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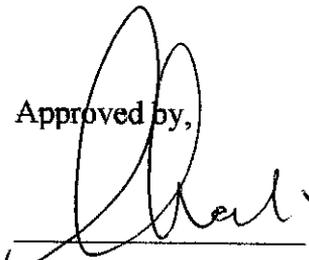
**Production of Granular Activated Carbon from Waste Oil-Palm Shells and Its
Adsorption Characteristics on Benzene**

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.



EE CHANG LIH

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Emission of volatile organic compounds (VOC) has posed serious negative impacts to human health and environment. Studies have recognized their contribution to cancer, reproductive problems, developmental effects, formation of ground level ozone (LaCoss, 2000), stratospheric ozone depletion, and enhancement of the global greenhouse effect. Exposure to benzene is found to result in headache, dizziness, a fast heart rate, tremors, drowsiness and confusion. Benzene can affect the bone marrow by decreasing red blood cells (anemia) or by decreasing platelets, which causes excessive bleeding. High-level exposure to benzene for a long duration is known to cause leukemia and other cancers of the blood-forming organs in humans.

VOCs are chemicals containing carbon that volatilize when they are exposed to air. Organic compounds that have a boiling point $< 100^{\circ}\text{C}$ and/or a vapor pressure $> 1\text{mmHg}$ at 25°C are generally considered to be volatile organic compounds. VOCs are used as fuels (gasoline) and are components of many common household items like cosmetics, perfumes and cleansers. In industry, VOCs are used as degreasers and solvents in dry cleaning. In offices, VOCs can be found in correction fluid. More commonly known VOCs are carbon tetrachloride (CCl_4), benzene and toluene.

The occurrence of VOCs in surface and groundwater can originate from solvents, gasoline, aromatic hydrocarbons, herbicides and pesticides (Cisniega et al., 2002). VOCs are among the most commonly found contaminants in groundwater. Their volatility is the reason they are not often found in concentrations above a few micrograms per liter in surface waters, but in groundwater their concentrations can

be hundreds or thousands of times higher (Masters, 1991). In petroleum refineries (generally before 1990), samples of various process streams were often taken from sample lines by allowing the stream being sampled to flow into the sewer long enough to flush the line and then rinsing and emptying the sample container into the sewer several times to ensure that a representative sample had been collected. After analysis, the remaining sample was usually dumped to the sewer. With a large number of samples collected in various process units, sample stream losses became a significant source of VOC's leak to environment (Michelle Payne, 2002). VOCs readily dissolve and leach into ground water. VOCs occur in numerous products including fuels, solvents, paints, adhesives, deodorants, refrigerants, and combustion exhausts. They are usually released into the environment during their production, distribution, storage, handling, and use and can enter both surface water and ground water supplies from many point and non-point sources (Lopes and Bender, 1998). To make the condition worse, VOCs which have percolated groundwater usually reside from several years to several decades, depending on the flow of the groundwater.

Several technologies are currently available to reduce the concentrations of VOCs in water. Adsorption by granular activated carbon has long been recognized as one of the most versatile adsorbents for the effective removal of organic contaminants in wastewater treatments. Findings that activated carbon could be produced from oil-palm shell (Guo and Lua, 2000, 2002) and the abundant availability and low cost of palm oil-palm shells make granular activated carbon stands up above other VOCs removal methods.

As the largest producer of palm oil in the world, Malaysia generates a large amount of oil palm wastes, an agricultural by-product from palm-oil processing mills. According to a study by Yatim (1996), Malaysia generated 2.4 million tons of palm oil shell every year as waste. However, only about 30% of the shell is utilized, namely for power and fertilizer purposes. This makes oil-palm shell as an appropriate and attractive precursor for activated carbon production to be used in VOCs removal.

1.2 PROBLEM STATEMENT

In recent decades, the extensive amount of VOC used by industrial processes and its existence in water has presented a direct health risk to human. The aspiration of removing VOC using activated carbon produced from waste oil-palm shell is driven by its abundant availability thus lowering the cost of precursor for activated carbon production. Hence, this study aims to examine the technical feasibility of VOC removal using activated carbon by oil-palm shells via evaluation of a number of adsorption parameters. They are carbonization temperature, adsorbent concentration, pH and temperature of synthetic wastewater.

