss of balance, respiratory failure and even death. In the Unites States the Environmental Protection Agency (EPA) has identified 1,350 hazardous waste sites as the most serious in the nation. Toluene and n-hexane have been found in at least 851 and 60 of the sites, respectively. (http://www.osha.gov/SLTC/healthguidelines)

Because of the severity of toluene and n-hexane to human health, the Occupational Safety and Health Administrator (OSHA) has set a limit of 100 ppm of toluene in the workplace, average of an 8-hour exposure per day over 40-hour work per week. OSHA has also set a limit of 500 ppm for n-hexane in workplace air. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a Threshold Limit Value (TLV) of 50 ppm.

The severity of toluene and n-hexane to environment and health has been identified. However, there are very scarce published literatures found relating the study of adsorption process for these two chemicals, especially for n-hexane, which are very common chemicals in industry usage. This is due to the fact that adsorption from aqueous solution is a difficult phenomenon to be measured experimentally. The concern of industrial waste disposal to the environment has led to the investigation and study of separation and treatment the wastes before discharging them.

In adsorption, temperature and adsorbent type are among the most important parameters which affect the adsorption capacity and effectiveness. Amount adsorbed is usually decreased with increase in temperature. Therefore, studying the effect of temperature on adsorption is important to determine the optimum operating temperature for the adsorption process. Moreover, adsorbents are characterized by their surface area and distribution of pore volume. Each type of adsorbent is unique in terms of its adsorption capacity. As a result, different types of adsorbent have different adsorption capacity although they are used at the same temperature.

Models or correlations for adsorption are crucial to the design of adsorptive separation processes. They could be capable of predicting the equilibrium amount adsorbed from the isotherms within given ranges of operating temperature and concentration.

In conclusion, the study of adsorption isotherm of toluene and n-hexane using activated carbon is very useful because through the isotherm, the adsorption capacity, i.e. the effectiveness of pollutants removal by selected adsorbents, can be identified. This information is very important in choosing the most suitable type of activated carbon to be employed in any treatment process in industry. The wealth knowledge of the effect of adsorbent's shapes and temperature to adsorption is also significant to determine the optimum operating condition of a certain process. In addition to adsorption isotherm measurement, developing a suitable model to represent experimental data in mathematical form gives a good prediction in the adsorption design process.

1.3 OBJECTIVES

The objectives of this project are:

- To determine the adsorption isotherms of toluene and n-hexane on activated carbon through the adsorption process
- To investigate the effect of temperature on the adsorption capacity of toluene and n-hexane
- To model the experimental adsorption isotherm data by using the established adsorption isotherm equations

1.4 SCOPE OF STUDY

The project focuses on the determination of the toluene and n-hexane adsorption isotherms. The adsorption isotherm shows the equilibrium between the concentrations of a solute (toluene and n-hexane) in the fluid phase and its concentration in the solid adsorbent. The adsorption isotherms which also show the adsorption capacity of a particular adsorbent in an adsorption process will be evaluated in three different temperatures, 35°C, 55°C and 65°C. There are three types of activated carbon that have been use which are granular activated carbon of diameter sizes 2.5 and 0.25mm and powder activated carbon. The solutions are prepared with different initial concentrations. The maximum concentration of the solution depends upon the solubility of that chemical in water. The concentrations of toluene solutions are 10, 25, 50, 100, and 200ppm whereas the concentrations of n-hexane solutions are ranging from 20 to 120 ppm. From the adsorption measurement, the effect of temperature on adsorption can be determined and the most suitable absorbent is chosen.

There are many adsorption correlations that describe the adsorption process. Among them, Freundlich is the most widely used adsorption isotherm model for aqueous solution. In this study, the adsorption measurements are used to fit into the Freundlich model. Sips isotherm, which is the combination between Langmuir and Freundlich equations, is an alternative model. The goodness of fit between the experimental data and the model is analyzed by using graphical method through analyzing the parity plots.

the micropores. Type I is of the classical Langmuir form. This type of isotherm is usually observed at sufficient low concentrations, and will revert to type I to V at higher concentrations. (Azmi, 1995)

Type II isotherms are most frequently encountered when adsorption occurs on nonporous powders or on powder with pore diameters larger than micropores. The inflection point or knee of isotherm usually occurs near the completion of the first adsorbed monolayer and with increasing relative pressure or concentration, second and higher layers are completed until at saturation the number of adsorbed layers become infinite (Lowell et al., 1991)

Type III behavior corresponds to the situation where the adsorbate-surface interaction is weaker then the sorbate-sorbate interaction, for instance, in the adsorption of water vapor on a carbon surface.

Type IV isotherms can be obtained when characterized by the condensation hysteresis. They occur on porous adsorbents which possessed pores in the radius range of approximately 15-1000 Å. The slope increases at higher elevated concentrations indicated an increased uptake of adsorbate as the pores are being filled. The knee of the type IV isotherm generally occurs near the completion of the first monolayer (Lowell et al., 1991)

Type V isotherms result from small adsorbate-adsorbent interaction. Type V isotherms are also associated with pores in the same range as those of type IV isotherm. (Lowell et al., 1991)

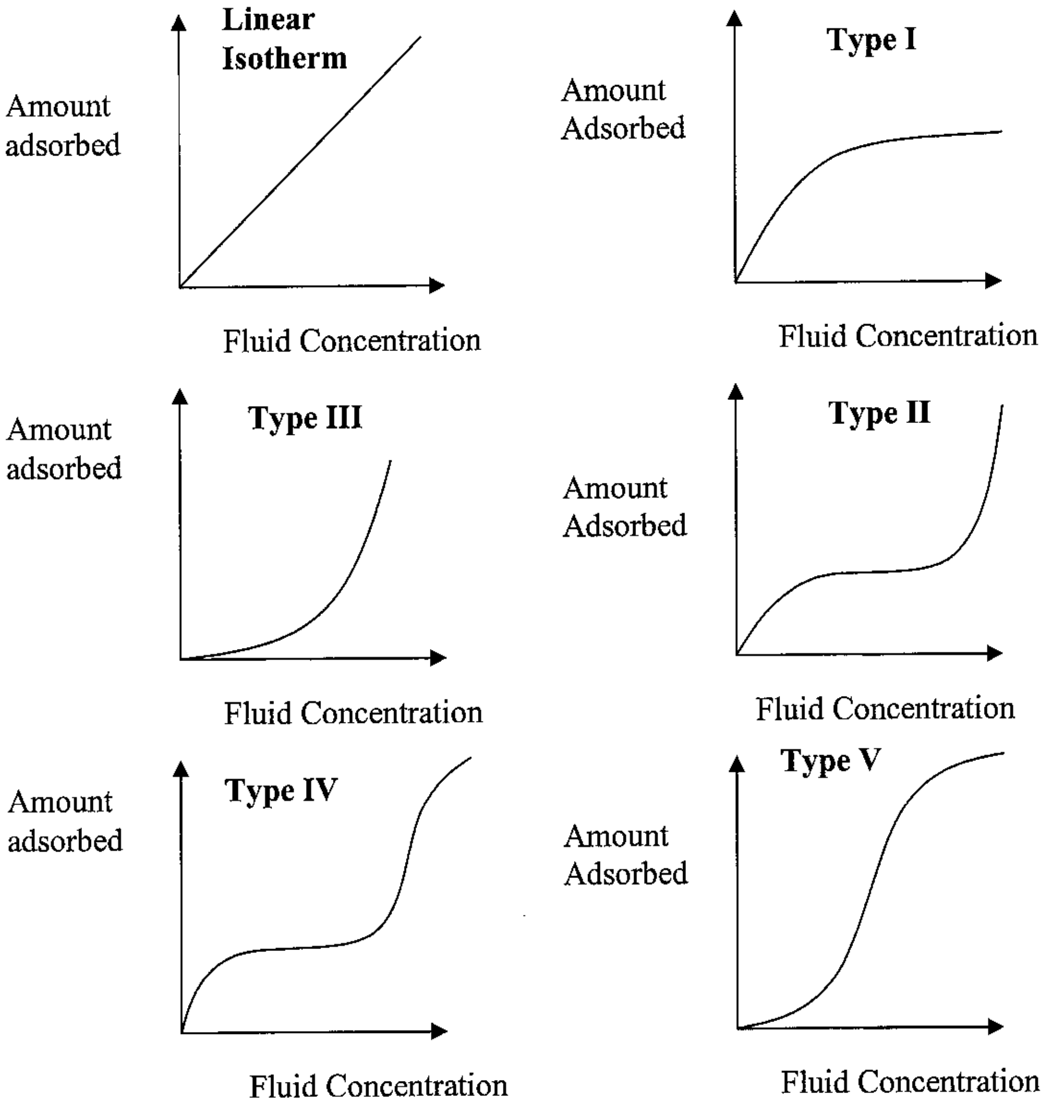

Figure 2.1: The six types of equilibrium isotherms based on BDDT classifications (Basmadjian, 1997)

Based on Yang (1987), the numerous isotherm models which have been discussed so far are based on three different approaches.

Langmuir in 1918 generated his approach called Langmuir approach. It is originally a kinetic one, assuming the adsorption system is in dynamic equilibrium, where the rate of evaporation is equal to that of condensation. The Langmuir isotherm remains the most useful for data correlation in separation processes.

The Gibbs approach employs the Gibbs adsorption isotherm which is $-Ad\pi + nd\mu=0$, where π is the spreading pressure, A is the surface area, n is the number of moles and μ is the chemical potential.

The potential theory was first formalized by Polanyi in 1914 (Yang, 1987). Based on Polanyi, there is a relationship between the potential field,ε and the volume above the surface, W. The forces operative in adsorption are assumed to be temperature-independent dispersion forces. That is the reason that the potential theory is mostly applied to activated carbon adsorption.

2.2 LIQUID-PHASE ADSORPTION OF TOLUENE AND N-HEXANE

When a liquid mixture is brought into contact with a microporous solid, adsorption of certain components in the mixture takes place on the internal surface of the solid. If a liquid is a homogeneous binary mixture, it is often differentiate between solute and solvent. In liquid adsorption, it is assumed that the change in composition of the bulk liquid in contact with the porous solid structure is due to entirely to adsorption of the solute. From Kipling (1965), if experimental data are obtained over the entire concentration range, the distinction between solute and solvent is arbitrary and the resulting adsorption isotherms can exhibit curious shapes that are unlike those obtained from pure gases or gas mixtures.

Seader (1998) states that when data for the binary mixture are only available in the dilute region, the amount of adsorption of the solvent maybe constant and all changes in the total amount adsorbed are due to just the solute. The adsorption isotherms are of the forms which are shown in Figure 2.2.

Liquid-phase adsorption includes a variety of substances as adsorbates: organic compounds, inorganic material, protein and other polymeric substances. Applications of liquid adsorption include removal of organic compounds from water or organic solutions, colored impurities from organics, and various fermentation products from fermentor effluents.

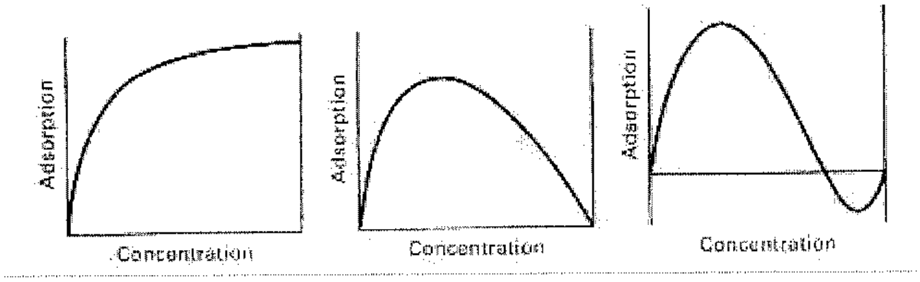

Figure 2.2: Representative isotherms of concentration change for liquid adsorption (Seader, 1998)

The adsorption process is an exothermal nature. With increasing temperature and decreasing adsorbate concentration the adsorption capacity decreases. Degel et al., 1990 has shown his study on adsorption and desorption of different types of solvent using activated carbon. The adsorption measurements are plotted using Freundlich isotherm, which is a very popular isotherm used in description of adsorption of organics from aqueous streams onto activated carbon.

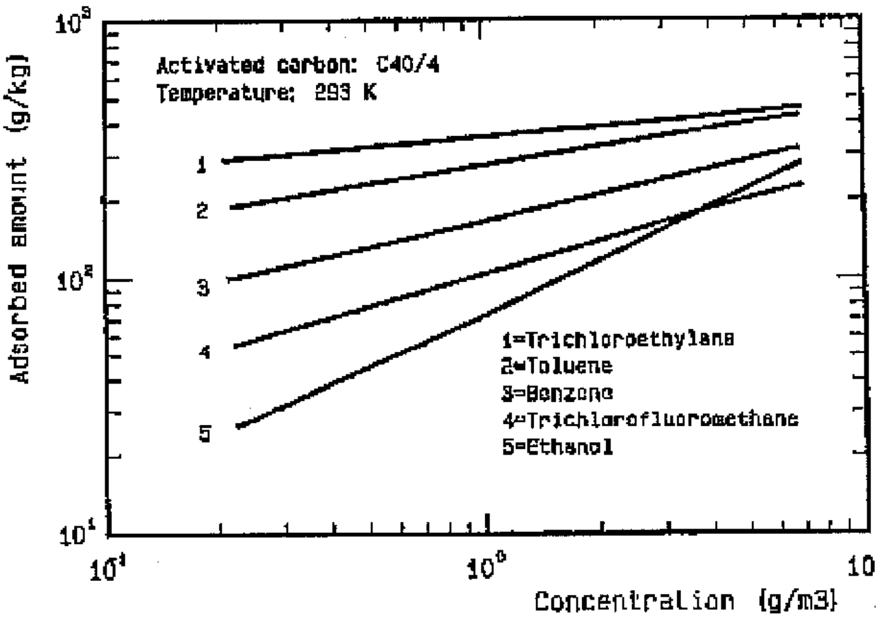

Figure 2.3: Adsorption isotherm of different solvents (Degel et al., 1990)

Adsorption process for these solvents is called physical adsorption process which can form multilayers of adsorbate molecules on top of another due to Van der Waals forces. It is shown that various solvents are adsorbed differently depending on the strength of the interaction forces between adsorbate and adsorbent.

Chatzopoulos et al. (1993) have studied the adsorption of toluene on GAC particles. They were able to fit experiments for variety of initial toluene concentrations and other experimental conditions.

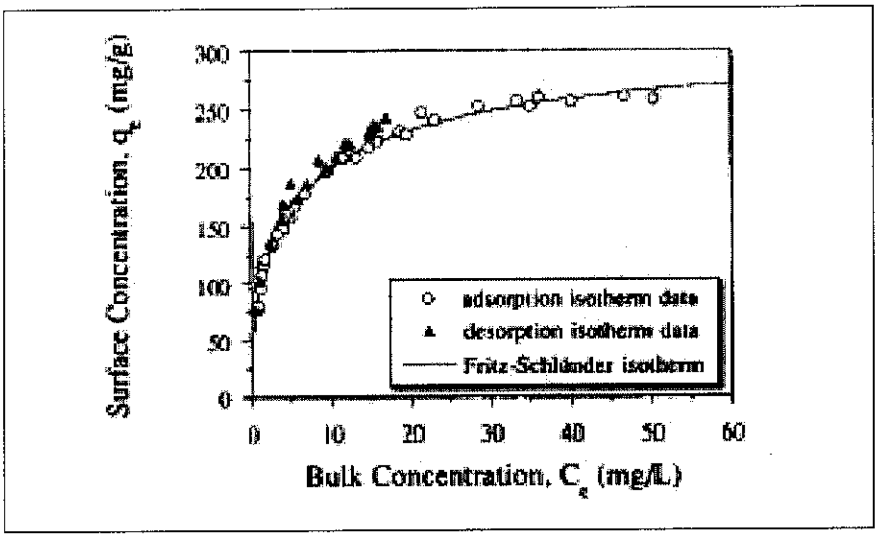

Figure 2.4: Adsorption and desorption isotherms for Toluene/F300 activated carbon system at 25°C (Chatzopoulos et al., 1993)

There are very scarce published literatures on n-hexane adsorption isotherm in aqueous system as most of the studies were based on gas adsorption.

2.3 CHARACTERIZATION OF ACTIVATED CARBON

Adsorption takes place at the interface boundary. The surface area is one important factor in the adsorption process. In general, the bigger the surface area is, the higher the adsorption capacity will be. However, that surface area has to be available within the activated carbon. At low concentration, the surface area in the smallest pores into which the solvent can enter is the most efficient one. With higher concentrations the larger pores become more efficient. With higher concentrations, capillary condensation will take place within the pores and the total micropore volume will become the limiting factor. These molecules are retained at the surface in the liquid state, because of intermolecular or Van der Waals forces. Figure 2.4 shows the relationship between maximum effective pore size and concentration for the adsorption of toluene according to the Kelvin theory.

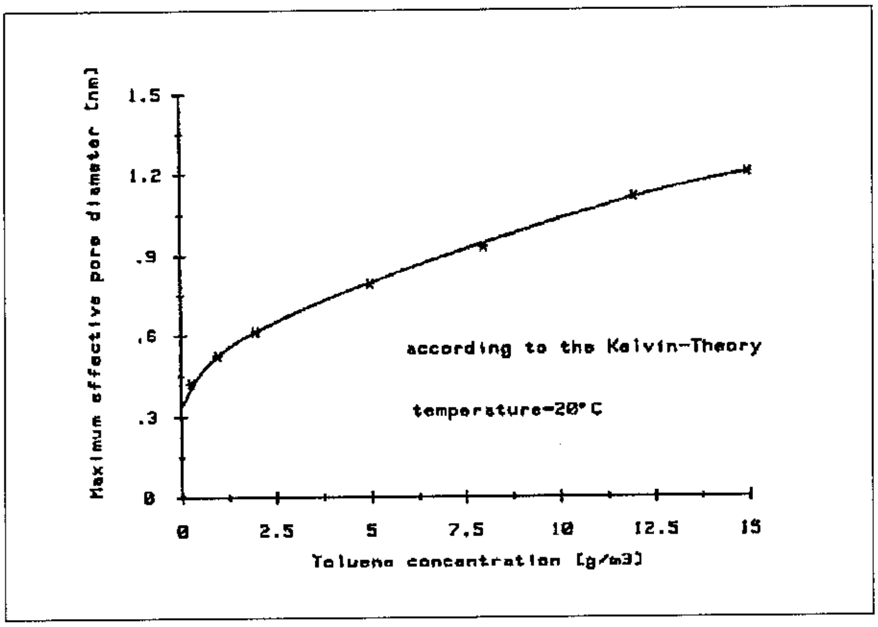

Figure 2.5: Relationship between pore size and toluene concentration (Degel et al., 1990)

Degel et al., 1990 also proved that one of the factors affecting the adsorption capacity of a given activated carbon is its surface area and its pore volume distribution. Through the study of toluene adsorption isotherms using three different types of activated carbon, which are large pores, medium pores and small pores predominant, Degel et al., 1990 found that these adsorption lines intersect at different concentrations depending on the pore size distribution of the activated carbon.

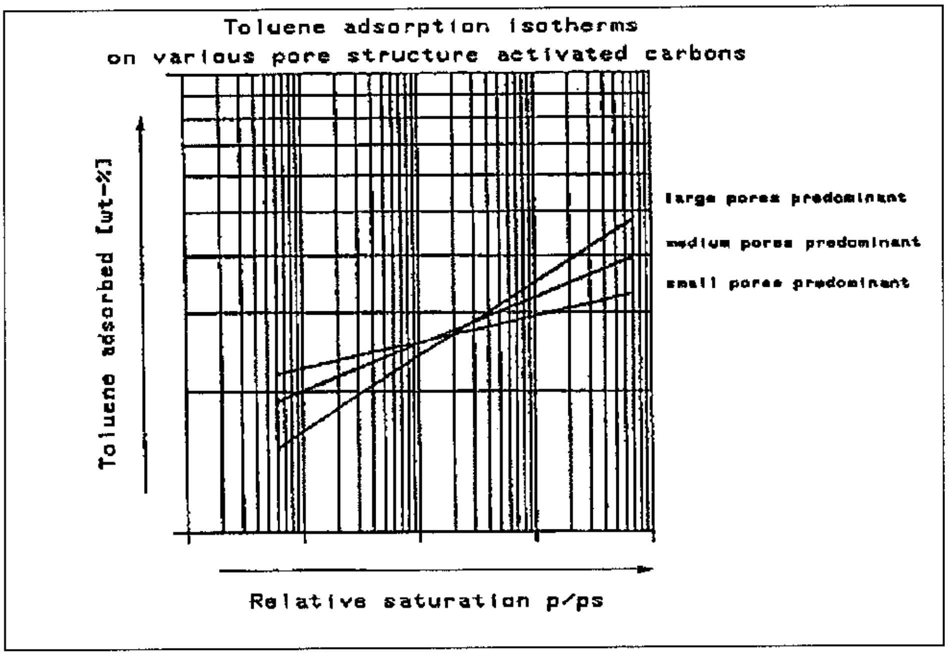

Figure 2.6: Idealized Toluene adsorption isotherm (Degel et al., 1990)

2.4 HEALTH HAZARD INFORMATION OF TOLUENE AND N-HEXANE

2.4.1 Health Hazard Information of Toluene

Toluene is a central nervous system depressant and an irritant of the eyes, mucous membranes, and skin in humans. In contact with the eyes, toluene causes reversible corneal injury; prolonged skin contact causes defatting and dermatitis (Hathaway, 1991). Volunteers exposed to a 200ppm concentration of toluene for 8 hours experienced mild upper respiratory tract irritation; at 400ppm, subjects experienced mild eye irritation and tearing and laughed inappropriately; at 600ppm, the volunteers developed slight nausea and lassitude; and at 800ppm, they experienced drowsiness, incoordination, and a metallic taste in the mouth (Clayton, 1981). Some volunteers exposed to a 100ppm concentration of toluene for 6 hours reported eye and nose irritation, and some reported headache and dizziness (Hathaway, 1991). An employee exposed to very high (concentration not specified) levels of toluene for 18 hours collapsed and lost consciousness; this individual showed clinical signs of liver and kidney damage but later recovered (Clayton, 1981). Painters exposed repeatedly to toluene at concentrations between 100 and 1100ppm developed enlarged livers, macrocytosis, a moderate decrease in erythrocyte count, and lymphocytosis, but showed no signs of leucopenia (ACGIH, 1986). Studies of workers chronically exposed to toluene or mixtures of solvents containing toluene have shown minor abnormalities in neuropsychological test results and decrements in performance, although a recent study of rotogravure printers exposed to an average toluene concentration of 117ppm for approximately 22 years detected no significant neurophysiologic or psychological differences compared with these parameters in controls (Hathaway, 1991)

2.4.2 Health Hazard Information of n-Hexane

Based on Sittig (1991), exposure to n-hexane can occur through inhalation, ingestion, and eye and skin contact.

n-Hexane is a narcotic agent; an irritant to the eyes, upper respiratory tract, and skin; and a neurotoxin. Exposure of humans to 5,000ppm n-hexane for 10 minutes causes marked vertigo; exposure to 1,500ppm results in headache and slight nausea (Hathaway et al., 1991). In industrial settings, exposure to levels exceeding 1,000ppm has been reported to cause mild symptoms of narcosis (Hathaway et al., 1991). Eye and upper respiratory tract irritation has been reported to occur in humans exposed to 880ppm n-hexane for 15 minutes (Clayton, 1982). Dermal contact with n-hexane results in immediate irritation characterized by erythema and hyperemia; exposed subjects developed blisters 5 hours following dermal exposure to n-hexane (Hathaway et al. 1991). The neuropathic toxicity of n-hexane in humans is well documented; cases of polyneuropathy have typically occurred in humans chronically exposed to levels of n-hexane ranging from 400 to 600ppm, with occasional exposures up to 2,500ppm (Hathaway et al., 1991). Distal symmetrical motor weakness is common in most cases; however, in severely affected individuals, motor weakness may extend to the pelvic and high musculature .Nerve biopsies in affected individuals show swelling of the nerve and thinning of the myelin sheath. Functional neurological disturbances usually progress for a few months after termination of exposure. Although recovery is expected to occur within a year, clinical polyneuropathy has been reported in some cases to remain after 2 years (Hathaway et al., 1991). Blurred vision, restricted visual field, and optic nerve atrophy has been reported to occur in association with n-hexane-induced polyneuropathy. Twelve of 15 individuals working with hexane for 12 years were found to have abnormal color discrimination (Grant, 1986)

CHAPTER 3

THEORY

Many theories and correlations have been developed to interpret different types of isotherms, but very few are appropriate over the temperature and pressure (or concentration) range found in most process situations. The correlations vary from those which are totally empirical to ones that have some theoretical basis. This chapter focuses on the adsorption equilibrium and some adsorption equilibrium models that are normally used.

3.1 ADSORPTION EQUILIBRIUM

In practical operations, maximum capacity of adsorbent cannot be fully utilized because of mass transfer effects involved in actual fluid-solid contacting processes. In order to estimate practical or dynamic adsorption capacity, it is important to have information on adsorption equilibrium.

According to Suzuki (1989), when an adsorbent is in contact with the surrounding fluid of a certain composition, adsorption takes place and after a sufficiently long time, the adsorbent and the surrounding fluid reach equilibrium. Adsorption isotherm is important to describe how solutes interact with adsorbents. It is the equilibrium relation between the quantity of the adsorbed material, q and the pressure or concentration (C) in the bulk fluid phase at constant temperature T.

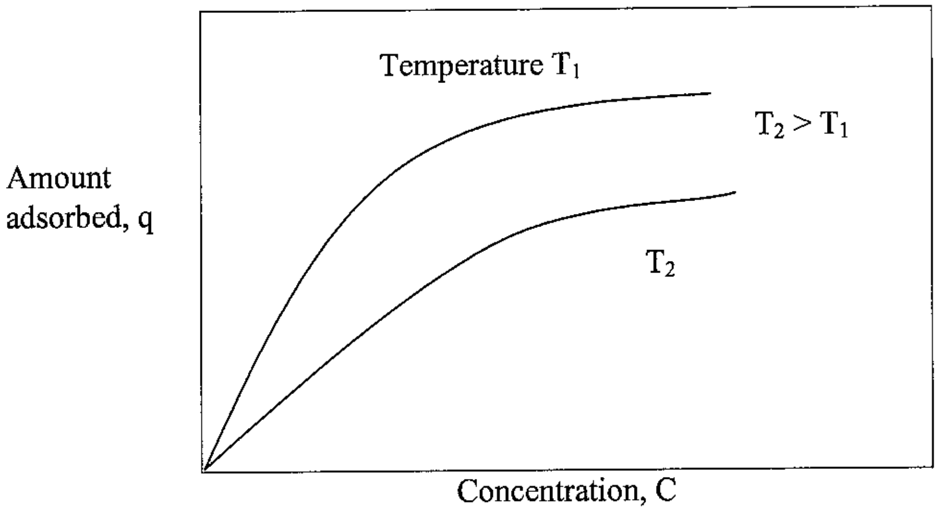

Figure 3.1: Adsorption Isotherm

The amount of adsorbates adsorbed on activated carbon is calculated according to the following equation:

$$q_e = \frac{V(C_o - C_e)}{W}$$

where C_0 and C_e are initial and equilibrium liquid concentration (mg/l), respectively

V is the volume of solution (l)

W is the weight of adsorbents (g)

3.2 DETERMINATION OF ADSORPTION CORRELATIONS

Adsorption isotherms are described in many mathematical forms, some of which are based on simplified physical pictures of adsorption and desorption, while the other are purely empirical and correlate the experimental data in simple equations. Various isotherm expressions for liquid phase adsorption are

Linear isotherm $q = Kc$ [3.1]

Langmuir isotherm $\frac{q}{q_s} = \frac{bc}{1+bc}$ [3.2]

Freundlich isotherm $q = bc^{1/n}$ [3.3]

Toth isotherm $\frac{q}{q_s} = \frac{c}{(b' + c^t)^{1/t}}$ [3.4]

Langmuir-Freundlich isotherm $\frac{q}{q_s} = \frac{bc^{1/n}}{1 + bc^{1/n}}$ [3.5]

Based on Do (1998), the Freundlich equation is very popularly used in description of adsorption of organics from aqueous streams onto activated carbon.

Langmuir Isotherm

For microporous adsorbents the isotherm can often be represented, at least, approximately, by the ideal Langmuir model (Ruthven, 1994)

$$\frac{q}{q_s} = \frac{bc}{1 + bc} \quad [3.6]$$

where q is the amount adsorbed; c is the equilibrium concentration;

b is an equilibrium constant that is directly related to the Henry constant ($K = bq_s$). Since adsorption is exothermic, it follows that b will decrease with temperature so at higher temperature the isotherms become less sharply curved. This form maybe derived from the simple mass action considerations by considering the balance between occupied and unoccupied sites.

Although there are relatively few systems that conform accurately to the Langmuir model, there are many systems that show approximately conformity, and this model has further advantage that it reduces to Henry's law in the low-concentration limit, which is a requirement for thermodynamic consistency in any physical adsorption system.

Freundlich Isotherm

Based on Ruthven (1994), an alternative expression that is sometimes used to present a favorable (type I) isotherm is the Freundlich equation.

$$q = bc^{1/n} \qquad \text{where } n > 1.0 \tag{3.7}$$

This form of expression can be derived from plausible theoretical arguments based on a distribution of affinity among the surface adsorption sites, but it is probably better regarded simply as an empirical expression.

Both the Freundlich and Langmuir equations contain two parameters, but, unlike the Langmuir expression, the Freundlich form does not reduce to Henry's law in the low concentration limit.

Langmuir-Freundlich isotherm (Sips isotherm)

Based on Ruthven (1994), Sipps suggested that the Langmuir and Freundlich equations can be combined,

$$\frac{q}{q_s} = \frac{bc^{1/n}}{1+bc^{1/n}}$$

where b and 1/n are empirical constants which are function of temperature.

This isotherm can be derived from the Langmuir isotherm by assuming each sorbate molecule occupies n sites (Yang, 1987). It can also be considered as the Langmuir isotherm on nonuniform surfaces.

CHAPTER 4

METHODOLOGY AND EXPERIMENTAL PROCEDURE

This chapter provides the detailed description of the experimental procedure including the apparatus required and the method of doing analysis. The experiment involves batch adsorption process for toluene and n-hexane on activated carbon. The adsorption isotherm measurements have been carried on for two adsorbates at three different temperatures (33°C, 55°C and 65°C) using three different types of adsorbents. Two adsorbates are toluene and n-hexane. Three adsorbents are GAC 2.5mm, GAC 0.25mm and PAC.

4.1 APPARATUS, EQUIPMENT AND RAW MATERIALS

4.1.1 Apparatus and equipment

For the apparatus and equipment used, please refer to Appendix I.

4.1.2 Adsorbates

The adsorbates that have been used in this study are toluene and n-hexane. Both are obtained from Merck Darmstadt, Germany. The properties of toluene and n-hexane are obtained form Perry's Chemical Handbook and summarized in Table 4.1.

Table 4.1: Properties on Toluene and n-Hexane (Source: Perry's Chemical Handbook)

Properties	Toluene	n-Hexane
Molecular Weight (g/mol)	92.14	86.18
Density (kg/m3)	866	659
Boiling Point (°C)	110.8	69
Solubility (g/L)	0.5	0.14

Toluene

Toluene is a clear, colourless liquid with a benzene-like odour. It is a flammable liquid and vapor. The liquid can accumulate static charge by flow or agitation. The vapour is heavier than air and may spread long distances and distant ignition and flashback are possible. Liquid can float on water and may travel to distant locations and/or spread fire. Toluene can decompose at high temperatures forming toxic gases.

Signs and symptoms of exposure

Toluene exposure can be classified as acute exposure and chronic exposure. For acute exposure, toluene can cause redness and inflammation of the eyes and eyelids, runny nose, scratchy throat, fatigue, weakness, incoordination, confusion, headache, dizziness, and drowsiness. For long term, the chronic exposure can be incoordination; tremors; impaired speech, vision, hearing, or memory; nausea; lack of appetite; and defatting of the skin. (http://www.osha.gov/SLTC/healthguidelines/toluene/recognition.html)

n-Hexane

n-Hexane is a colorless, volatile liquid with a mild, gasoline-like odor. Commercial n-hexane is a mixture of n-hexane isomers with a small amount of cyclopentane, pentane, and heptane isomers. Benzene may be present in concentrations ranging from one to six percent. Air odor threshold concentrations for n-hexane ranging from 65 to 130 parts per million (ppm) parts of air have been reported.

Signs and symptoms of exposure

n-Hexane can cause serious effect to health if the time and amount of exposure to n-hexane is over its exposure limit. The acute exposure can cause dizziness, confusion, nausea, headache, and irritation of the eyes, nose, throat, and skin (Hathaway et al., 1991) while the chronic exposure can cause disturbances in sensation, muscle weakness, and distal symmetric pain in the legs. Changes in vision may also be a symptom of chronic exposure to n-hexane (Hathaway et al., 1991)

4.1.3 Adsorbents

The purpose of this project is to study the adsorption process onto different types of activated carbon, including granular and powder types. The granular activated carbons (GAC) are NORIT PK 0.25-1 and Merck. The powder activated carbon is obtained from Merck.

Table 4.2: Specification of GAC NORIT PK 0.25-1 (Source: NORIT Nederland B.V)

Properties	Value
Iodine number	700
Methylene Blue Adsorption	11g/100g
Total surface area (BET)	775 m^2/g
Apparent Density	325 kg/m^3
Effective size	0.3mm
Uniformity coefficient	1.9
Ash content	15 mass- %
pH	Alkaline
Moisture (as packed)	2 mass-%

Table 4.3: Specification of GAC Merck 2.5mm (Source: Merck. Germany)

Properties	Value
Iodine number (mg/g min)	900
CTC (%min)	50
Bulk Density (gm/cc)	0.42-0.48
Ash (%max)	12-13
Moisture (%max)	5
Hardness (%min)	90
pH	6-9

Table 4.4: Specification of Powder Activated Carbon (Source: Merck. Germany)

Properties	**Value**
Moisture (%max)	5
pH	9-12
Ash (%max)	8
Iodine (mg/g min)	1000
Arsenic (mg/L max)	5

4.2 EXPERIMENTAL PROCEDURE

4.2.1 Preparation of activated carbon

The experiment began with the preparation of activated carbons. The activated carbons were washed several times with distilled water to remove dust. They were then dried in the oven at 150°C in the oven overnight. The carbons were then stored in a sealed bottle along with a silica gel to prevent the re-adsorption of moisture before use.

4.2.2 Preparation of the solutions

Both toluene and n-hexane are obtained from Merck Darmstadt, Germany. The solubility of toluene and n-hexane, which are obtained from the Perry's Chemical Engineer Handbook, are 0.5g/L and 0.14 g/L, respectively. The solubility is a very important parameter in preparing the solutions because it indicates the maximum solute that can be dissolved in water. Therefore, the solutions which are prepared with different concentrations with the maximum concentration will not exceed the solubility of the chemical. Each chemical has been prepared with different concentrations. Sample calculation is shown in the Appendix II.

4.2.3 Determination the concentration of toluene and n-hexane using UV-VIS Spectrophotometer

The water bath shaker was filled with distilled water and the temperature is set to 35°C.

100 ml of toluene was measured using 100 ml-measuring cylinder and the solution was poured into 100ml-volumetric flask. A fixed amount of 0.2g of activated carbon was added to the of 100 ml volumetric flasks with stopper. The glass-stopper flask was then placed in a water bath shaker at a speed of 120 rpm until it reached equilibrium condition, approximately 24 hours. The initial and equilibrium concentrations were analyzed by using UV-VIS Spectrophotometer. The experiment was repeated at temperature 55°C and 65°C. The experiment was then carried on with other types of activated carbon (GAC 2.5mm from Merck, GAC 0.25-1mm from Norit, and PAC)

4.2.4 Sample Analysis using UV-VIS Spectrophotometer

Before analyzing the sample, all cuvettes were cleaned using distilled water and dried to avoid contaminating the samples. In the UV probe window, the connect button was pressed to ensure there is a connection between the equipment and the software. The system is ready to use when it passes all the tests and all items in the test list are selected in green color. The 'method' button was pressed and the parameters were changed accordingly including wavelength range, scan cycle and number of samples. The wavelength of toluene and n-hexane were entered at 261.8nm and 206nm, respectively. The cuvette was filled with the sample about two third of the cuvette's height and was covered with its cap. It is important to avoid finger print on the smooth sides of the cuvette by wiping with soft tissue paper. After the cuvette was put into the chamber, 'Start' button is pressed and the data is shown on the monitor.

4.2.5 Sample Analysis using Gas Chromatography with Purge and Trap

Gas Chromatography with purge and trap is able to analyze the composition of an aqueous solution. There are three main steps involved, including purging, desorbing, and baking. At first, the equipment is at the stand-by mode. The sample is injected into the GCMS by using a syringe. The 'Start' button is pressed to begin the purging process which takes 11 minutes to complete. The main purpose of purging is to remove any contaminants in the samples. After that, the desorbing process which takes about 4 minutes will heat the solution to 220°C to vaporize the components and send the components to the gas chromatography to analyze. At this stage, the spectrums of each component are shown on the monitor with a predetermined retention time. Baking is continued for about 10 minutes before the equipment returns back to stand-by mode. The components in the sample can be determined from the build-in library of spectrums which available in the software.

CHAPTER 5

RESULTS AND DISCUSSION

This chapter provides the findings of the adsorption isotherms measurement for toluene and n-hexane at three different temperatures (35°C, 55°C, and 65°C) with three different adsorbents (GAC 2.5mm from Merck, GAC 0.25-1mm from NORIT and PAC from Merck). The results are presented in the form of graphs of amount adsorbed of each chemicals versus the equilibrium concentration of that chemical in aqueous solution.

5.1 STANDARD CALIBRATION CURVE

5.1.1 Standard Calibration Curve using UV-Vis Spectrophotometer

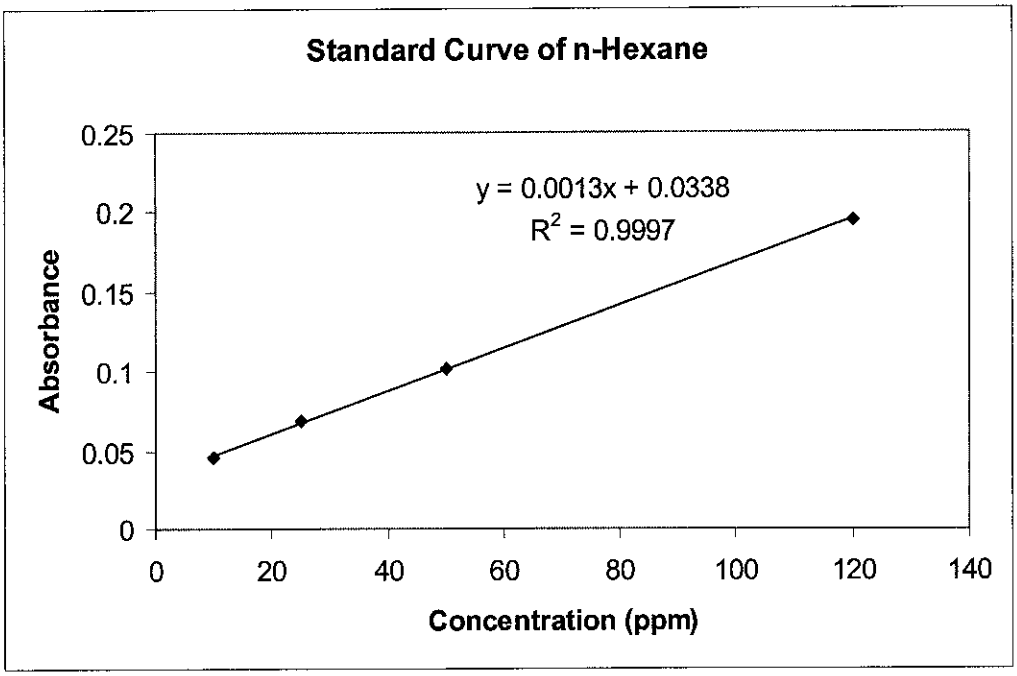

Figure 5.1: Calibration Curve of n-Hexane

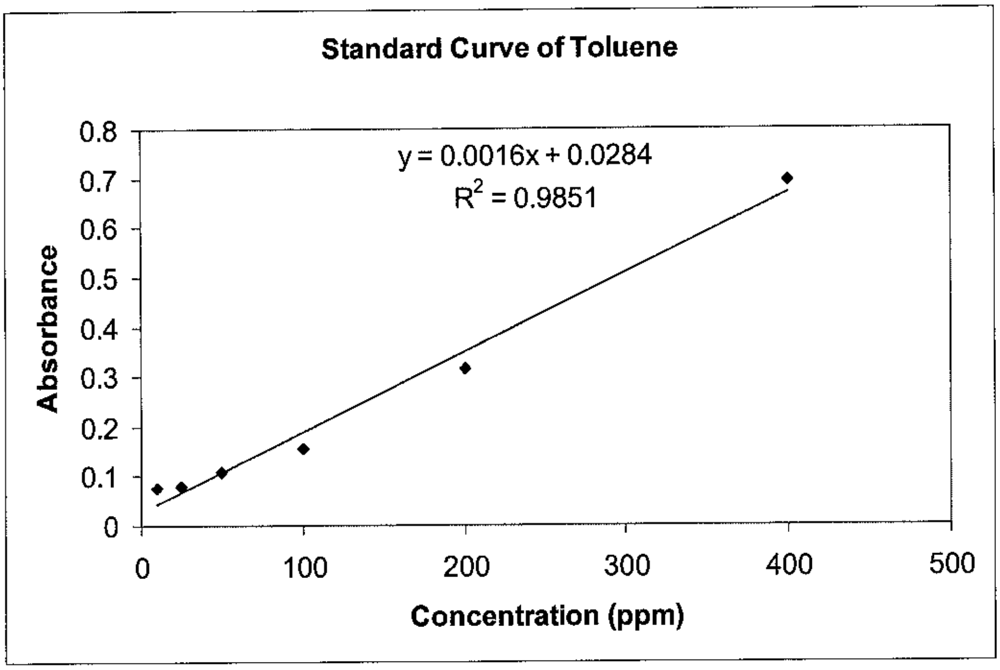

Figure 5.2: Calibration Curve of Toluene

The calibration curves for toluene and n-hexane on the UV-Vis Spectrophotometer are given in Figure 5.1 and 5.2. The use of adsorption spectroscopy and spectrometry has long been a mainstay of the refining, petrochemical, fine chemicals, materials and pharmaceutical industries. In laboratory scale, adsorption spectroscopy is also a useful analyzing method.