1.3 OBJECTIVES AND SCOPE OF STUDY

The objectives of this study are:

- a) To produce granular activated carbon from waste oil-palm shell under different preparation conditions.
- b) To study the effect of carbonization temperature on benzene and n-hexane uptake by the activated carbon produced.
- c) To study the effect of adsorbent concentration on benzene and n-hexane uptake by the activated carbon produced.
- d) To study the effect of initial solution pH on benzene and n-hexane uptake by the activated carbon produced.
- e) To study the effect of adsorption temperature on benzene uptake by the activated carbon produced.

CHAPTER 2

LITERATURE REVIEW / THEORY

2.1 VOLATILE ORGANIC COMPOUND (VOC)

2.1.1 Definition of VOC

VOC represents photochemical smog precursors, and as such can be generally defined as “any organic compound that participates in atmospheric photochemical reactions.” VOC is in recognition of the combined effect of compounds that contribute to smog formation that may not otherwise have been captured due to individual substances not meeting a usage threshold in their own right. The most common sources of VOCs emissions are from the storage and use of liquid and gaseous fuels, the storage and use of solvents and the combustion of fuels. A pragmatic definition of VOCs is *any chemical compound based on carbon chains or rings (and also containing hydrogen) with a vapor pressure greater than 2mm of mercury (0.27 kPa) at 250 C, excluding methane*. These compounds may contain oxygen, nitrogen and other elements, but specifically excluded are carbon monoxide, carbon dioxide, carbonic acid, metallic carbides and carbonate salts (Australian Government Department of the Environment and Heritage, 2003).

Most fossil fuels consist of a mixture of a number of different carbon compounds and other substances. In many fuels, some of these carbon compounds will meet the above VOC definition, while others will not. Hence it is not possible to describe a particular fuel as a VOC. Rather it is necessary to describe what percentage of the fuel is made up of VOCs.

In a similar way to fuels, VOCs are often a component of products such as paints and solvents. They are found in everyday household items such as paints, paint strippers,

varnishes, lacquers, wood preservatives, craft kits, glues, fuels, aerosols, cleaners, pesticides, cigarette smoke and dry-cleaned clothes. They act as carriers and can dissolve grease. Formaldehyde, benzene, toluene and acetone are all considered volatile organic compounds. VOCs are released into the environment in a number of ways. Paint, furnishings, gasoline, smokes from fires and even stored products such as closed paint canisters may release large amounts of VOCs into the air. Renovation of homes and buildings leads to an accumulation of VOCs within enclosed spaces, thus accounting for higher levels of VOCs indoors compared to outdoors. Once VOCs are released into the environment in the form of gases, they can react with sunlight to form ozone or smog.

Other substances that meet the VOC definition are listed below. They are known for their toxicity to plant, animal and human health.

Table 2-1 Examples of volatile organic compounds

Substance	Substance
Acetaldehyde	Ethyl butyl ketone
Acetic acid (ethanoic acid)	Ethylbenzene
Acetone	Ethylene oxide
Acetonitrile	Formaldehyde (methyl aldehyde)
Acrylonitrile (2-propenenitrile)	n- Hexane
Acrylic Acid	Methanol
Aniline (benzenamine)	2- Methoxyethanol
Benzene	2- Methoxyethanol acetate
1,3 - Butadiene	Methyl ethyl ketone
Chloroethane (ethyl chloride)	Methyl isobutyl ketone
Chloroform (trichloromethane)	Methyl methacrylate
Cumene (1-methylethylbenzene)	Methylenebis (phenylisocyanate)
Cyclohexane	Styrene (ethenylbenzene)
1,2- Dibromoethane	1,1,1,2- Tetrachloroethane
1,2- Dichloroethane	Tetrachloroethylene
Dichloromethane	Toluene (methylbenzene)
Ethanol	1,1,2- Trichloroethane
2- Ethoxyethanol	Trichloroethylene
2- Ethoxyethanol acetate	Vinyl Chloride Monomer
Ethyl acetate	Xylenes (individual or mixed isomers)

There are two thresholds relating to VOCs (Australian Government Department of Environment and Heritage, 2003):

Category 1a

This threshold is tripped if, at a facility, 25 tonnes or more of Total VOCs is used in the reporting period. For example, if a facility uses 300 tonnes per year of a fuel that consists of 10% VOCs by weight, then it is said to use 30 tonnes ($300 \times 10/100$) of VOCs and hence trips this threshold. There is one exemption to this definition. For bulk storage facilities, the threshold is only exceeded if their design capacity also exceeds 25 kilotonnes. It is important to note that this only applies to facilities solely engaged in bulk storage.

Category 2

This threshold is tripped if, at a facility, 400 tonnes or more of fuel or waste is burnt in the reporting period, or 1 tonne or more of fuel or waste is burnt in any hour (peak hourly usage) during the reporting period. If this threshold is tripped, the facility is required to report emissions of a range of substances, including VOCs.

Industry handbooks provide emission estimation techniques for estimating VOCs from fuel burning, fuel storage and other solvent use. For fuel storage, all losses from breathing and refilling are to be regarded as VOCs emissions. For use of solvents, paints and other such products, the VOCs emissions often are equal to the VOCs content of the product.

2.1.2 Some Studies Done for VOC Removal from Water

Table 2.3 shows some studies done previously on the area of VOC removal from water.

Table 2-2 Studies Done on VOC Removal from Water

Reseachers	Mechanisms
Li <i>et al.</i> , 2003	Adsorption using walled carbon nanotubes as an adsorbent
Blume <i>et al.</i> , 1990	Pervaporation
Feng <i>et al.</i> , 1994	
Yang <i>et al.</i> , 1995	
Lan <i>et al.</i> , 1997	
Hitchens <i>et al.</i> , 2001	
Dubray <i>et al.</i> , 2003	Combination of absorption and adsorption
Urutiaga <i>et al.</i> , 2001	Vacuum membrane distillation and pervaporation

2.1.3 Exposures to VOC in Water

Historically, the primary concern of drinking water has been microbial contamination since public health inevitably suffers when control of microbial contaminants is compromised (Craun *et al.*, 1993). Chemical contamination of drinking water, however, is also of concern and has caused national, regional and international regulatory and advisory authorities to set standards and guidelines for acceptable levels of many chemicals, including VOC in water sources.

Exposure to VOC in water occurs when the water is ingested and according to Olin (1998), this has been assumed to be the major or sole route of exposure in the past. However, evidence accumulated from experimental measurements and modeling of exposures to VOC in recent years shows that uptake through the skin and/or by inhalation also contributes significantly to the total adsorbed dose. These findings revealed the VOC threat as there are many uses of water that present opportunities for skin contact or inhalation of VOC. Showering, bathing, cooking, washing clothes or dishes and swimming are examples.

The extent of exposure to VOC in water is a function of fundamental characteristics of the contaminant like chemical structure and functionality and molecular weight, and secondary characteristics like partition equilibria, complex formation, and reactivity. Partition equilibria are critically important in assessing a chemical's tendency to migrate from one environmental medium to another and also in determining the permeability of human tissue to the chemical. Among the partition equilibrium values of interest are solubility in water (the maximum dissolved concentration of a chemical in water at a given temperature) and vapor pressure (a measure of the volatility of a chemical, expressed as the temperature). Most of these values can be found in general sources such as Lange's Handbook of Chemistry (1992), the Handbook of Environmental Data on Organic Chemicals (Vershueren, 1996) and Illustrated Handbook of Physical-Chemical properties and Environmental Fate for Organic Chemicals, Vol I-IV (Mackay *et al.*, 1992a, 1992b, 1993, and 1995).

Impact of plumbing and appliances on water quality characteristics is little known but study done by Weisel and Chen (1994) suggested that it represents a potential source of VOC contamination. Precipitation of calcium carbonate in pipes and plumbing fixtures allows the presence of certain VOC in the water.

Another significant pathway of VOC exposure is through the volatilization of contaminants from water to indoor air. Andelman (1985a, b) reported the release of VOC from drinking water. Experimental and field studies in the later years further explaining this exposure route (Andelman, 1990). Related theoretical assessments were made by McKone (1987), Little (1992), and Wilkes *et al.* (1992, 1996).