The UV-Vis Spectrophotometer was calibrated by analysis of a known concentration of toluene and n-hexane. In this study, UV-Vis Spectrophotometer from Shimadzu is used to determine the equilibrium concentration of toluene and n-hexane. The equipment is suitable for analyzing solutions within the visible region, which wavelength is from 400 to 180 nm and the UV region is from 400-200nm. From Du, (1998), the maximum wavelength of toluene is 261.8nm and based on Chalmers, (1999), that of n-hexane is 201 nm. Determination of the wavelength of each chemical is the first important step to obtain the standard curve. The standards prepared range from 10ppm to 120ppm and 10ppm to 400ppm for n-hexane and toluene, respectively. The different range of the standards depends on the solubility of each chemical.

Based on Chalmers, (1999), the basis in an adsorption method for quantitative determination of absorbing species is expressed in the relationship between the absorbance (A) and the analyte concentration (c), known as *Beer's law*, which can be written as:

$$A= \log(P_0/P) = abc$$

Where a is the proportionality constant called the absorptivity and b is the pathlength through the absorbing medium.

The calibration curves for both toluene and n-hexane are straight lines which show the linear relationship between the concentration and the absorbance value. This is in agreement with Beer's law discussed above.

5.1.2 Standard Calibration Curve obtained from GCMS

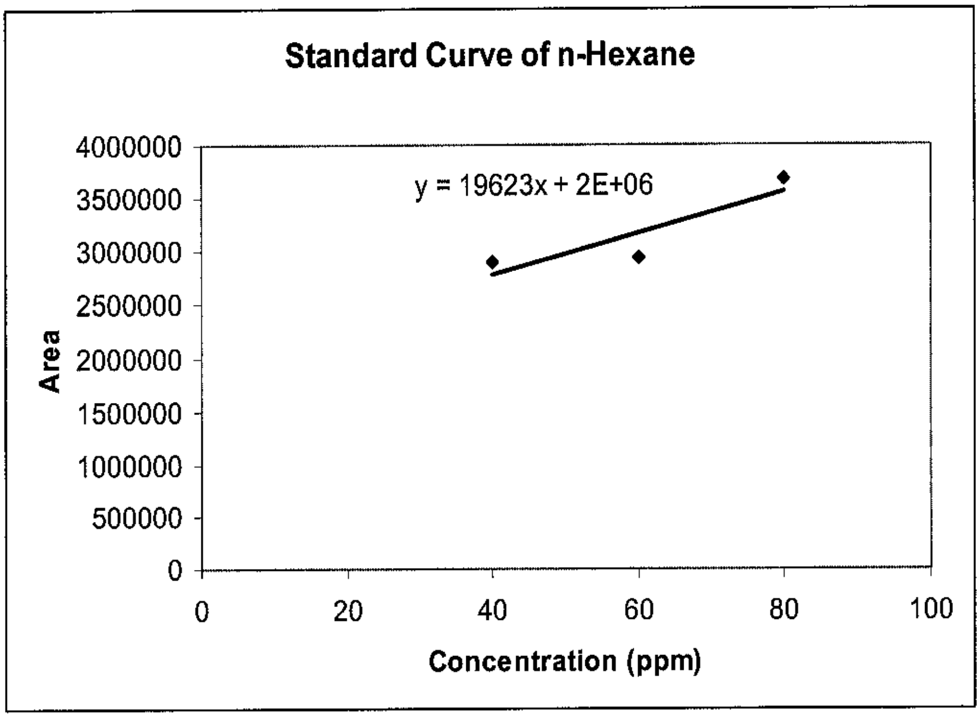

Figure 5.3: Calibration Curve of n-Hexane (for GCMS)

The calibration curves for n-hexane on the GCMS are given in Figure 5.3. The calibration curve for n-hexane is linear which indicates the linear relationship between the concentration and the area.

5.2 ADSORPTION ISOTHERM OF TOLUENE

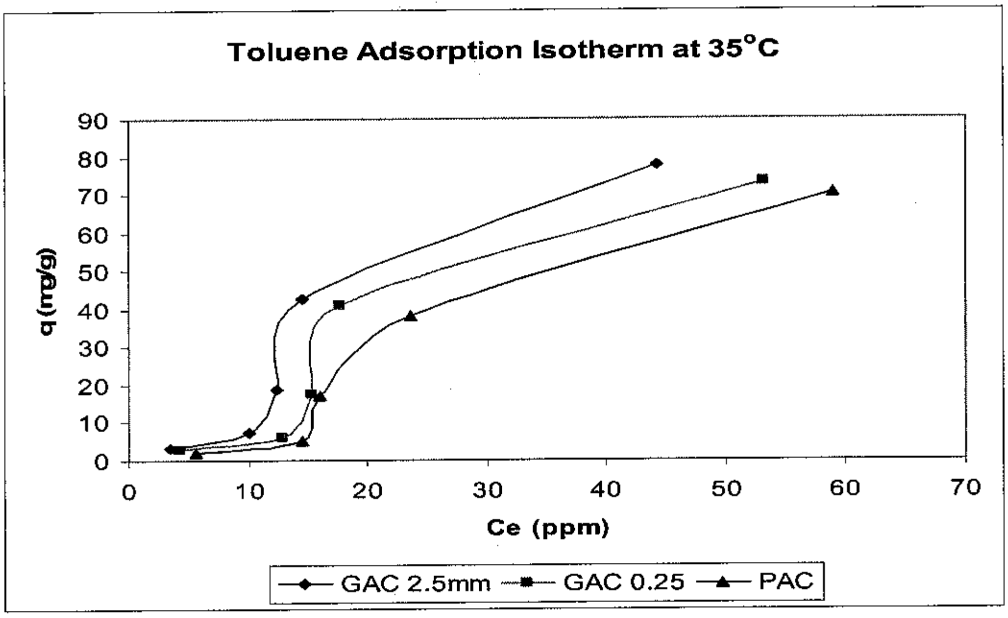

Figure 5.4: Toluene adsorption isotherm at 35°C

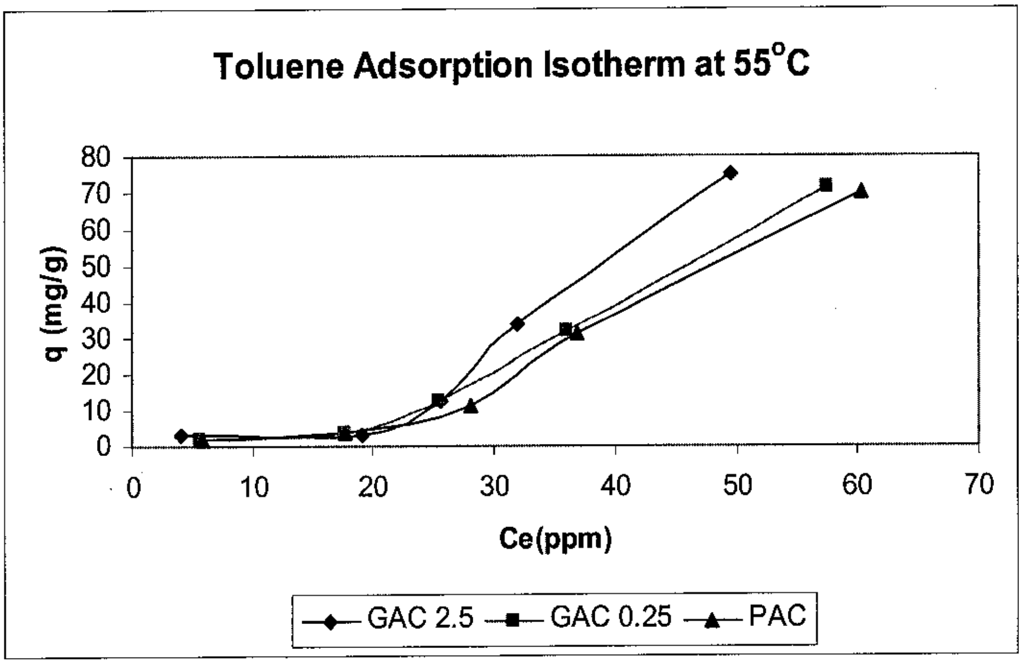

Figure 5.5: Toluene adsorption isotherm at 55°C

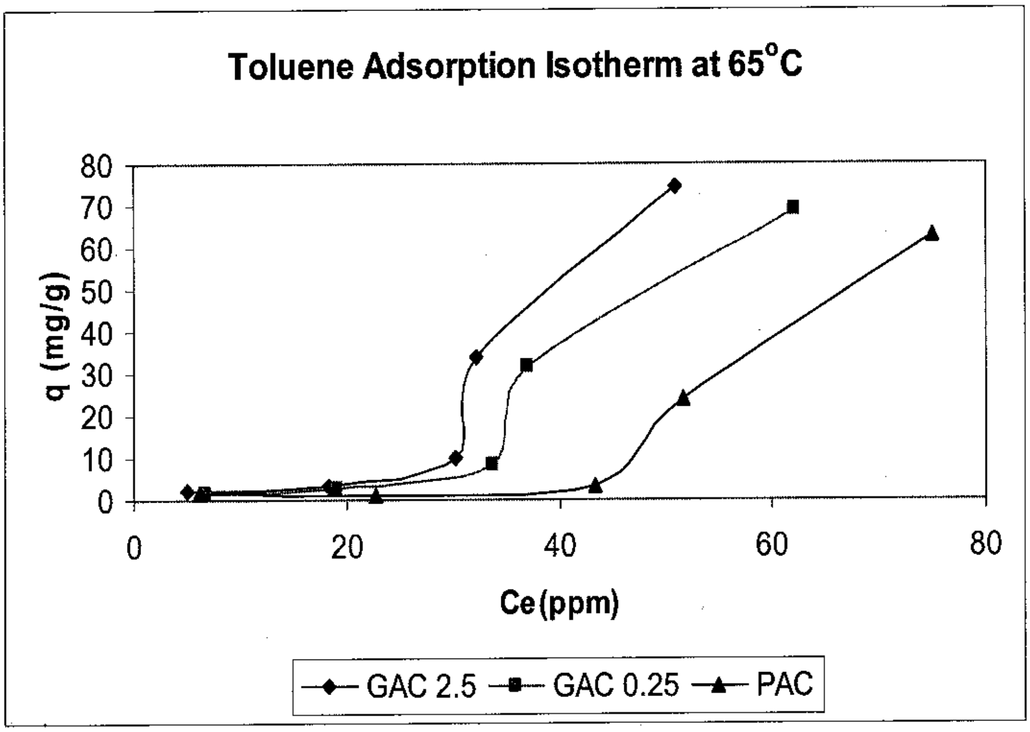

Figure 5.6: Toluene adsorption isotherm at 65°C

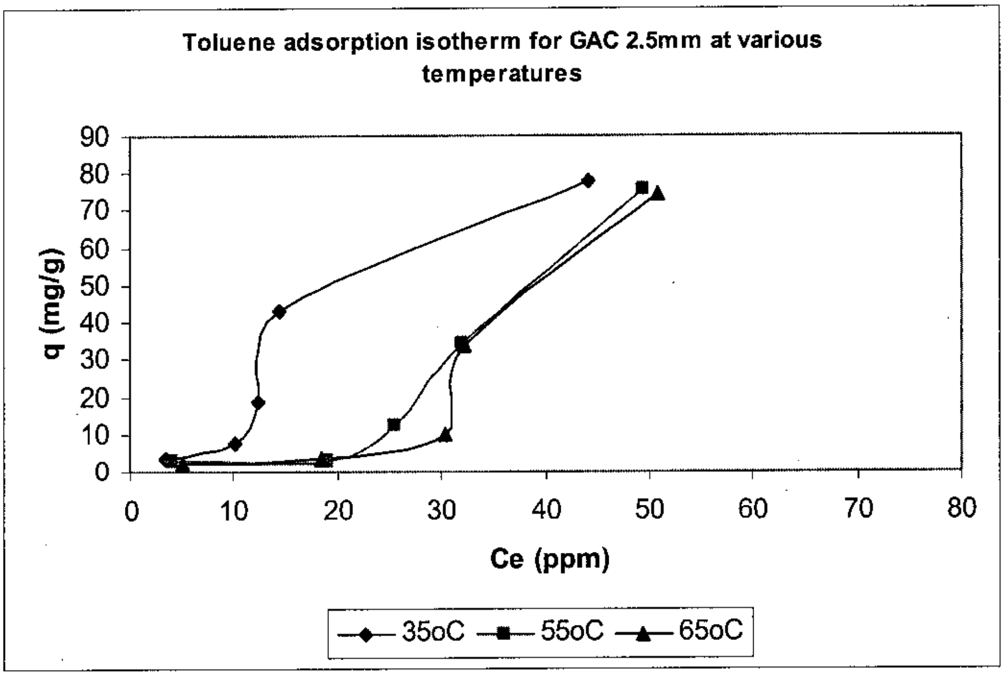

Figure 5.7: Toluene adsorption isotherm for GAC 2.5mm at various temperatures

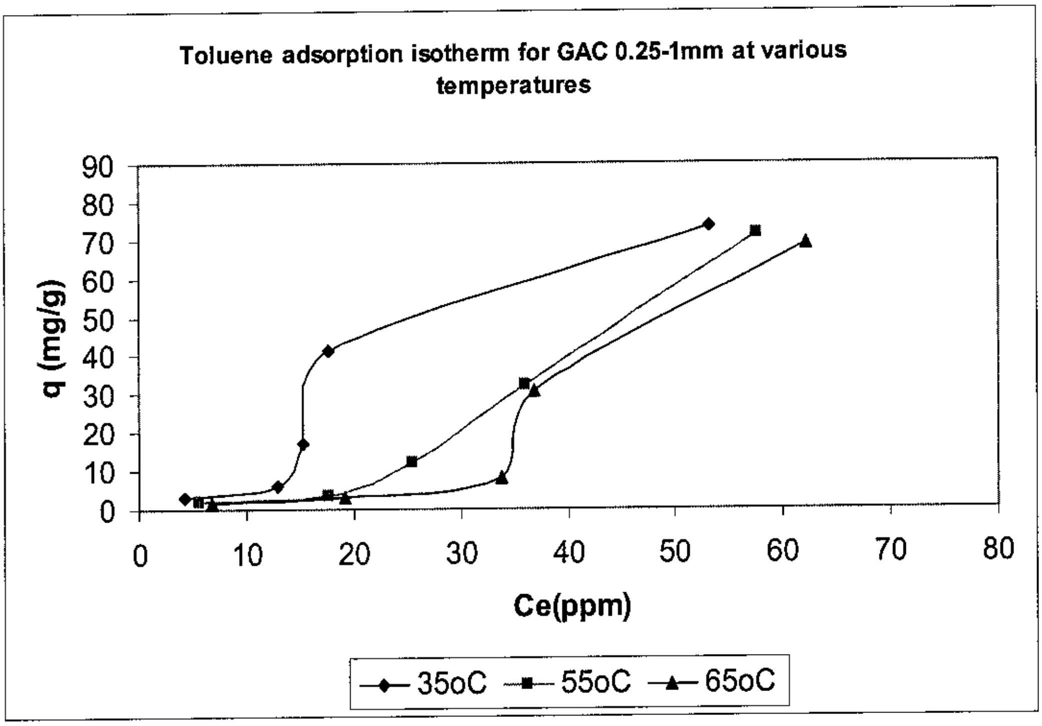

Figure 5.8: Toluene adsorption isotherm for GAC 0.25-1mm at various temperatures

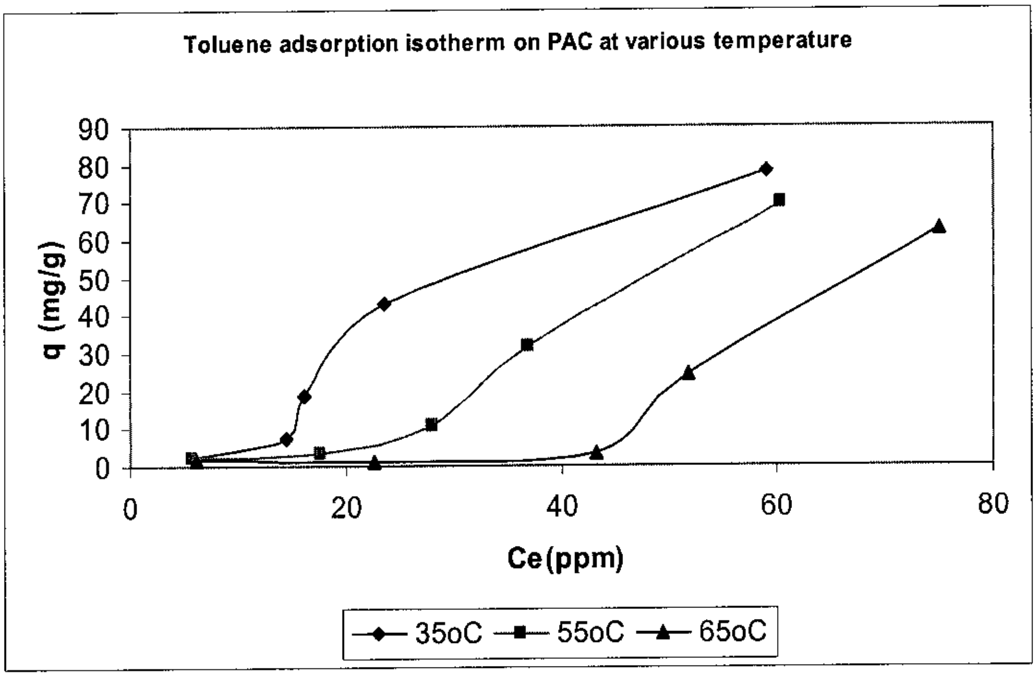

Figure 5.9: Toluene adsorption isotherm for PAC at various temperatures

Liquid adsorption is more complicated as compared to gas adsorption. It is different from gas adsorption where the amount of gas adsorbed is determined by the decrease in total pressure, in liquid adsorption, the pressure does not change. It is assumed that the change in composition of the bulk liquid in contact with the porous solid is due entirely to adsorption of solute. That is the adsorption of the solvent is assumed not to occur.

The experimental results for the adsorption equilibria of toluene on three types of activated carbons at 35°C, 55°C and 65°C are presented in Figure 5.4 to Figure 5.9. The tabulated results are given in Appendix IV. The isotherm is a graph of amount toluene adsorbed versus equilibrium concentration. The toluene isotherms are of type V in the BDDT classification (Refer to Figure 2.1 in Chapter 2) and having an S-shaped form. As the concentration increases, the isotherm rises sharply prior to saturation. The sharp rise in the isotherm occurs earlier for the low temperature isotherm compared with adsorption at higher temperature. For example, for toluene adsorption isotherm using GAC 2.5, the sharp rise occurs at C_e=12.889 for 35°C as compared with C_e = 17.613 for 55°C.

It can be seen that the last measured points of the isotherms give the plots that curve slightly upwards. The upwards tail to the amount adsorbed could be attained if the data are measured above the saturation limit of the system. Once the activated carbon is saturated, no more liquid can be adsorbed and there will be no more increase in the equilibrium concentration. Unfortunately, it is difficult to estimate accurately the exact amount of initial concentration required for saturation.