2.2 ADSORPTION

2.2.1 Introduction of Adsorption

Adsorption is the change in concentration of a given substance at the boundary between two phases. Adsorption is used to remove components present at low concentration on nonadsorbing solvents or gases and to separate the components in

gas or liquid mixtures by selective adsorption on solids and is normally followed by desorption to regenerate the adsorbents, which include activated carbon, aluminum oxide and silica gel (Seader, 1998). Adsorption generally involves the accumulation of solute on adsorbents' surface area. Naturally, highly porous adsorbents with high surface area are desired to achieve better adsorption. Adsorbents are material that adsorbs solutes to be separated from a solvent. They can be natural or synthetic material of amorphous or microcrystalline structure. The basis of separation of adsorption processes is phase equilibrium between the fluid and sorbed phases for one or many components in adsorption. Sorption equilibrium of single component adsorption is normally depicted in isotherm form.

Depending on the type of phases in contact, adsorption process can occur in the following systems: liquid/gas, liquid/liquid, solid/gas and solid/liquid. However, two main types of adsorption process are solid/gas adsorption and solid/liquid adsorption. Solid/gas adsorption is a condensation process where the adsorption forces the molecules from the bulk phase to within the pores of the activated carbon. The driving force for gas phase adsorption is the ratio of the partial pressure and the vapor pressure of the compound. Solid/liquid adsorption is a process where the molecules move from the bulk phase to being adsorbed in the pores in a semi-liquid state. The driving force of liquid phase adsorption is the ratio of the concentration to the solubility of the compound.

2.2.1.1 Adsorption Isotherms

The most important conception in adsorption science is the adsorption isotherm. It is the equilibrium relation between the quantity of the adsorbed material and the pressure or concentration in the bulk fluid phase at constant temperature. Three common adsorption isotherms are plotted in the Figure 1 below. The concentration in the solid phase is expressed as q , and in the fluid phase as c .

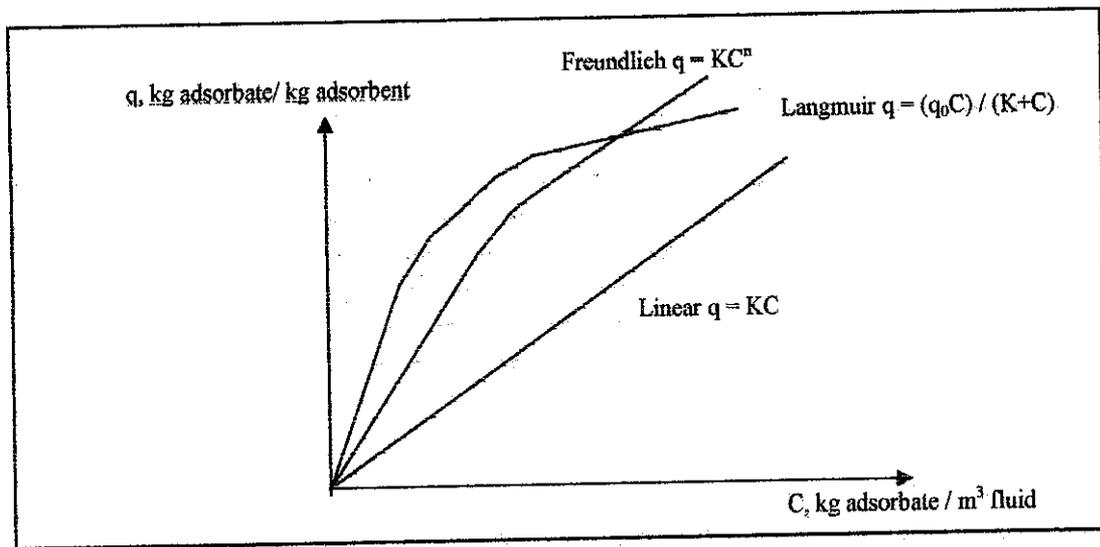


Figure 2-1 Adsorption Isotherms (Seader, 1998)

Data that follows a linear law can be expressed by an equation similar to Henry's law, $q=KC$, where K is an experimental constant, m^3/kg adsorbent. Data that follows Freundlich isotherm equation can be expressed by, $q=KC^n$, where K and n are experimental constant. This isotherm is empirical and approximates data for many physical adsorption systems and is particularly useful for liquids. Data that follows Langmuir isotherm is given by, $q = \frac{q_0 C}{K + C}$, where q_0 is a constant, kg adsorbate/kg solid; and K is a constant in kg/m^3 . This equation was derived assuming that there are only a fixed number of active sites available for adsorption, only a monolayer is formed, and the adsorption is reversible and reaches an equilibrium condition (Geankoplis, 1993).

2.2.1.2 *Physisorption and Chemisorption*

Adsorption process which results from van der Waals universal interactions is known as physical adsorption or physisorption while that from chemical process is known as chemical adsorption or chemisorption. Physical adsorption is a reversible process occurring at a temperature lower or close to the critical temperature of an adsorbed substance. It is always accompanied by a decrease in free energy and entropy of the adsorption system which results from the decrease of freedom degrees of adsorbed molecules. Hence, physical adsorption is always an exothermic process. Chemisorption occurs only as a monolayer (Oscik, 1982). It usually occurs at temperatures much higher than the critical temperature and is a specific process which can occur only if the fluid is capable of forming a chemical bond with the adsorbent. Unlike physisorption, chemisorption is an irreversible process.

2.2.2 *Factors Affecting Adsorption*

As the essential components in an adsorption process, it is natural that the characteristics of adsorbate, adsorbent and the solution affect adsorption process significantly.

2.2.2.1 *Characteristics of Adsorbate*

Adsorbate can affect adsorption process due to its size and molecular form. As adsorbate molecular size increases, its solubility in water tends to decrease. This in turn grants the adsorbate higher affinity for solid surfaces. Hence, the tendency of adsorption to occur is higher. Other than that, it is known that adsorption depends highly on the internal surface area of adsorbent. Large molecular size increases the possibility of adsorption site block and decreases the adsorption performance significantly. Large molecules also tend to diffuse much slower in solution and hence the equilibrium adsorption would be achieved in longer time.

The molecular form of adsorbate include whether an adsorbate is in ionic or neutral state, branched isomer or straight chain. These factors have been known to affect the solubility of the adsorbate, its diffusivity and more importantly, the energy of adsorption. They also determine whether the adsorption is an endothermic or exothermic process, which is vital in determining the best adsorption temperature. Endothermic adsorption is more efficient at higher adsorption temperature. The opposite is true for exothermic adsorption.

2.2.2.2 *Characteristics of Adsorbent*

Adsorbent can affect an adsorption process through its two main properties, physical and chemical properties.

Physical properties include the shape of the adsorbent, surface area, and the composition of pores in the adsorbent. In terms of shape, activated carbon has been produced in granular, particle, and also powder forms. The variety of shape offers differing degree of adsorption performance and hence can be applied in different type of application. Adsorbent surface area and the composition of pores in the adsorbent often directly affect adsorption performance due to the fact that the larger the adsorbent surface area, the more adsorption sites that are available for adsorption.

Chemical properties include the types of functional groups which are present on the adsorbent. Studies have found that the presence of active functional groups on the adsorbent surface allows chemical interactions which usually result in either advantageous or otherwise effect to the adsorption process, depending on other factors involved in the process.

2.2.2.3 *Characteristics of Solution*

Two main solution characteristics which may affect an adsorption process are the pH and temperature.

The pH of a solution is essentially the concentration of hydrogen ions in the solution. With a change in pH, carbon surface properties and hence its behavior change. Carbons behave as a base when $\text{pH} < \text{pH}_{\text{zpc}}$ (zpc, zero point charge) by adsorbing H^+ ions and behave as an acid when $\text{pH} > \text{pH}_{\text{zpc}}$ by adsorbing OH^- ions. Increase of pH decreases the competition between the protons and metal ions for surface sites and results in increased uptake of metal ions by the activated carbon (Savova et al., 2003). Cation adsorption is favorable at pH values greater than that of pH_{zpc} . pH_{zpc} is the pH at which the charge of the surface is zero. pH zero point of charge for different carbons normally lie between pH 3.5 and 5.5. In short, cations sorb at high pH, anions sorb at low pH.