5.2.1 Effect of Temperature

To investigate the effect of temperature, the adsorption measurement has been done with three different temperatures, 35°C, 55°C, and 65°C. It is shown that as the temperature is increased, the amount adsorbed by the adsorbent decreases strongly. Increasing the temperature from T_1 to T_2 will decrease the equilibrium loading from q_1 to q_2 because the most strongly adsorbed species have the greatest heat of adsorption a relatively large decrease in loading can be achieved by a relatively modest increase in temperature. Based on Crittenden, (1998), adsorption isotherms tend to become unfavorable for adsorption at increased temperature and hence they become more favorable to desorption.

Roostaei et al., 2003 states that adsorption is an exothermic process. As the adsorption process takes place, heat is released to the surroundings. According to the Le Chatelier's principle, a system at equilibrium adjusts so as to minimize any stress applied to it. Therefore, the adsorption process will favor low temperature to shift the adsorption equilibrium to adsorption rather than desorption. That is the reason why in industry, adsorption is normally at room temperature.

Because adsorption is exothermic, high temperatures would seem to inhibit or slow adsorption. An explanation for this may be revealed by considering the rate-limiting factor for adsorption. In porous particles like activated carbon, adsorption is limited primarily by the diffusion of solute into the carbon particles. When adsorbed molecules are mobile on the surface of the adsorbent, especially in the case of volatile organic compound in activated carbon, diffusion due to migration of the adsorbed molecules may contribute more than pore diffusion. This type of diffusion which is called surface diffusion together with molecular diffusion make liquid phase more complicated because of the interaction between diffusing molecules and the surrounding molecules. Higher temperatures may impede adsorption at the adsorption site, but they significantly speed up the pace of diffusion, offsetting any negative temperature effect.

5.2.2 Effect of Adsorbents on Adsorption

There are three adsorbents that have been used to determine the adsorption isotherm. From the experimental results, it is seen that GAC 2.5mm has the largest adsorption capacity, followed by GAC 0.25mm and PAC.

Based on Suzuki (1989), for large adsorption capacity, large surface area is preferable, as a result of large number of pores, as fine as possible, are needed. Surface area and the distribution of area with respect to pore size are primary determinants of adsorption capacity and the molecular size which can be adsorbed. The smaller particles of a given mass of carbon would have a greater surface area than larger particles; the huge internal surface area of carbon dominates the calculation so much that the particle size essentially has no effect on capacity.

Although the characterization of adsorbents is not one of the objectives of the project, information on surface area of the adsorbents from the previous studies is obtained. The physical properties of the adsorbents are summarized in Table 5.2.

Table 5.1: Physical Properties of GAC 2.5mm and PAC (Source: Sheema, 2004)

Sample	Specific surface area, Sg (m^2/g)	Average pore diameter, d_p (nm)	Micropore analysis		
			Micropore volume (cm^3/g)	Micropore surface area (m^2/g)	Average pore width (nm)
GAC 2.5mm	3419.66	1.995	1.868	5255	5.641
PAC	1927.00	2.114	1.018	2865	4.51

Due to unavailability of the equipment and the data, the physical properties of GAC 0.25mm cannot be achieved. However, the data from the previous study shows that GAC 2.5mm has the largest micropore volume which is 1.868 cm^3/g and micropore surface area of 5255 m^2/g as compared to PAC. This is in agreement with the experimental data which shows that GAC 2.5mm has a higher adsorption capacity as compared to PAC.

5.3.1 Fitting adsorption isotherm measurement into correlations

Freundlich model

Many theories and models have been developed to interpret the adsorption isotherms. The correlation of the adsorption equilibrium was performed by fitting a single equation to the experimental data for all temperatures together. The most popular model which is widely used in the correlation of liquid adsorption is Freundlich. (Do, 1998)

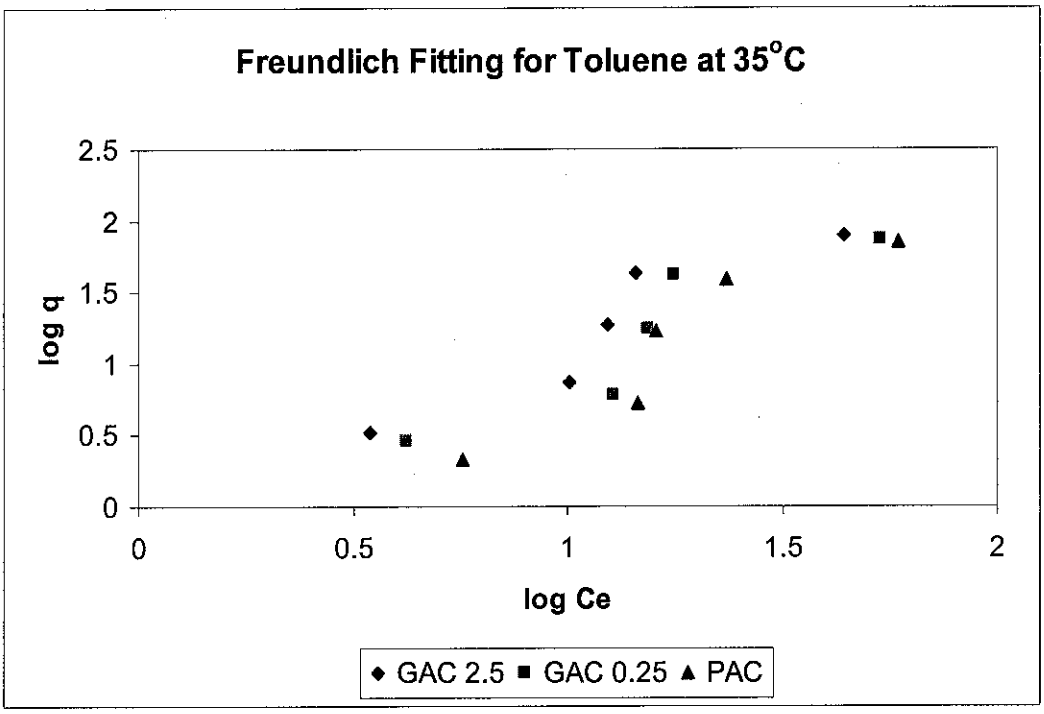

Figure 5.10: Freundlich Fitting for Toluene at 35°C

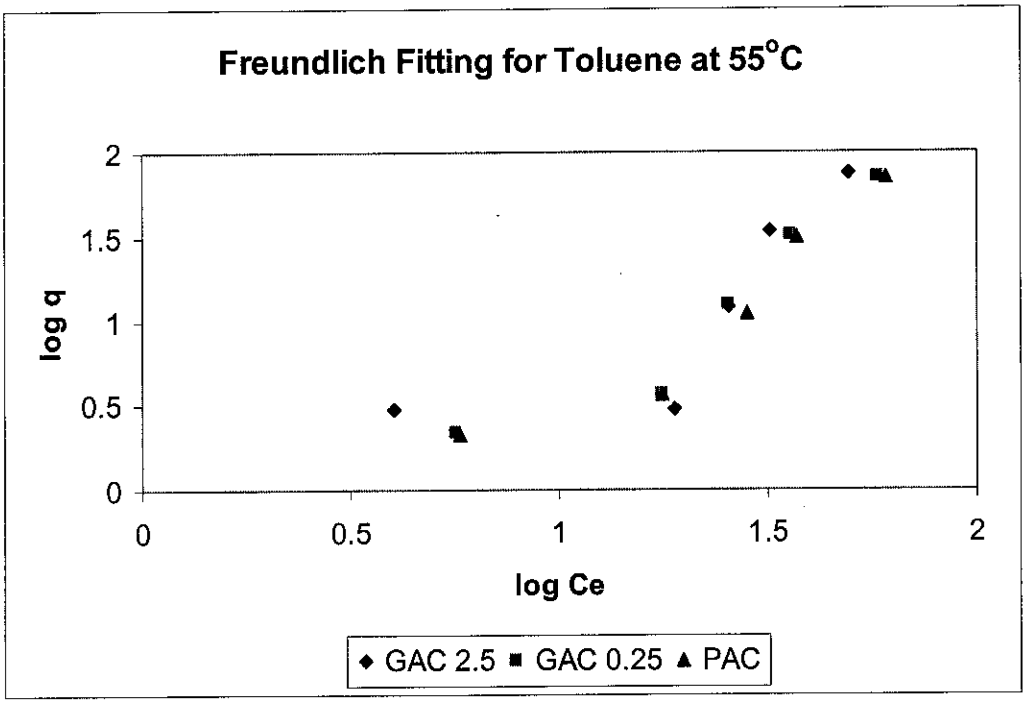

Figure 5.11: Freundlich Fitting for Toluene at 55°C

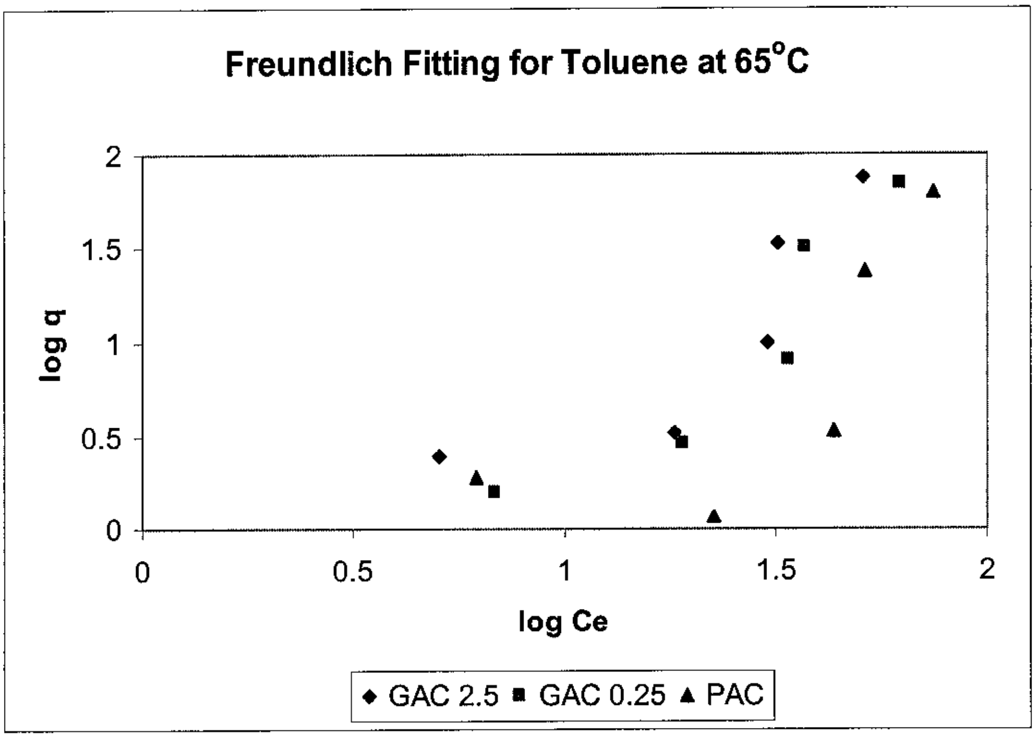

Figure 5.12: Freundlich Fitting for Toluene at 65°C

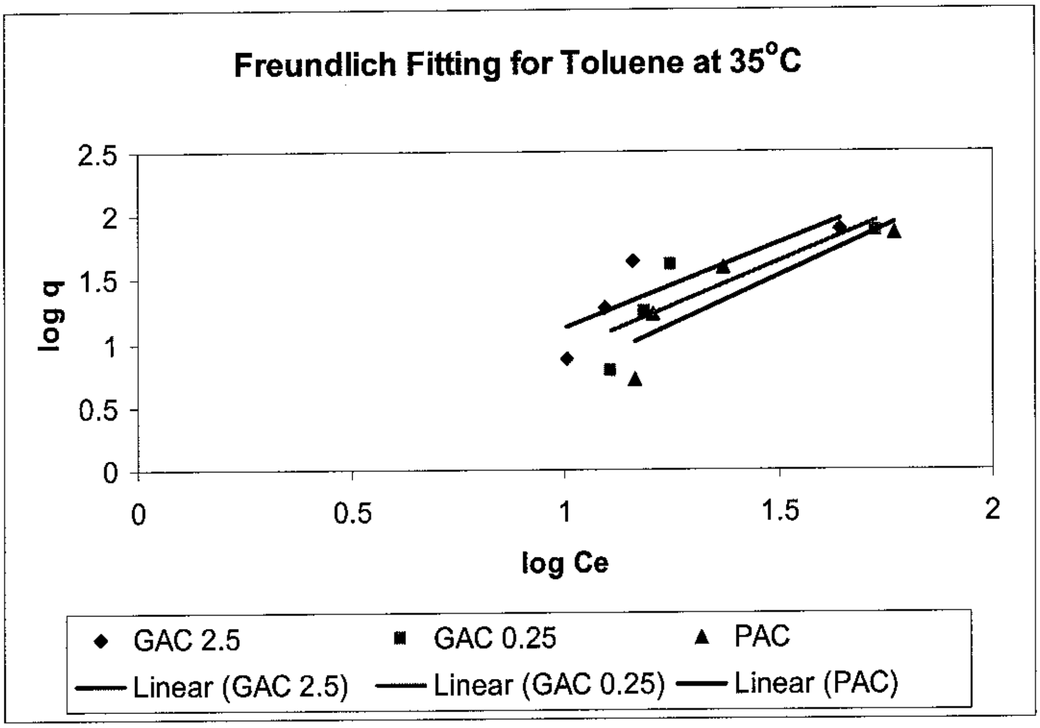

Figure 5.13: Freundlich Fitting for Toluene at 35°C (omit the first data point)

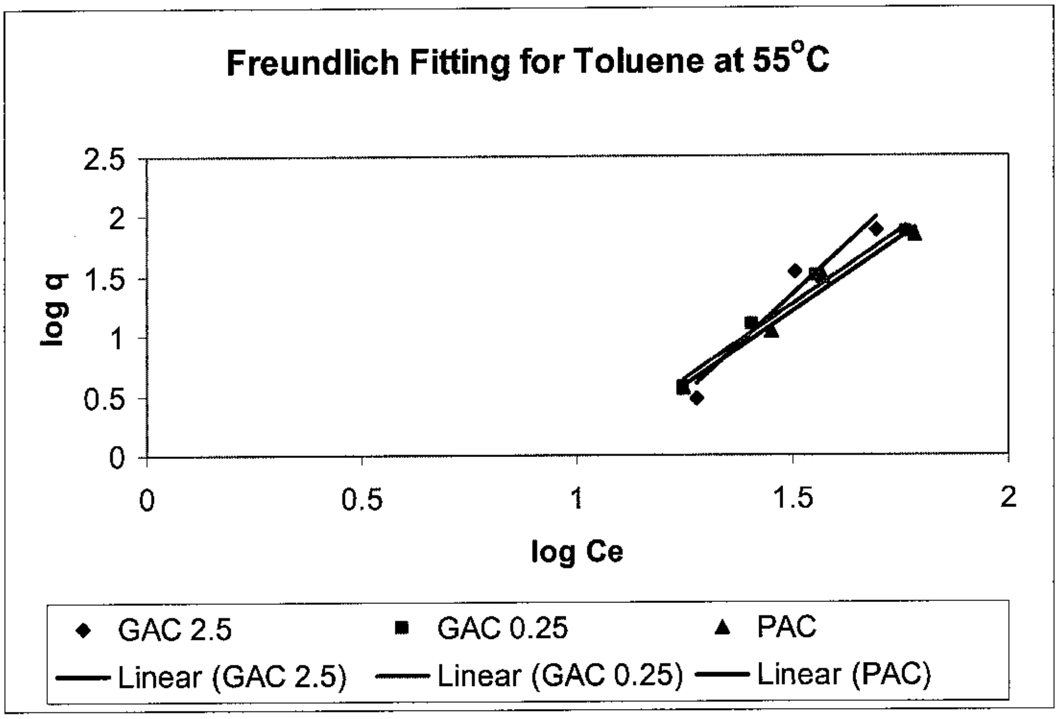

Figure 5.14: Freundlich Fitting for Toluene at 55°C (omit the first data point)

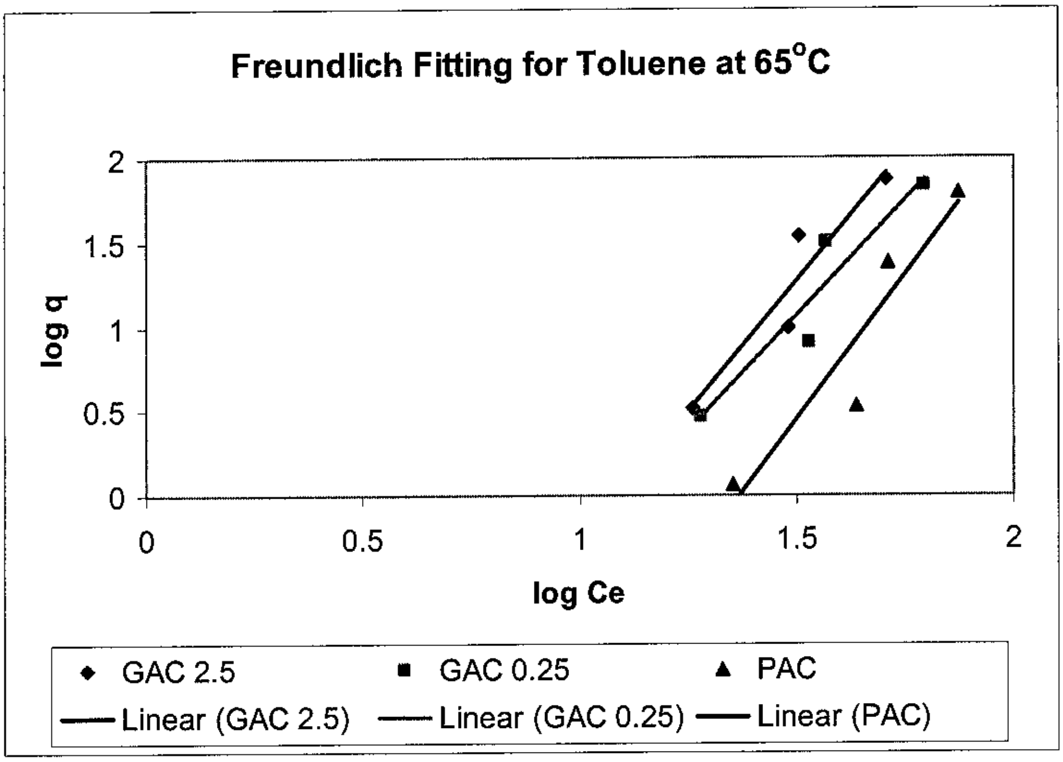

Figure 5.15: Freundlich Fitting for Toluene at 65°C (omit the first data point)

The graphs correlated by Freundlich model for all experimental data are given from Figure 5.10 to Figure 5.12, whereas the graphs that omitted the first data point for all temperatures are given in Figure 5.13 to Figure 5.15. Comparing the graphs, it is seen that the graphs in which the first data points are omitted give better fit to almost the experimental data except for the data near saturation. Unfortunately, the error of the fitting is very high. The inaccuracy of the fitting shows that Freundlich model did not fit the experimental data very well. Looking back at the shape of the adsorption isotherm, it shows that the isotherm has an S-shape, which is similar to type V isotherm, whereby the shape of Freundlich isotherm is similar to type I isotherm.

The correlated parameters for the toluene adsorption at three different temperatures are summarized in table below. The model parameters are obtained by neglecting the first data point at all temperatures. The model for 55°C has the best fit compared with other temperatures.

Table 5.2: Freundlich constants for the adsorption of Toluene

GAC 2.5			
Temperature(°C)	K	n	R^2
35	0.636	0.76	0.7252
55	0.00021	0.299	0.9425
65	0.00086	0.364	0.8933
GAC 0.25			
35	0.319	0.714	0.6808
55	0.0033	0.4	0.9776
65	0.00038	0.321	0.9014
PAC			
35	0.176	0.656	0.7469
55	0.0032	0.405	0.9776
65	0.000021	0.293	0.8863

There are several graphical methods for examining goodness of fit between a model and data. However, all graphical methods suffer the drawback of being qualitative rather than quantitative. In spite of that, it is much easier to spot a discrepancy between data and a model from a graph than it is from a statistic analysis.

To analyze the accuracy between the model predictions and the data, the parity plots have been used. A parity plot is a plot of the results from the model against measured experimental results under the same conditions. The parity plots for the model prediction are shown from Figure 5.16 to Figure 5.18.

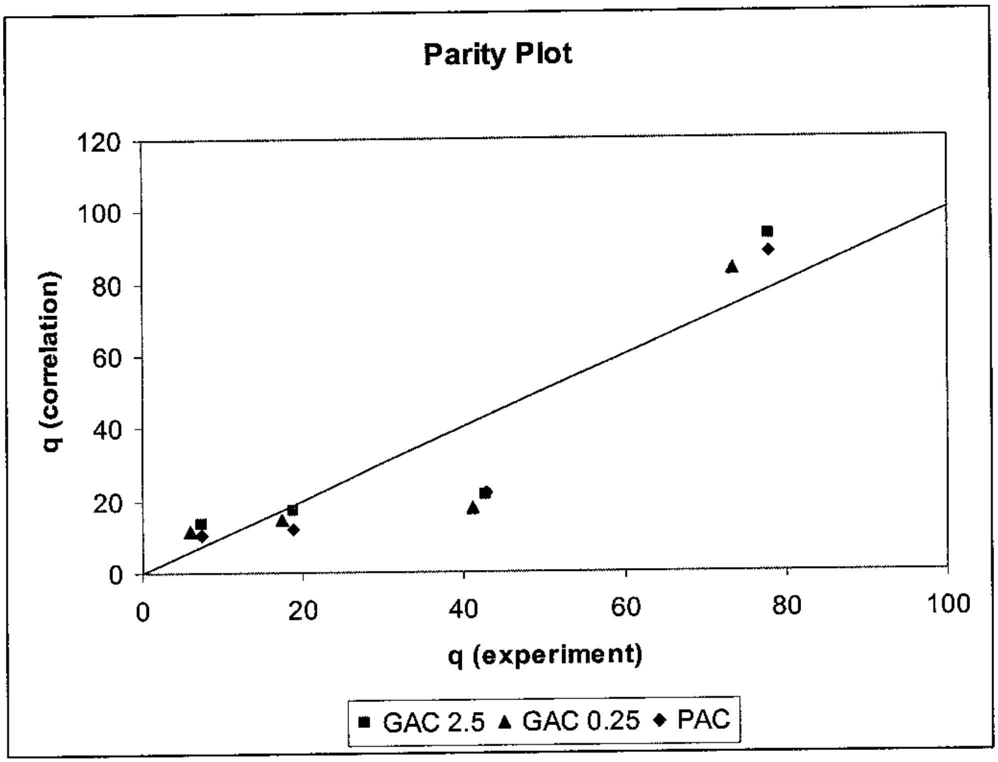

Figure 5.16: Parity Plot for Toluene Adsorption Isotherm at 35°C

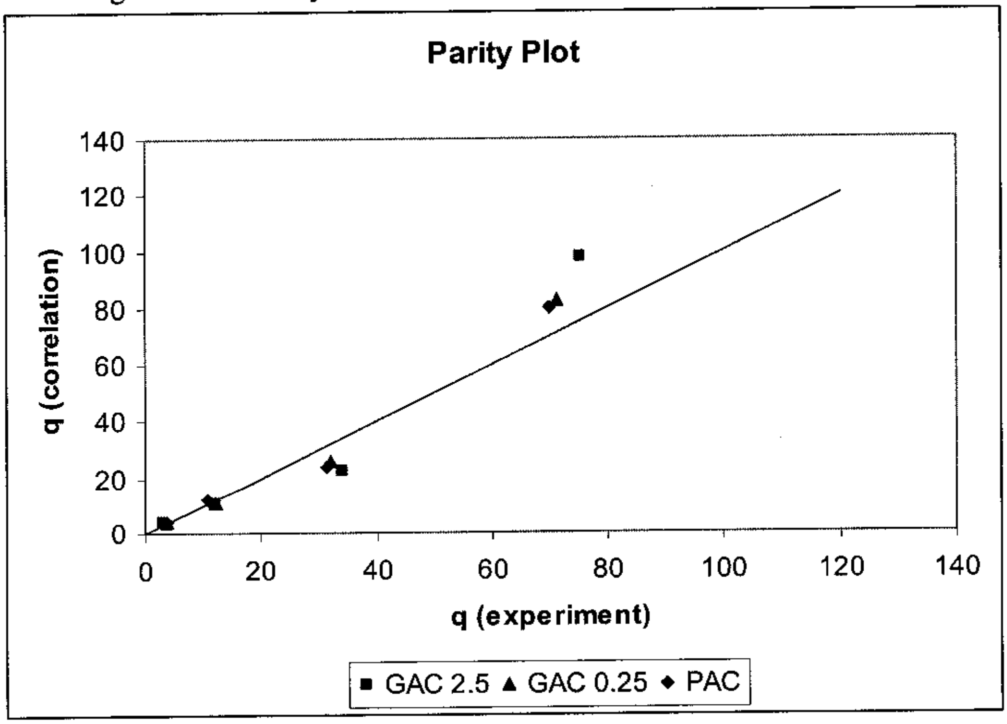

Figure 5.17: Parity Plot for Toluene Adsorption Isotherm at 55°C

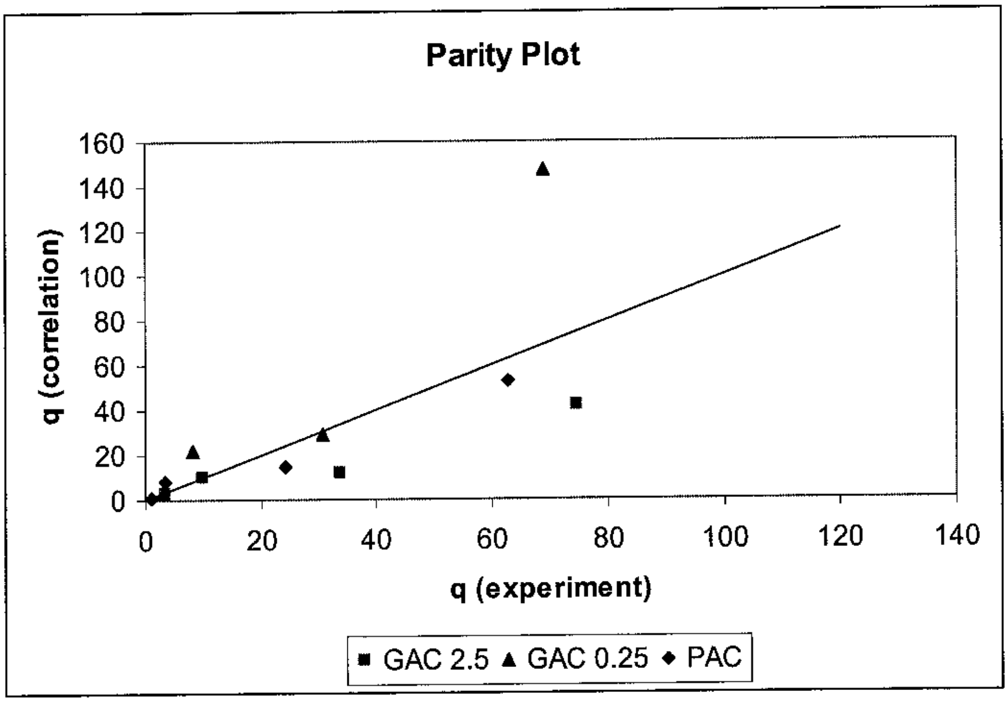

Figure 5.18: Parity Plot for Toluene Adsorption Isotherm at 65°C

The model perfectly predicts the data when all the points will fall on the diagonal. On the other hand, if the model overpredicts the data then the points lie above the diagonal. Likewise, if the model underpredicts then the points lie below the diagonal. The parity plot for the adsorption isotherm at 35°C shows that the data are overpredicted at the second and the last point and underpredicted for the third and fourth data point. The parity plot for 55°C is shown to have the relatively better predict as compared to the parity plot for 35°C and 65°C. Most of the data points at high values are overpredicts which further proved the inaccuracy of the correlation obtained Freundlich. It is possibly because the system has not reached equilibrium or was just about to reach equilibrium by the time the solutions were analyzed.

Sips model

Sips equation or Langmuir-Freundlich equation is similar in the form to the Freundlich equation, but it has a finite limit when the pressure is sufficiently high (Do, 1998). The experimental data were used to fit the Sips model using the build-in Matlab program.

Unfortunately, the technique was not successful with the toluene isotherm measurement. It gave a very poor fit to the experimental data as shown in Figure 1 to Figure 3 in Appendix VIII. The residual was found to be very large which indicates that Sips equation is not suitable to fit S-shape isotherm.

Toluene adsorption isotherm follows type V isotherm which is also similar to water adsorption isotherm which was studied by Azmi (1995). The interactions between activated carbon and water are so weak that the nature of the adsorption of water is the same as for the condensation of water vapor in the bulk phase (Dubinin, 1980) The most popular models which are widely used in the correlation if water adsorption isotherms are based on the Dubinin-Serpinski equations, (Dubinin and Serpinski, 1954, 1981; Barton et al., 1991). The equation can give good fit to the S-shape isotherm for water on most porous and nonporous carbons (Azmi, 1995). It is recommended that further study on the Dubinin-Serpinski isotherm should be done to determine the best fitting for toluene adsorption isotherm.

5.3 ADSORPTION ISOTHERM OF N-HEXANE

The adsorption isotherm measurement of n-Hexane on activated carbon has been carried out using the same method as that has been used for toluene. The results obtain from UV-Vis Spectrophotometer is shown in Figure 5.19. The amount adsorbed is negative in value indicated that the equipment cannot be used to analyzed the equilibrium concentration as the results obtained shown that UV-Vis Spectrophotometer cannot detect the n-hexane spectrum, which is 201 nm.

n-Hexane solution was then analyzed using Gas Chromatography with Purge and Trap. This equipment has the capability to analyze the components in the solution. However, the results obtained do not give any difference. The Gas Chromatography can analyze the equilibrium concentration although the amount is very small (less than 1 ppm) which can be negligible.

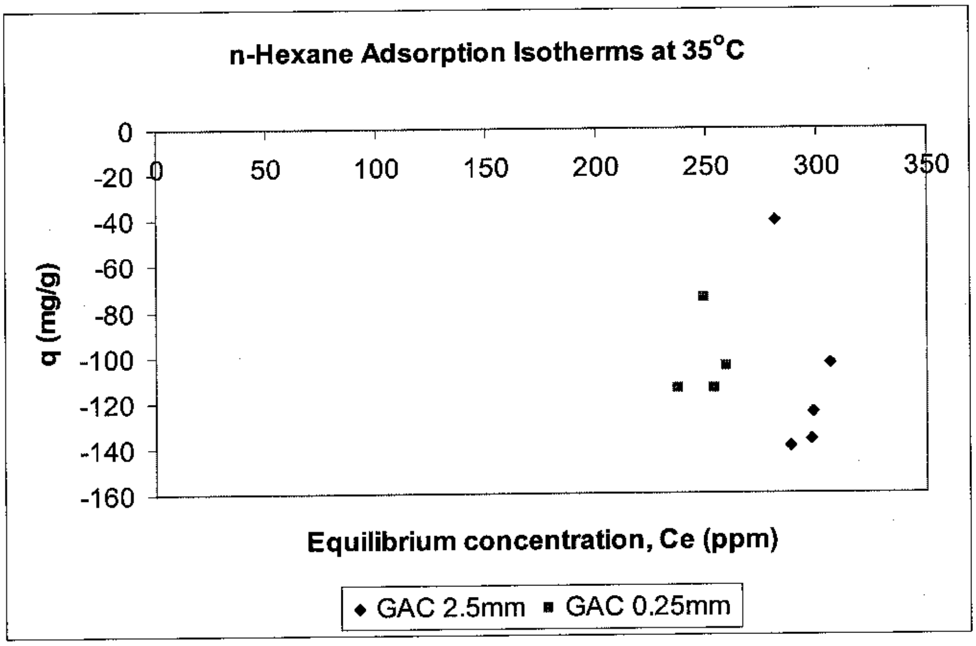

Figure 5.19: n-Hexane adsorption isotherm at 35°C (analyzing using UV-Vis Spectrophotometer)

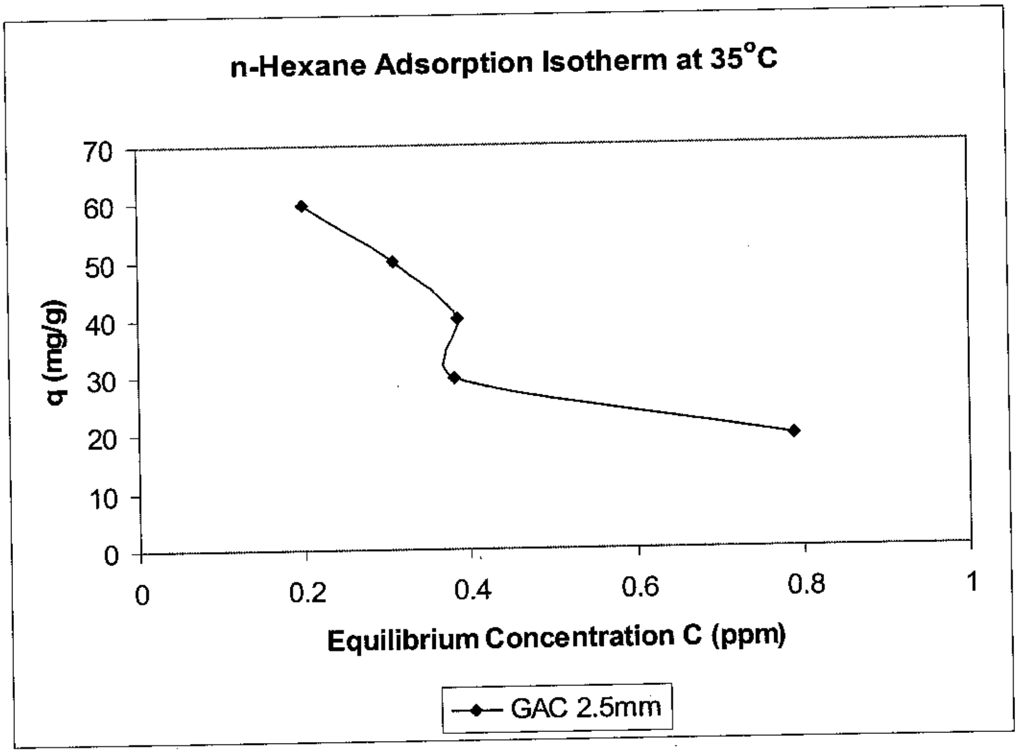

Figure 5.20: n-Hexane adsorption isotherm at 35°C (analyzing using GCMS

Volatility of n-hexane

The high volatility of n-hexane is the main reason for the inconsistent in the results obtained from UV-Vis Spectrophotometer and GCMS. Because of its high volatility, n-hexane is ready to vaporize during vigorous shaking in the solution preparation and when the adsorption process takes place. Its high volatility is proved in the volatility test where the n-hexane solution is analyzed at different time interval at room temperature. The concentrations were plotted versus time as shown in Figure 5.21. The concentration of n-hexane has dropped tremendously after two and a half hours. (Refer to Appendix VI for the results obtained from GCMS). At elevated temperatures, it is even easier for the n-hexane molecules to escape from the solution leading to the extremely small equilibrium concentration after the adsorption process takes place.

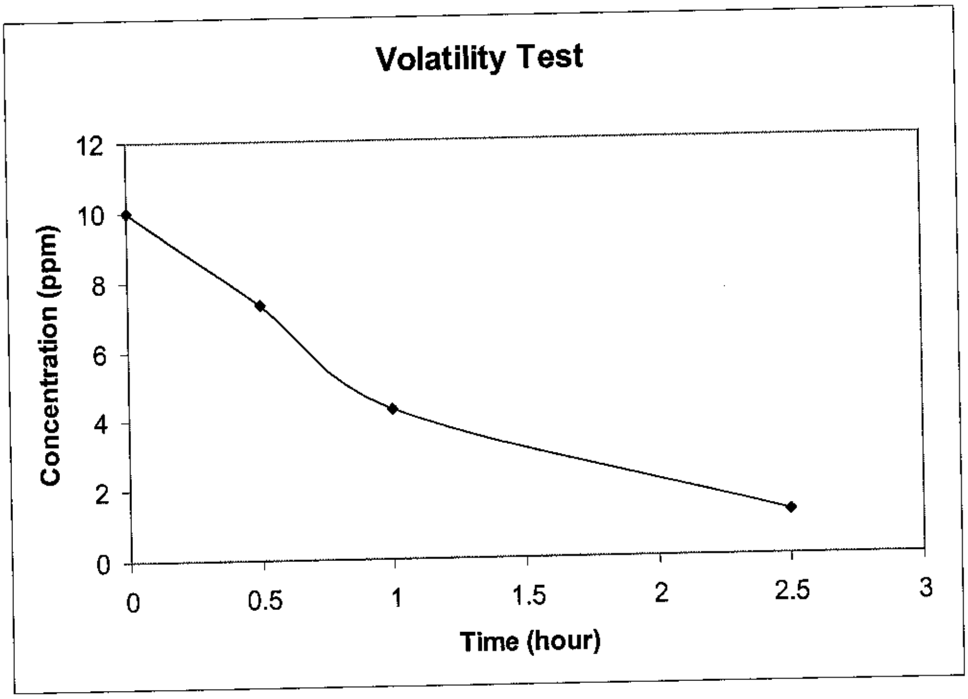

Figure 5.21: Volatility Test of n-Hexane

n-Hexane and Environmental Facts

According to the Toxics Release Inventory (TRI), in 1996, the estimated releases of *n*-hexane of 58,649,487 pounds (26,603,233 kg) to air from 534 reporting facilities accounted for about 82.9% of total environmental releases (TRI96 1998). On the other hand, the estimated releases of *n*-hexane of 215,775 pounds (97,875 kg) to water from reporting facilities accounted for less than 1 percent of total environmental releases (TRI96 1998). It is obvious that most releases of *n*-hexane to environmental media are to air. Based on its Henry's law constant, *n*-hexane discharged to water will volatilize rapidly; however, the amount volatilized will vary depending on a number of factors including the temperature, turbulence, and depth of the receiving water. n-Hexane spilled onto surface soils will also volatilize to the air.

This and other findings which have been discussed so far imply that n-hexane can be negligible in liquid form and adsorption process is not required.

5.4 EFFECT OF ADSORBATE ON ADSORPTION

The purpose of selecting toluene and n-hexane for this study is to compare the effect of hydrocarbon of different classes but having the same number of carbon on adsorption. Generally, straight-chain organic compounds are less adsorbable than branched-chain organics, while the type of attached functional group has been shown to affect adsorption. These phenomena are attributed to the influence of the molecular structure on the polarity and/or solubility of the compound of interest. Several authors have documented the fact that large molecules (with more adsorption sites) tend to be more sorbable than small molecules, but most also document cases in which large molecular size inhibits adsorption. This occurs when the molecular size approaches the size of the smaller carbon pores, and the pores screen out large numbers of molecules which might otherwise be strongly adsorbed. This occurrence is often referred to as the "molecular sieve" effect.

Besides, the solubility of the adsorbates is also an important factor that contributes the adsorption ability. The solubility of n-hexane given in the Perry's Chemical Engineers Handbook is 0.14 g/L. However, the solubility of n-hexane in water from the specification of the supplier is only 0.0095 g/L which is much lower than the value that has been used before. In other words, the amount of n-hexane that can be dissolved in the water is very small which can be negligible. This also explains the unexpected adsorption isotherms obtained for n-hexane.

CHAPTER 6

CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION

The adsorption isotherms for Toluene and n-Hexane have been developed for different temperatures using different adsorbents. The high volatility of n-Hexane has been proven from the solubility test done in the experiment; therefore, adsorption is not required to remove n-hexane from aqueous solution. Toluene, on the other hand, does require adsorption process. The adsorption isotherm of toluene follows type V isotherm as described by BDDT classification. The experiment has also proved that adsorption is an exothermic process. The adsorption process will favor low temperature to shift the adsorption equilibrium to adsorption rather than desorption. In industry, adsorption is normally at room temperature.

Among three adsorbents that have been used, granular activated carbon 2.5mm is found to have largest adsorption capacity due to its largest amount adsorbed from the adsorption measurement. The surface area and the distribution area with respect to pore size are the main contributions to the adsorption capacity.

The correlations using Freundlich isotherm were also determined. Freundlich isotherm is the most popular model which is widely used in the correlation of liquid adsorption. Sips isotherm which is the combination between Langmuir and Freundlich equation is an alternative. However, these techniques were not successful with toluene isotherm measurement.

6.2 RECOMMENDATIONS

Temperature and time have been the most critical parameters of the experiments. It is recommended to choose lower temperature for the adsorption study because adsorption process favors low temperature to push the equilibrium to adsorption rather than desorption process. The equilibrium condition is assumed to be reached after 24 hours throughout the project. However, the adsorption measurement shows that the system has not reached equilibrium condition or just about to reach saturated condition. Longer time is recommended to check whether 24 hours is sufficient for the system to achieve equilibrium.