Temperature of a solution may influence the rate of adsorption, either making it faster or slower, depending on the nature of the adsorption process. For an exothermic adsorption process, the rate decreases with temperature. It is the opposite for endothermic adsorption. Temperature also affects solubility of adsorbate in solution. Since solubility and adsorption are inversely related, change in temperature will change the solubility and in turn the extent of adsorption.

2.3 ADSORBENT

2.3.1 Adsorbent Porosity

Adsorbents are solids which have sufficient selectivity and capacity to adsorb species from gases and liquids. The most important criteria for adsorbent is specific surface area (area per unit volume), which is achieved by adsorbent manufacturing techniques resulting in solids with microporous structure (Seader, 1998). Total porosity is classified into three groups. According to the IUPAC recommendation (Everett, 1976), the micropores are defined as pores of a width < 2 nm, mesopores are pores of a width 2-50 nm, and macropores represent pores of a width of > 50 nm.

The significance of pores in adsorption processes depends largely on their sizes. Due to the similar sizes of micropores to those of adsorbate molecules, all atoms or molecules of the adsorbent can interact with the adsorbate species. Hence, adsorption

in micropores is a pore-filling process in which volume of the micropores is of utmost importance.

The basic parameters of mesopores character are specific surface area, pore volume and pore-size to pore-volume distribution. Mesopores have walls formed by a large number of adsorbent atoms or molecules at which the mono- and multilayer adsorption takes place successively. Mesopores and macropores also are essential in the transport of adsorbate molecules inside the micropores volume.

The specific surface area of macropores is very small and hence its contribution to adsorption is usually neglected (Keltsev, 1980).

According to Dubinin and Zaverina (1949), a microporous active carbon is produced when the degree of burn off (weight loss) is less than 50% and a macroporous active carbon when the extent of burn off is greater than 75%. When the degree of burn off is between 50 and 75%, the product has a mixed porous structure and contains all types of pores.

2.3.2 Types of Adsorbent

Carbon, molecular-sieve zeolites, silica gel, and activated alumina are four most widely used adsorbents commercially. Carbon adsorbent can be categorized into two: activated carbon and molecular-sieve carbon. Activated carbon is made by pyrolysis and chemical activation using carbon-rich raw materials, such as coconut shells, wood, coal, and oil-palm shells. Typical pore diameters of activated carbon starts from 10 Å. It is hydrophobic and has high specific surface area for processes involving nonpolar and weakly polar organic molecules. It is popular due to its low adsorption bonding strength which results in low heat of adsorption and hence ease of regeneration of adsorbent. Molecular-sieve carbon, or MSC, has pores sizes from 2 to 10 Å enabling its usage in adsorbing much finer particles.

Silica gel (SiO_2) is made from colloidal silica. Its high affinity for water and other polar compounds makes it highly effective for water removal. Examples of silicate adsorbent are calcium silicate, magnesium silicate and various clays.

Activated alumina (Al_2O_3) is made by removing water from hydrated colloidal alumina. It has moderately high specific surface area. Similar to silica gel, it has high affinity for water and hence is widely used for water removal.

Molecular-sieve zeolites are crystalline inorganic polymers of aluminosilicates and alkali. It is activated by removing water molecules by means of temperature increment or pulling a vacuum. Remaining atoms are left spatially intact in interconnected cagelike structures with six identical window apertures each. Typical aperture sizes are 3.8 to 10 Å. Due to the crystal structure and hence the equivalent size apertures, molecular-sieve zeolites are highly selective.

2.4 ACTIVATED CARBON

Activated carbon is one of the adsorbents used in adsorption processes. Activated carbon is highly efficient adsorbent due to its large number of pores. These produce a large surface area relative to the size of the carbon particles. According to a study, the approximate ratio is 1 g = 100 m² of surface area (Hoehn, 1996). Activated carbon uses attractive van der Waals forces to pull the solute out of solution and onto its surface (Reynolds and Richards, 1996). Activated carbon adsorption proceeds through three basic steps. First, substances adsorb to the exterior of carbon granules. Second, substances move into the carbon pores. Third, substances adsorb to the interior walls of the carbon.