In the study, the concentrations are limited to certain points which are 200ppm for toluene and 120ppm for n-hexane. This depends upon the solubility of each chemical. Higher concentrations are recommended to confirm whether the system is able to reach equilibrium at later stage of the adsorption process.

Finally, further study is strongly recommended to evaluate the possible reasons for the unsatisfactory data obtained from n-hexane adsorption. Different correlations should be attempted to find the best fit for the experimental data. For instance, the Dubinin-Serpinski isotherm should be considered to determine the best fitting for toluene adsorption isotherm.

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APPENDICES

APPENDIX I : Apparatus and Equipment

No	Description	Purpose
1	100ml Erlenmeyer flask/conical flask with cap	To put activated carbon and liquid solution during batch adsorption isotherm measurement
2	Glass funnel	To be used during gravity filter, to separate activated carbon from liquid solution
3	50ml beaker	For storage of activated carbon
4	Desiccators	For storage of activated carbon
5	Filter paper of 0.4-0.45 μm	To filter activated carbon from liquid adsorption solution
6	Parafilm	To seal volumetric flask containing sample
7	Silica gel	To be used in desiccators, for storage of activated carbon
8	Water bath shaker	To maintain temperature of system and shake activated carbon solution during batch adsorption isotherm measurement
9	Oven	To bake activated carbon
10	Analytical balance	To weigh activated carbon
11	UV VIS Spectrophotometer	To analyze concentration of adsorbate in sample
12	GCMS with purge and trap	To analyze concentration of adsorbate in sample
13	100ml measuring cylinder	To measure the volume of the solution
14	SEM	To study the microstructure of adsorbents

APPENDIX II: Sample Calculation of Solution Preparation

- n-Hexane

n-Hexane is prepared with a 120ppm stock solution.

The sample calculation is as followed:

$C_1V_1 = C_2V_2$

Where C_1 is the initial concentration ($6.6x10^5$ ppm)

V_1 is the initial volume

C_2 is the stock concentration (120ppm)

V_2 is the volume required (500ml)

The amount of n-hexane needed is

$$V_1 = \frac{C_2V_2}{C_1} = \frac{120x500}{6.6x10^5} = 9.0x10^{-2}\, ml \text{ or } 90.9\mu L$$

Different concentrations are prepared. The results are summarized in the table below:

Concentration(ppm)	Volume needed (mL)	Volume from stock(mL)
10	100	8.33
25	100	20.83
50	100	41.67
100	100	83.33
120	100	100.00

- Toluene

Toluene is prepared with a 400ppm stock solution.

The sample calculation is as followed:

$C_1V_1 = C_2V_2$

Where C_1 is the initial concentration ($8.7x10^5$ ppm)

V_1 is the initial volume

C_2 is the stock concentration (400ppm)

V_2 is the volume required (500ml)

The amount of n-hexane needed is

$$V_1 = \frac{C_2V_2}{C_1} = \frac{400x500}{8.7x10^5} = 2.29.0x10^{-1}ml \text{ or } 229.9\mu L$$

Different concentrations are prepared. The results are summarized in the table below:

Concentration(ppm)	Volume needed (mL)	Volume from stock (mL)
10	100	2.5
25	100	6.25
50	100	12.5
100	100	25
200	100	50

APPENDIX III: Standard Curve Data

n-Hexane

Sample ID	Concentration (ppm)	Absorbance
1	10	0.046
2	25	0.069
3	50	0.101
4	120	0.195

Toluene

Sample ID	Concentration (ppm)	Absorbance
1	10	0.077
2	25	0.081
3	50	0.109
4	100	0.154
5	200	0.314

APPENDIX IV: Toluene Adsorption Isotherm Results at Different Temperature

Experimental Results of Toluene Adsorption at 35°C

Adsorbent	C(ppm)	Absorbance	Ce (ppm)	V (L)	m (g)	q(mg/g)
GAC 2.5	10	0.034	3.473	0.1	0.2	3.2635
	25	0.045	10.117	0.1	0.2	7.4415
	50	0.048	12.393	0.1	0.2	18.8035
	100	0.052	14.477	0.1	0.2	42.7615
	200	0.099	44.179	0.1	0.2	77.9105
GAC 0.25	10	0.035	4.211	0.1	0.2	2.8945
	25	0.049	12.889	0.1	0.2	6.0555
	50	0.053	15.332	0.1	0.2	17.334
	100	0.057	17.728	0.1	0.2	41.136
	200	0.114	53.227	0.1	0.2	73.3865
PAC	10	0.037	5.685	0.1	0.2	2.1575
	25	0.052	14.555	0.1	0.2	5.2225
	50	0.054	16.062	0.1	0.2	16.969
	100	0.066	23.545	0.1	0.2	38.2275
	200	0.123	58.996	0.1	0.2	70.502

Experimental Results of Toluene adsorption at 55°C

Adsorbent	C (ppm)	Absorbance	Ce (ppm)	V (L)	m (g)	q (mg/g)
GAC 2.5	10	0.035	4.021	0.1	0.2	2.9895
	25	0.059	18.985	0.1	0.2	3.0075
	50	0.069	25.533	0.1	0.2	12.2335
	100	0.079	31.903	0.1	0.2	34.0485
	200	0.108	49.462	0.1	0.2	75.269
GAC 0.25	10	0.037	5.685	0.1	0.2	2.1575
	25	0.057	17.613	0.1	0.2	3.6935
	50	0.069	25.467	0.1	0.2	12.2665
	100	0.086	36.035	0.1	0.2	31.9825
	200	0.120	57.549	0.1	0.2	71.2255
PAC	10	0.038	5.767	0.1	0.2	2.1165
	25	0.057	17.686	0.1	0.2	3.657
	50	0.073	28.083	0.1	0.2	10.9585
	100	0.087	36.933	0.1	0.2	31.5335
	200	0.125	60.36	0.1	0.2	69.82

Experimental Results of Toluene adsorption at 65°C

Adsorbent	C (ppm)	Absorbance	Ce (ppm)	V (L)	m (g)	q (mg/g)
GAC 2.5	10	0.037	5.067	0.1	0.2	2.4665
	25	0.058	18.367	0.1	0.2	3.3165
	50	0.077	30.325	0.1	0.2	9.8375
	100	0.080	32.244	0.1	0.2	33.878
	200	0.110	50.931	0.1	0.2	74.5345
GAC 0.25	10	0.039	6.825	0.1	0.2	1.5875
	25	0.059	19.128	0.1	0.2	2.936
	50	0.083	33.823	0.1	0.2	8.0885
	100	0.087	36.933	0.1	0.2	31.5335
	200	0.128	62.152	0.1	0.2	68.924
PAC	10	0.038	6.167	0.1	0.2	1.9165
	25	0.065	22.654	0.1	0.2	1.173
	50	0.098	43.292	0.1	0.2	3.354
	100	0.111	51.703	0.1	0.2	24.1485
	200	0.148	74.9	0.1	0.2	62.55

APPENDIX V: Results Obtained from GCMS for n-Hexane Adsorption

CLASS-5000 *** Report No. = 10   Data : HOA.D01   04/09/09 10:37:49

ple   : std 40ppm
                : std01
e   : Standard
hod File Name : HOA.MET

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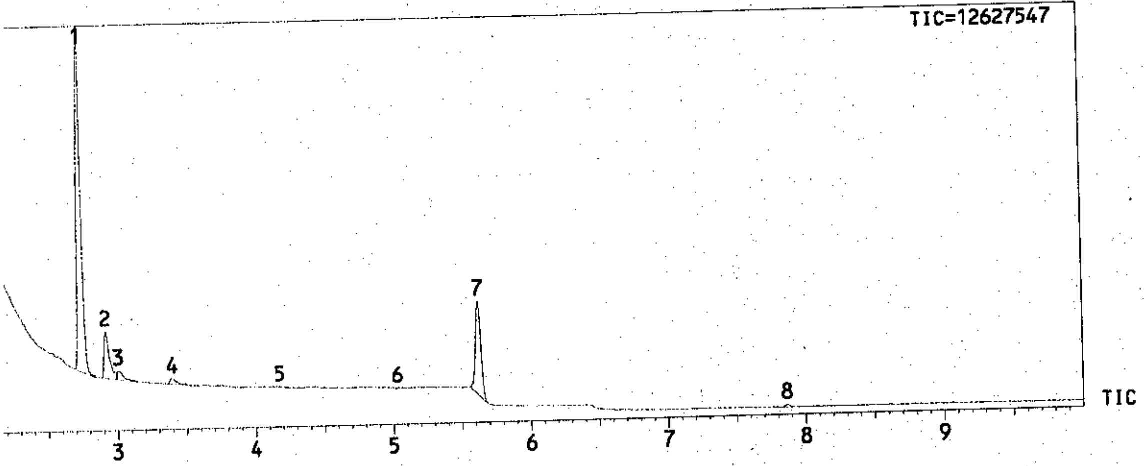

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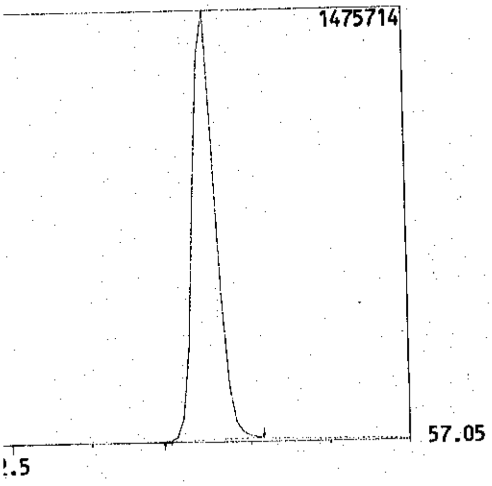

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Name   : hexane

Time   : 2.744
Area   : 2897116

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ample           : std 60ppm
)               : std02
ype             : Standard
ethod File Name : HOA.MET

** Chromatogram ***
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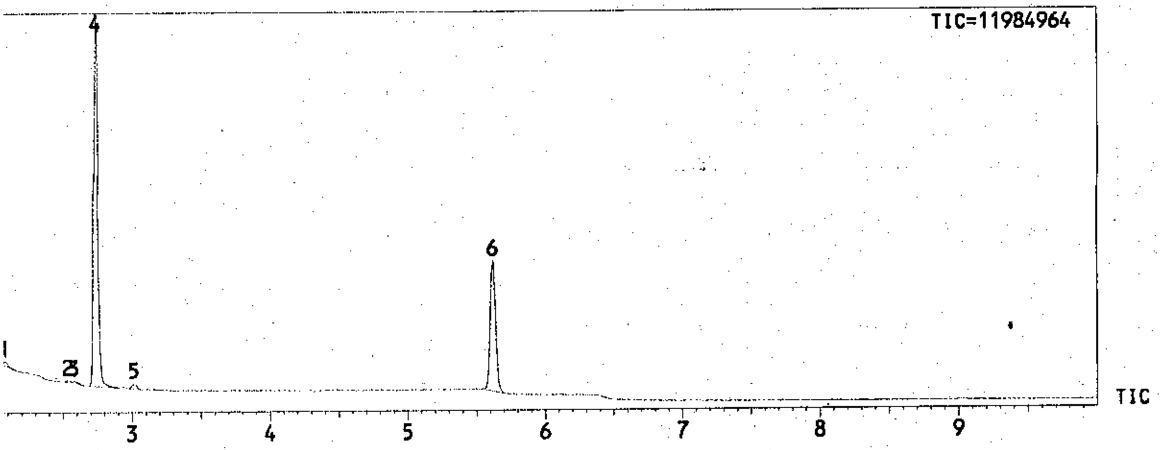

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** Quantitation ***
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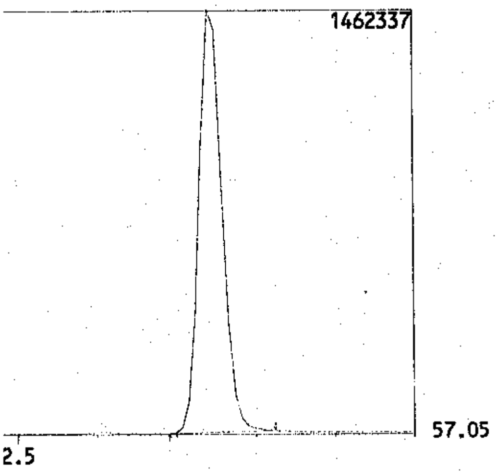

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ID    :  1     M/Z : 57.05
Type  : Target
Name  : hexane

Time  : 2.740
Area  : 2945613
```

```
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ample            : std 80ppm
)                : std03
ype              : Standard
ethod File Name  : HOA.MET

** Chromatogram ***
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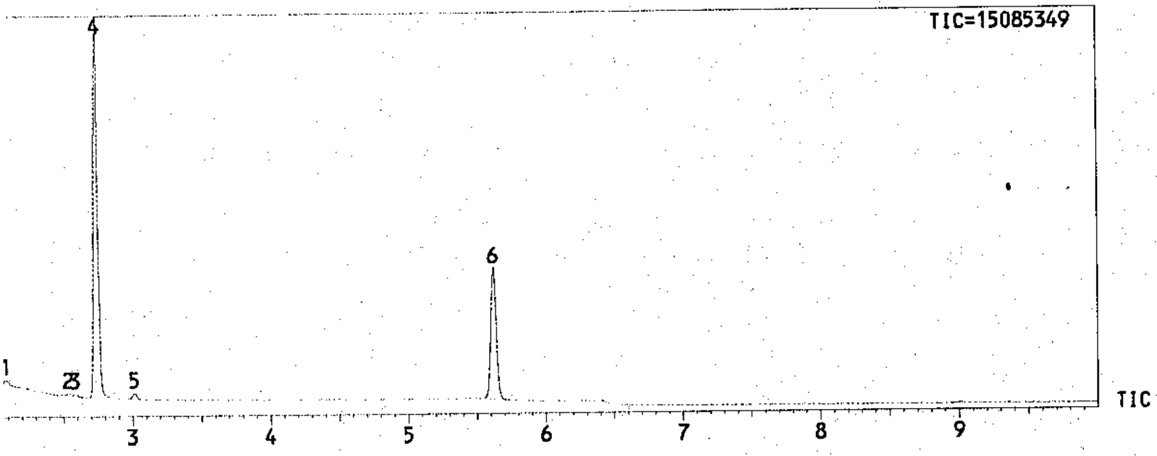

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** Calibration Curve ***

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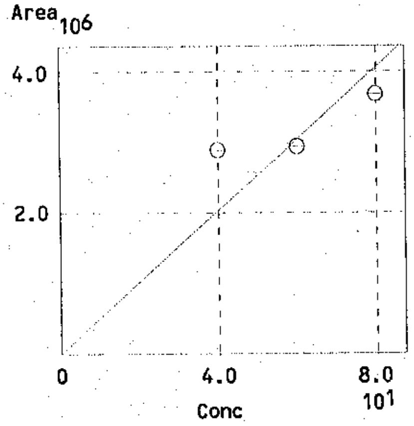
 Area = 50619.3 * (Conc.)    r2 = 0.796152
```



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          Conc.(ppm    )         Area
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2               60.000          2945613
3               80.000          3682035
```

```
*** Quantitation ***
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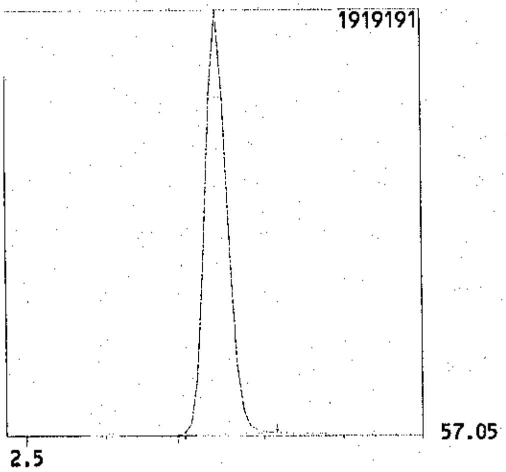

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Type    : Target
Name    : hexane

Time    : 2.737
Area    : 3682036
```
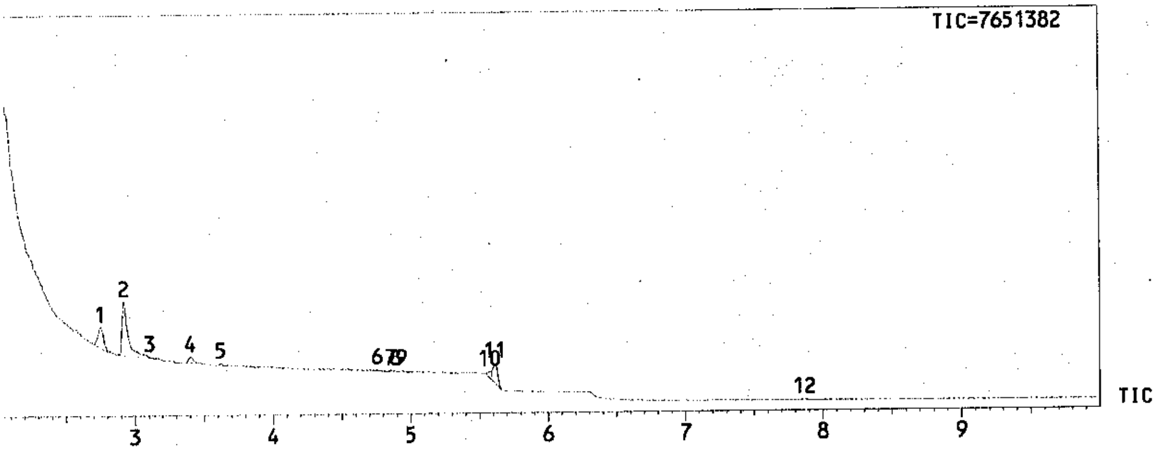

** CLASS-5000 *** Report No. = 13   Data : HOA.D06 04/09/10 10:53:01

```
ample            : sample1 40ppm
D                : sample1
ype              : Unknown
ethod File Name  : HOA.MET
```

** Chromatogram ***



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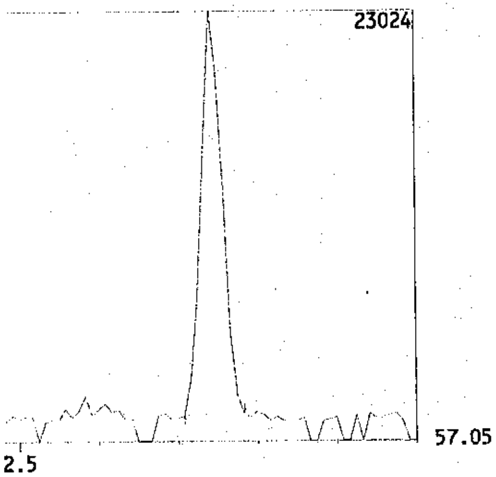

```
ID    :  1     M/Z : 57.05
Type  : Target
Name  : hexane

Time  : 2.739
Area  : 39934
Conc. : 0.789ppm
```

```
** CLASS-5000 *** Report No. = 14   Data : HOA.D07  04/09/10 11:22:39

ample            : sample2 60ppm
)                : sample2
ype              : Unknown
ethod File Name  : HOA.MET

** Chromatogram ***
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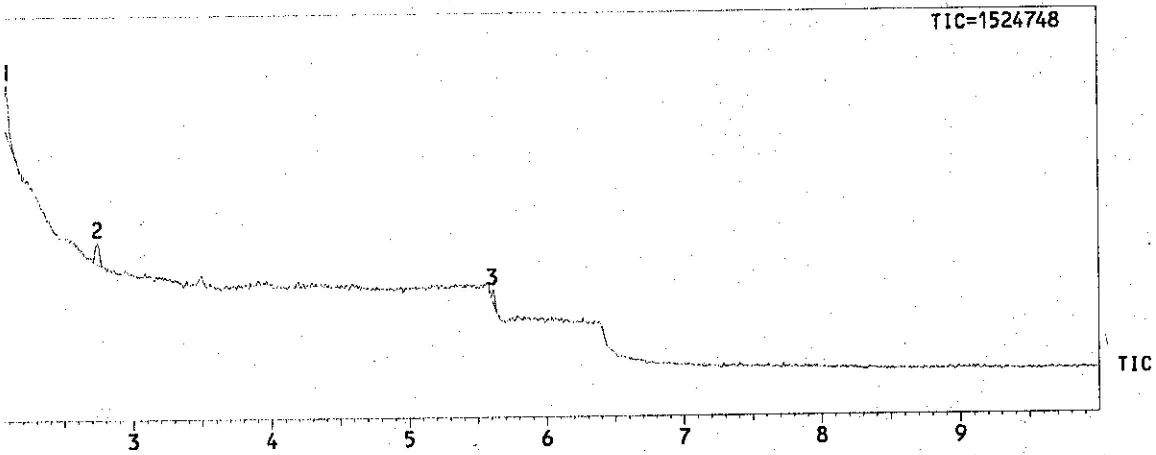

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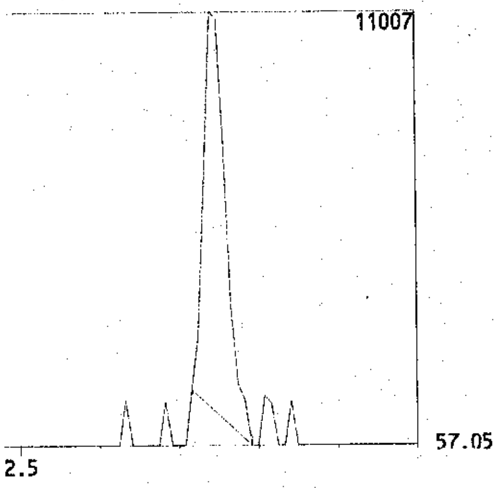

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ID     :  1     M/Z : 57.05
Type   : Target
Name   : hexane

Time   : 2.741
Area   : 19343
Conc.  : 0.382ppm
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CLASS-5000 *** Report No. = 15   Data : HOA.D08 04/09/10 11:55:40

le : sample3 80ppm
: sample3
: Unknown
od File Name : HOA.MET

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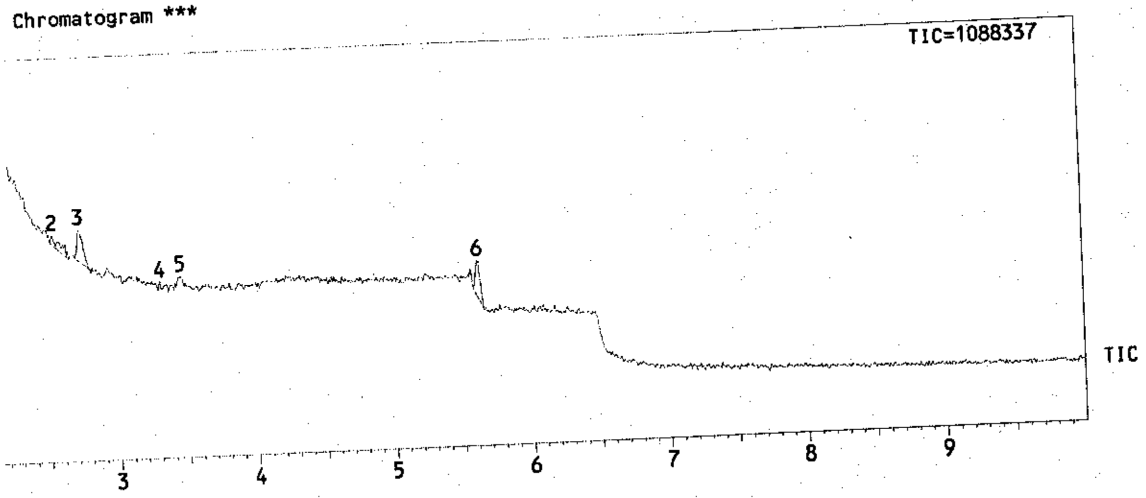

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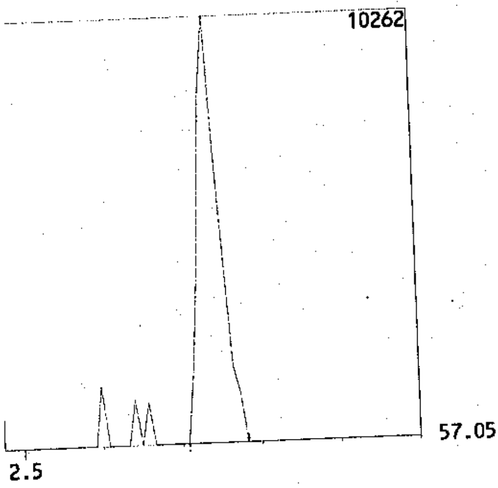

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Type : Target
Name : hexane

Time : 2.737
Area : 19559
Conc. : 0.386ppm

CLASS-5000 *** Report No. = 16   Data : HOA.D09 04/09/10 12:25:25

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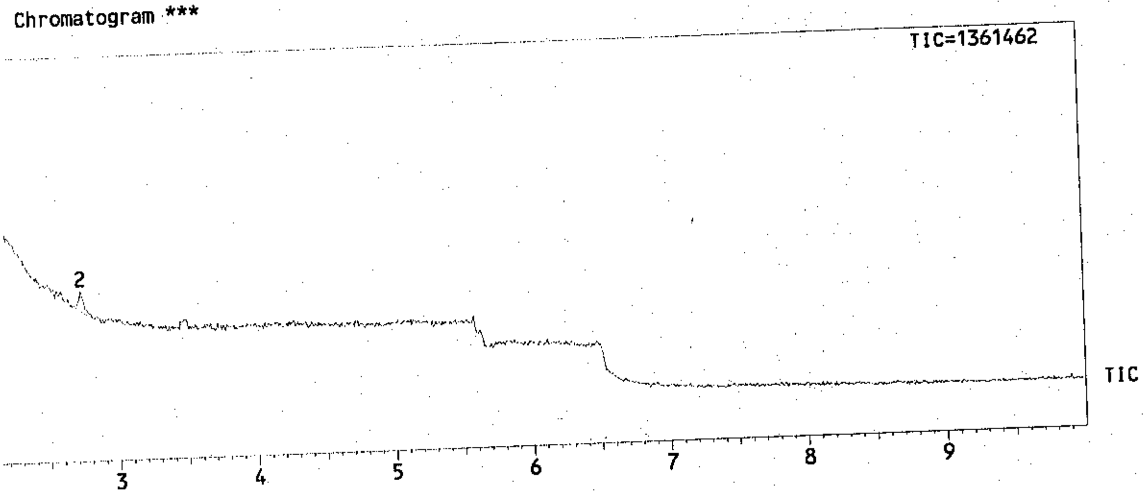
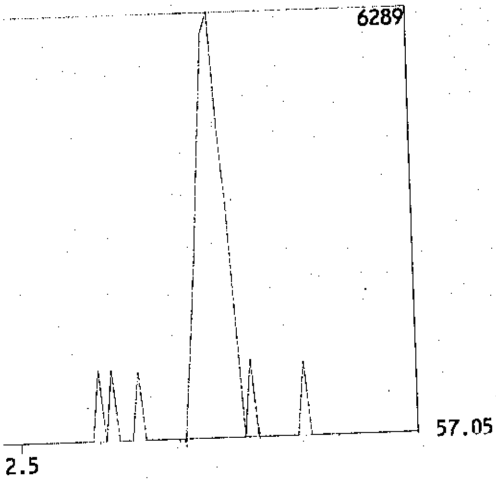
 : sample4
e : Unknown
od File Name : HOA.MET

Chromatogram ***



* Quantitation ***



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Type : Target
Name : hexane

Time : 2.743
Area : 15657
Conc. : 0.309ppm

```
LASS-5000 *** Report No. = 17   Data : HOA.D00  04/09/10 12:55:07

.e            : sample5 120ppm
              : sample5
              : Unknown
ɔd File Name  : HOA.MET
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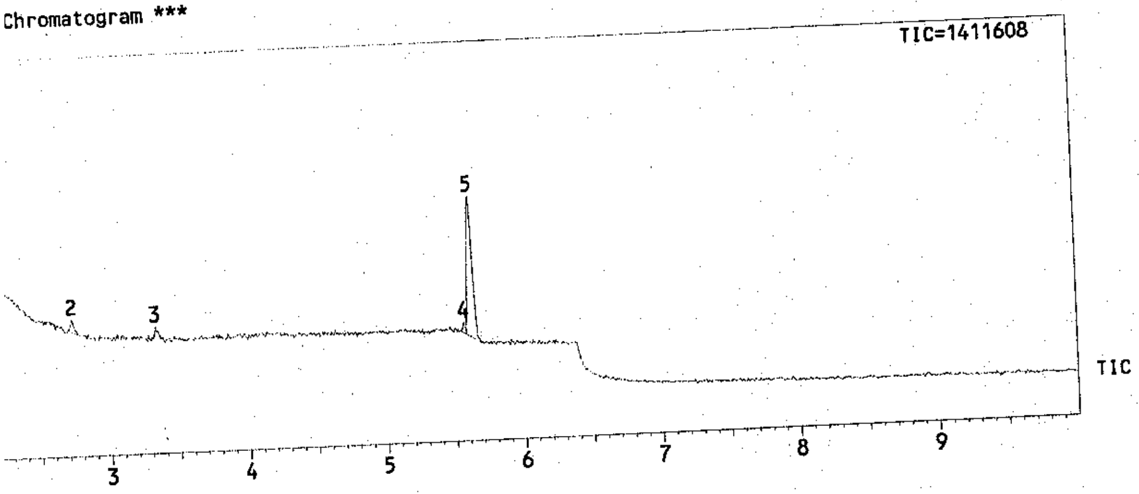
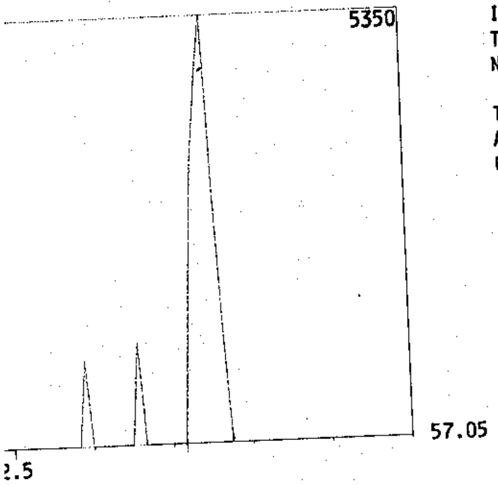
Chromatogram ***



‹ Quantitation ***



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ID      :  1      M/Z : 57.05
Type    : Target
Name    : hexane

Time    : 2.744
Area    : 10132
Conc.   : 0.200ppm
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LASS-5000 *** Report No. = 19   Data : HOA.D13 04/09/10 14:23:55

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: sample8
: Unknown
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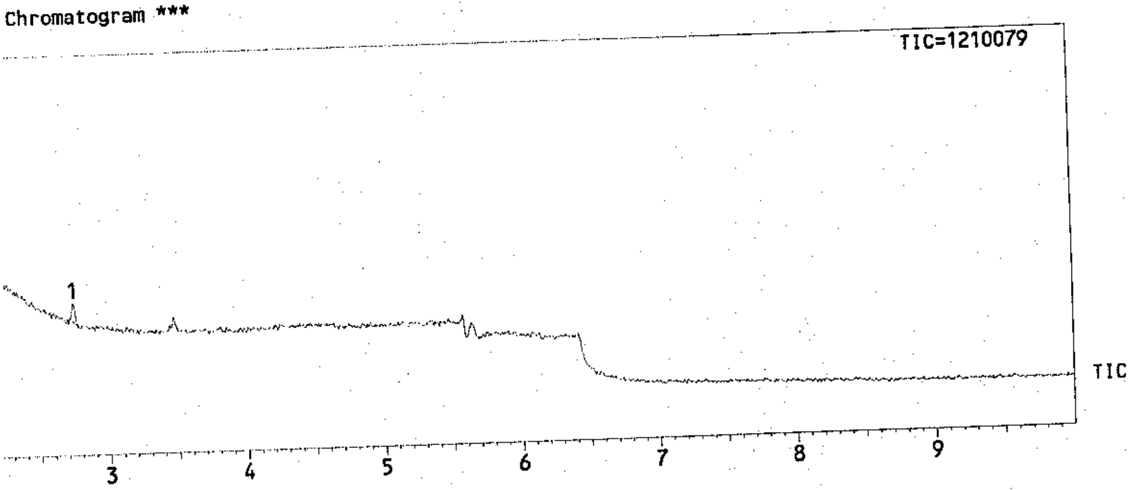
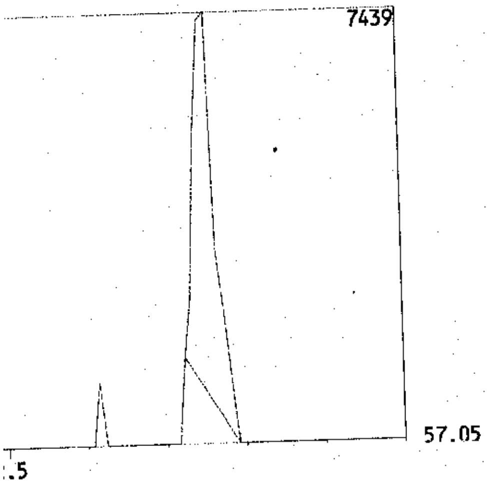
Chromatogram ***



Quantitation ***



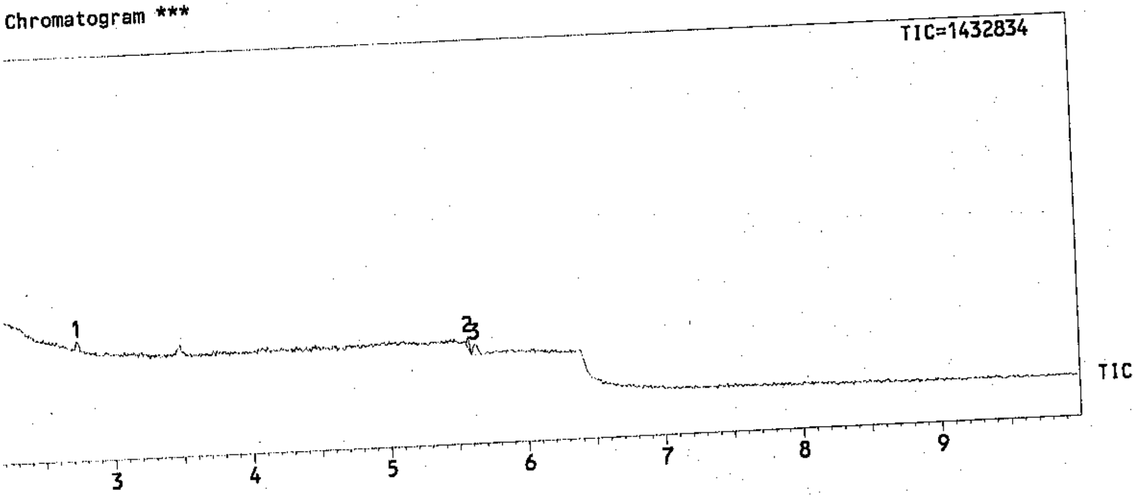
ID : 1   M/Z : 57.05
Type : Target
Name : hexane

Time : 2.750
Area : 11753
Conc. : 0.232ppm

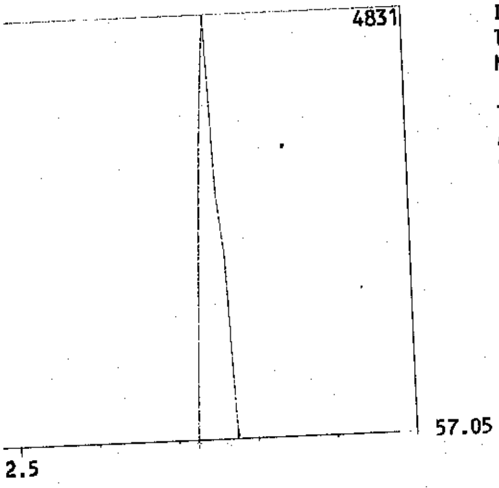
LASS-5000 *** Report No. = 20 Data : HOA.D14 04/09/10 14:53:58

le : sample9 100ppm
: sample9
: Unknown
od File Name : HOA.MET

Chromatogram ***



* Quantitation ***

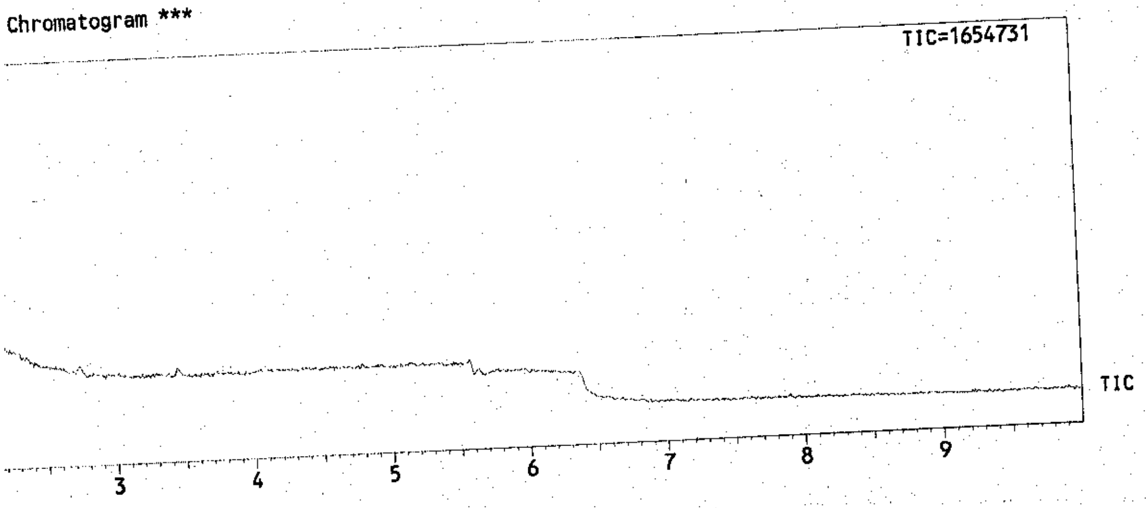


ID : 1 M/Z : 57.05
Type : Target
Name : hexane

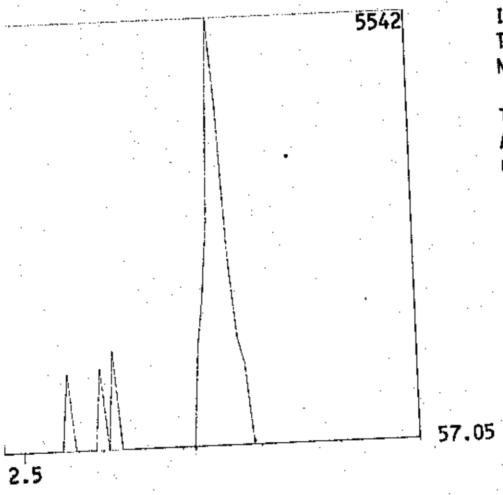
Time : 2.744
Area : 7687
Conc. : 0.152ppm

```
:LASS-5000 *** Report No. = 21   Data : HOA.D15  04/09/10 15:25:03

le              : sample10 120ppm
                : sample10
                : Unknown
od File Name    : HOA.MET
```

Chromatogram ***



* Quantitation ***



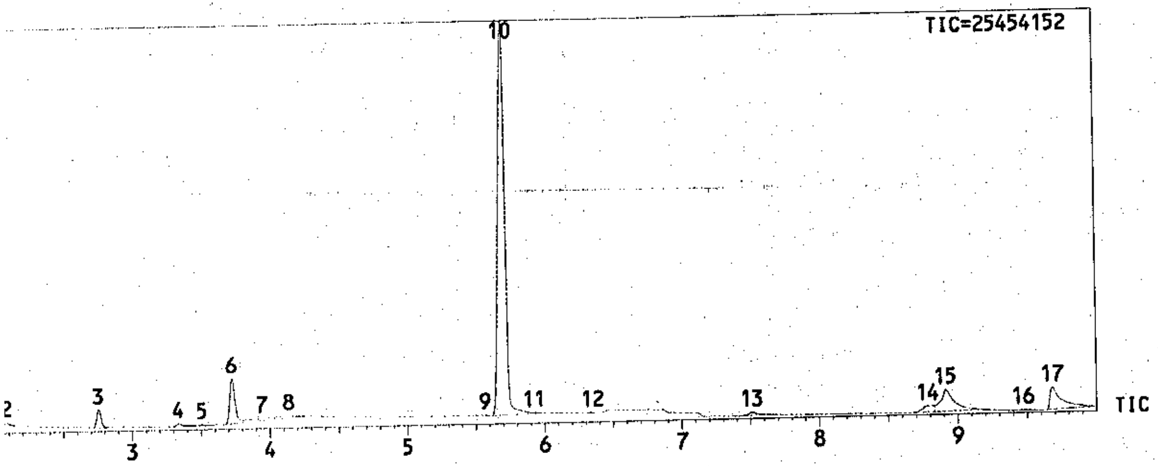
```
ID     :  1      M/Z : 57.05
Type   : Target
Name   : hexane

Time   : 2.747
Area   : 10480
Conc.  : 0.207ppm
```

APPENDIX VI: Results Obtained From GCMS for n-Hexane Volatility Test

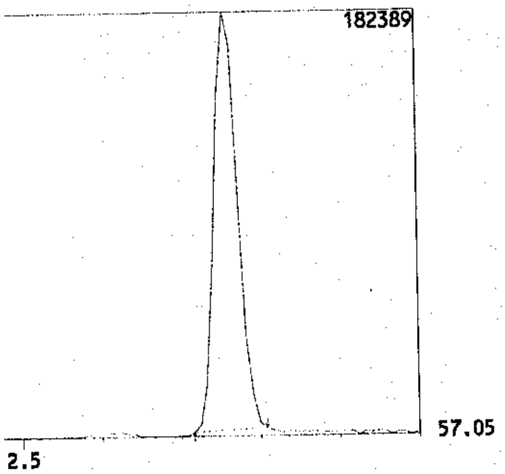
* CLASS-5000 *** Report No. = 22   Data : HOA.D10   04/10/01 10:02:42

mple : hexane30min
: hexane10ppm
pe : Unknown
thod File Name : HOA.MET

* Chromatogram ***



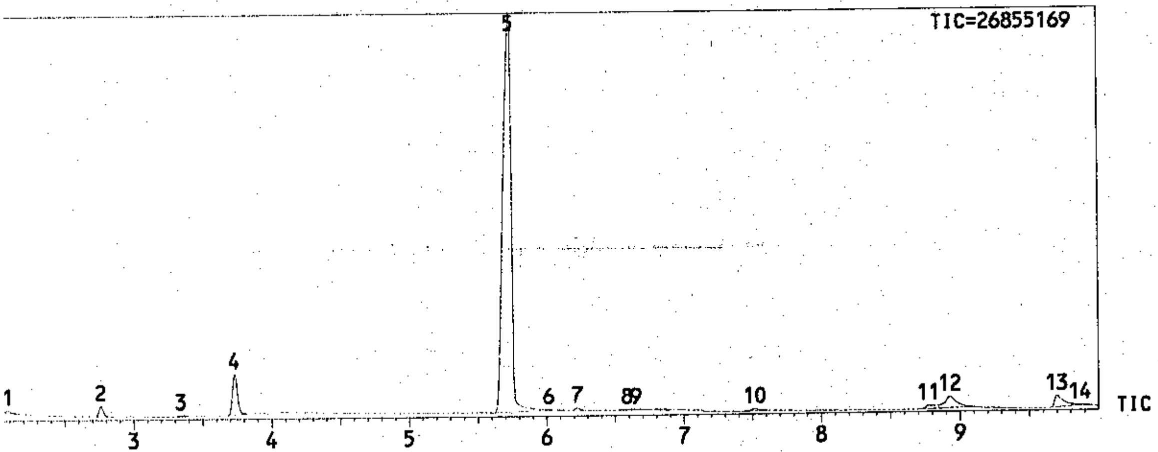
** Quantitation ***



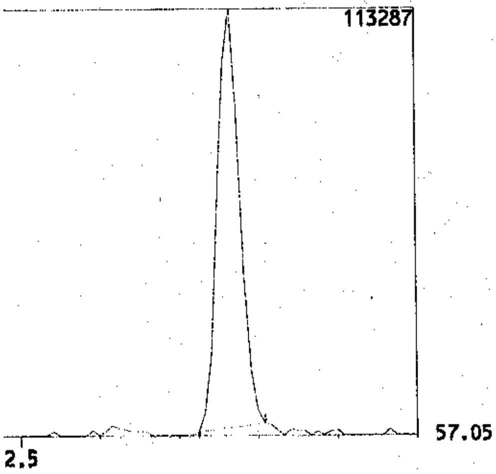
ID : 1   M/Z : 57.05
Type : Target
Name : hexane

Time : 2.756
Area : 369534
Conc. : 7.300ppm

```
** CLASS-5000 *** Report No. = 24   Data : HOA.D12  04/10/01 11:23:11

ample            : hexane1hr
)                : hexane10ppm
ype              : Unknown
ethod File Name  : HOA.MET

** Chromatogram ***
```

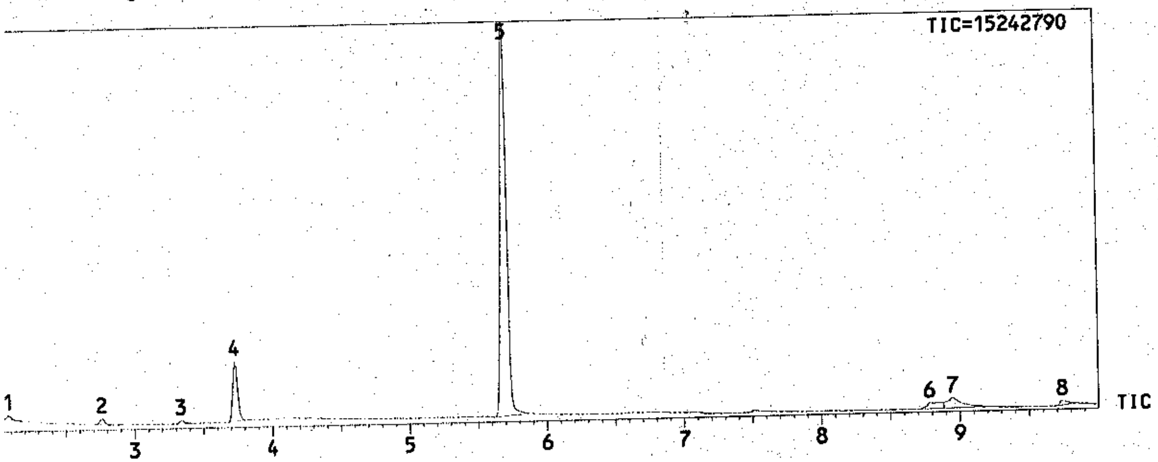


```
** Quantitation ***
```

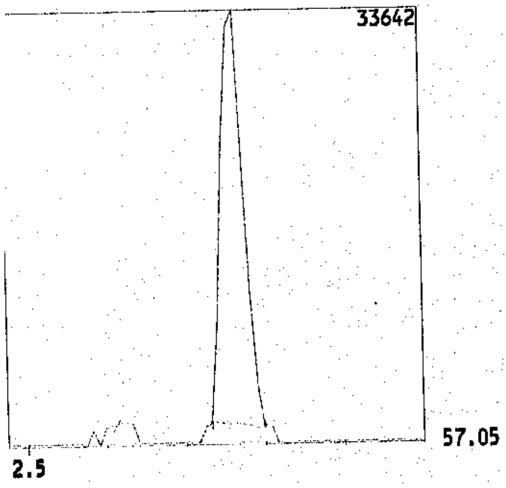


```
ID     :  1     M/Z : 57.05
Type   : Target
Name   : hexane

Time   : 2.761
Area   : 217738
Conc.  : 4.301ppm
```

```
* CLASS-5000 *** Report No. = 27   Data : HOA.D15  04/10/01 13:00:33

mple            : hexane0230hr
                : hexane10ppm
pe              : Unknown
thod File Name  : HOA.MET

* Chromatogram ***
```

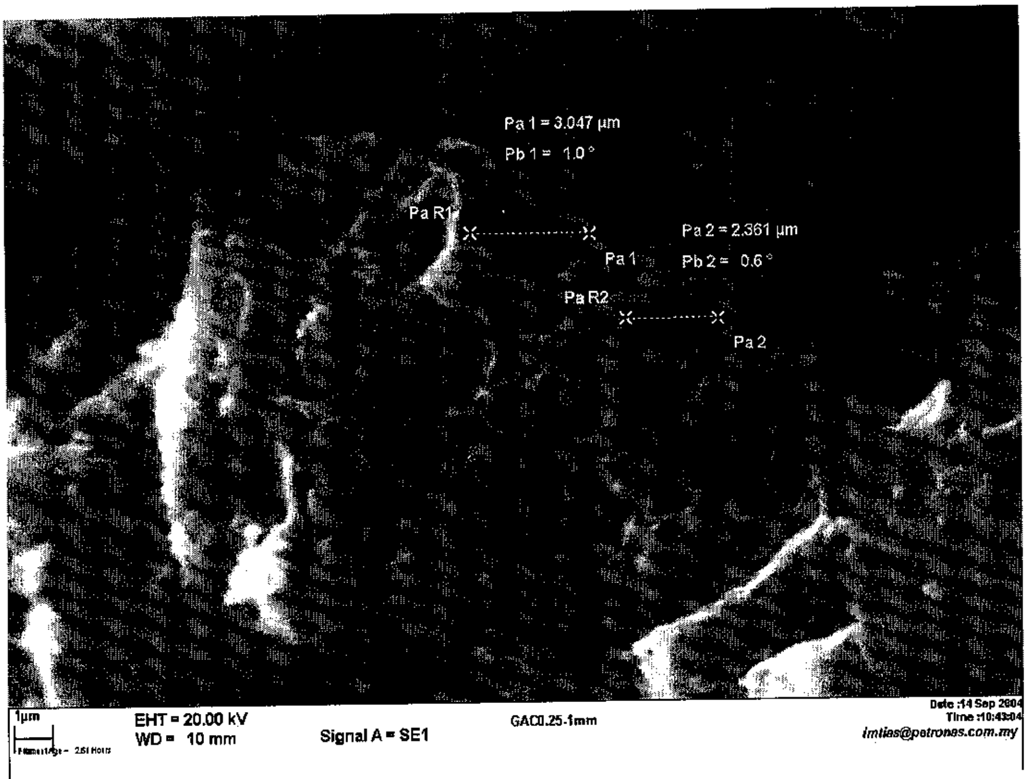


```
** Quantitation ***
```

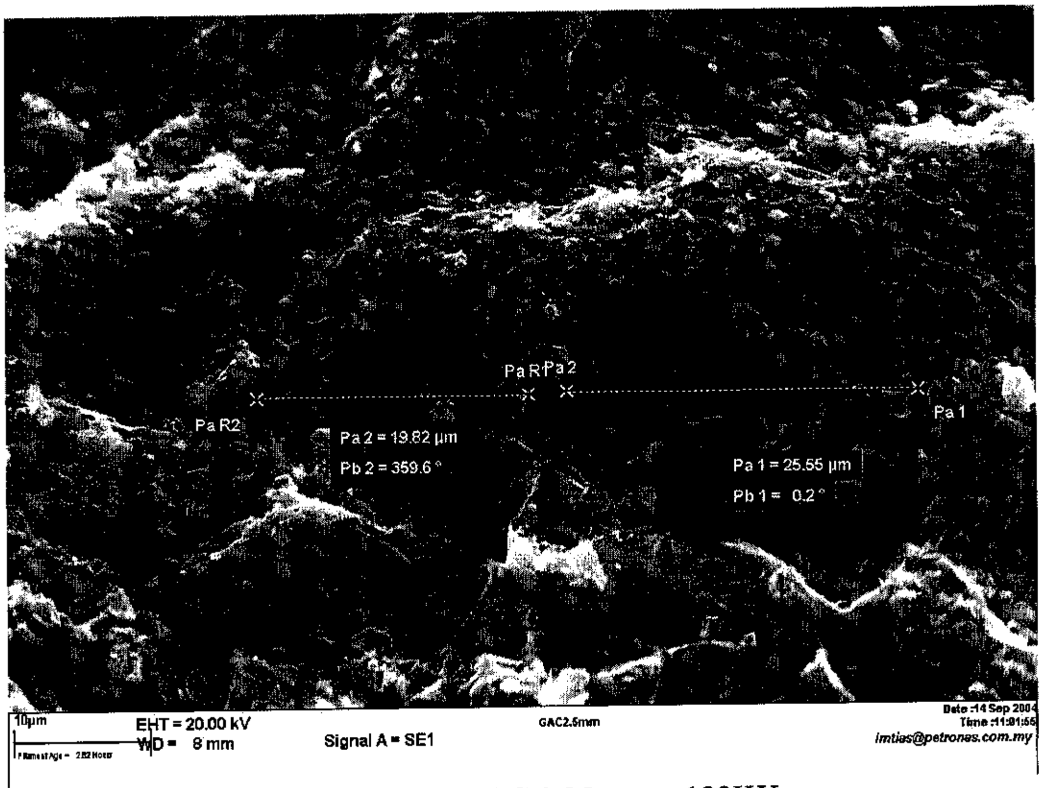


```
ID     :  1     M/Z : 57.05
Type   : Target
Name   : hexane

Time   : 2.759
Area   : 63221
Conc.  : 1.249ppm
```

APPENDIX VII: SEM Micrographs of GAC 2.5mm and GAC 0.25mm



Micrograph of GAC 2.5mm at 3.85KX



Micrograph of GAC 0.25mm at 133KX

APPENDIX VIII : Sips Isotherms for adsorption isotherm measurement at different temperatures using GAC 2.5

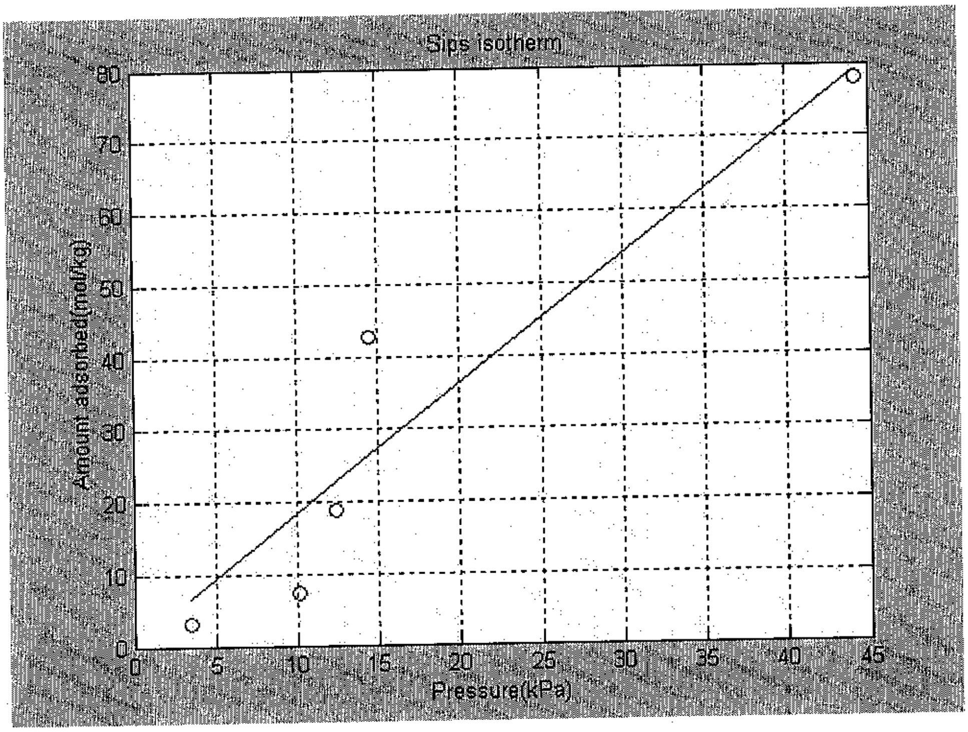


Figure 1: Sips isotherm at 35°C

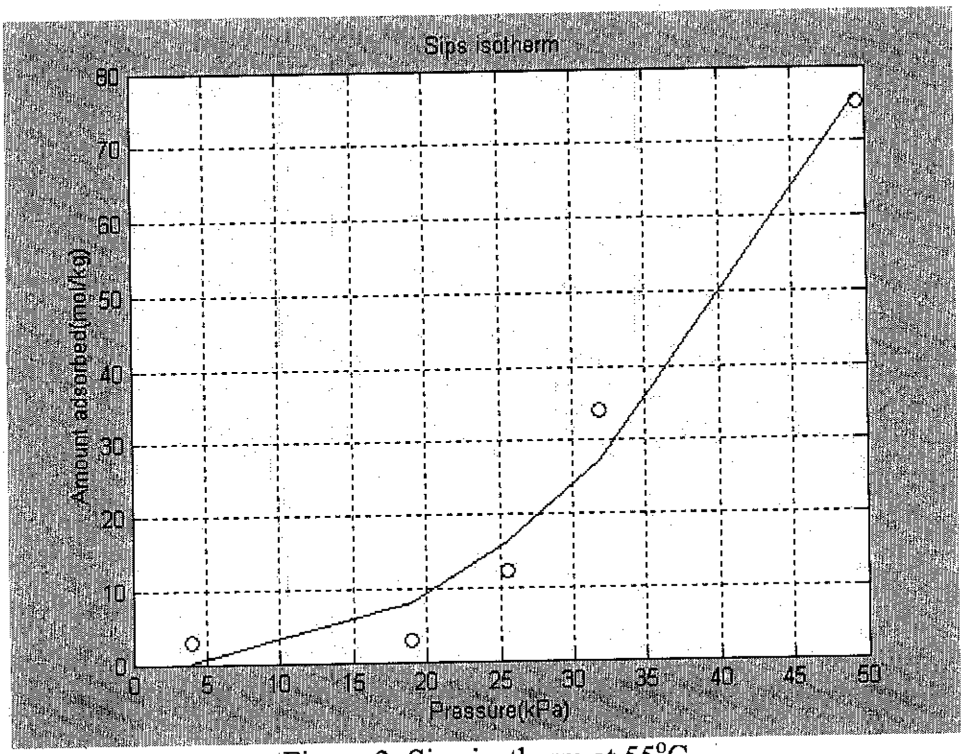


Figure 2: Sips isotherm at 55°C

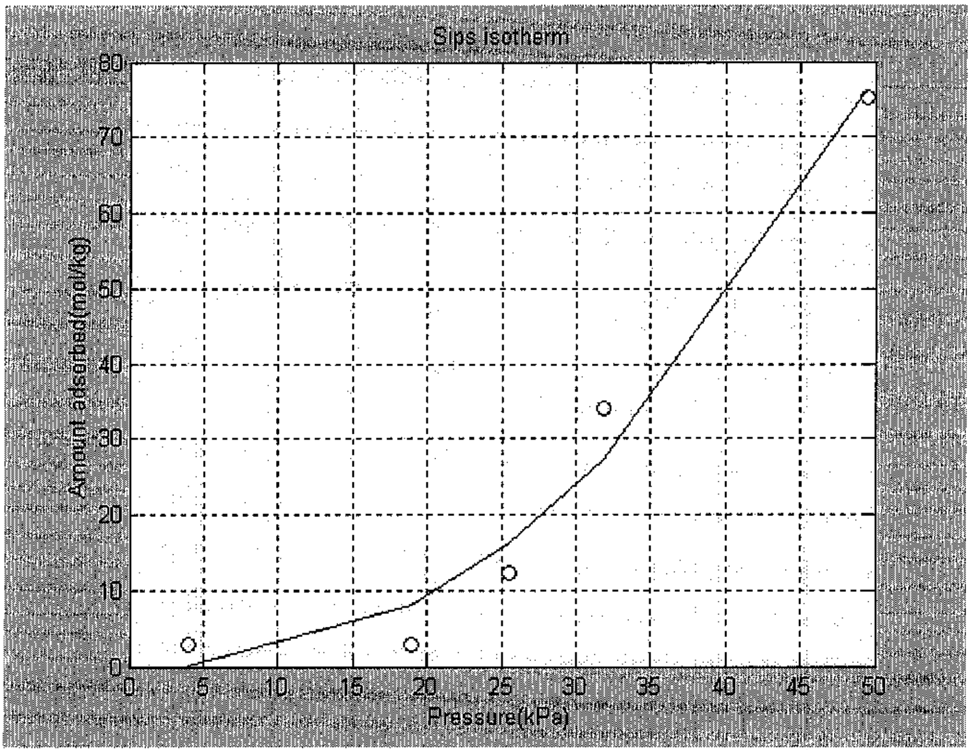


Figure 3: Sips isotherm at 65°C

MATLAB RESULTS

- **35°C**

The reference temperature T0 = 308
cmus0 = 0.82677
b0 = 2.3779
gamma = 3.5248
n0 = 1.02
alpha = 4.9045
deltaT0 = -0.00018264
Residual = 20.4406; Number of iteration = 330; CPU = 0.311 sec

- **55°C**

The reference temperature T0 = 308
cmus0 = 0.28855
b0 = 0.41516
gamma = 10.5162
n0 = 0.59938
alpha = 11.0586
deltaT0 = -0.0049813
Residual = 9.7994; Number of iteration = 403; CPU = 0.34 sec

- **65°C**

The reference temperature T0 = 308

```
cmus0 = 1.0872
b0            = 0.12922
gamma         = 2.0537
n0      = 2.6905
alpha   = 19.1188
deltaT0 = 0.00019204
Residual = 14.9673;   Number of iteration = 921;  CPU = 0.51 sec
```