Activated carbon adsorption efficiency decreases with time. Eventually, activated carbons need to be regenerated or replaced. Prediction of amount of solute adsorbed by activated carbon is done using empirical equations called isotherm, as mentioned before.

2.4.1 Preparation of Activated Carbons

Preparation of activated carbon involves the selection of raw material, followed by dehydration, carbonization in inert atmosphere and activation. Different raw material would result in different activated carbon characteristics which include pore structure, particle size, total surface area, and void space between particles (Clark, 1989).

Dehydration of precursors is followed by grinding and sieving into granules of size desired. Carbonization is a process by which solid residues with increasing content of carbon element are formed from organic material usually by pyrolysis in inert atmosphere. The final pyrolysis temperature controls the degree of carbonization and the residual content of carbon elements. Mass fraction of carbon content in solid residue increases as pyrolysis temperature increases. Through carbonization, volatile matters are eliminated, hydrogen is lost, and a fixed carbon mass with a rudimentary porosity is formed.

Pore structure is then further developed during activation. This step is to enhance the volume of pores, to enlarge the diameters of the pores created during the carbonization process, and to create new porosity. Two main types of activation are chemical activation and physical activation. Chemical activation usually is carried out when the raw material is of wood origin. Raw material is impregnated with the activating agent concentrated solution usually by physical contact with constant agitation. The most widely used activating agents are phosphoric acid, zinc chloride and sulfuric acid, although potassium sulfide, potassium thiocyanate hydroxides and carbonates of alkali metals, chlorides of calcium, magnesium, and ferric iron have also been suggested. On the other hand, NaOH and KOH have been used by Lozano et al. (2001), Lillo-Rodenas et al. (2001), Qiao et al. (1997) and Hu et al. (1999) to prepare activated carbons with high specific surface area. Physical activation is the process through which the carbonized product develops an extended surface area and a porous structure of molecular dimensions under high temperatures heating of between 800 and 1100°C in the presence of suitable oxidizing gases such as steam, carbon dioxide, air or any mixture of these gases. Of the two activation methods, chemical activation is preferred because it is performed in a single-step (in the

presence of chemical reagents), the process normally takes place at temperature lower than that used in the physical activation processes, and the yields of carbon are usually high (A. Garcia-Garcia). Table 2-3 below shows the activation processes and agents used for the production of activated carbon.

Table 2-3 Activation processes and agents used for the production of activated carbon

Researchers	Activation Process	Activating Agents
Guo and Lua, 2001	Physical activation	CO ₂ gas
Hu et al., 2002	Chemical Activation	ZnCl ₂ and KOH
Tsai et al., 2000	Chemical Activation	KOH and K ₂ CO ₃
Lafi, 2000	Chemical Activation	Phosphoric Acid
Hayashi et al., 2002	Chemical Activation	K ₂ CO ₃
Kim et al., 2001	Chemical Activation	ZnCl ₂ and CaCl ₂
Hu et al., 2000	Chemical Activation	ZnCl ₂
Hu and Vansant, 1994	Chemical Activation	KOH
Ng et al., 2002	Physical Activation	Steam
Sirichote et al., 2002	Chemical Activation	ZnCl ₂
D. Lozano-Castello et al., 2001	Chemical Activation	KOH and NaOH

2.4.2 Factors Affecting Activated Carbon Production

Carbonization temperature and time are known to have great influence on the micropore structures of activated carbon, which determines the adsorption capacity (Zhonghua et al., 1995). Higher carbonization temperature and time produces activated carbon with higher pore volume and surface area which result in better adsorption capacity. However, if the temperature and/or time are too high for the raw

material used, the yield of activated carbon decreases and possesses lower adsorption capacity due to thermal degradation (Zhonghua et al., 1995).

Study done by Lainé et al. (1991) showed that activation temperature determines the development of microporous structure of activated carbon. Well developed micropores can provide the adsorbent with a high specific surface area and adsorbability. At low temperature, activation is not sufficiently accomplished and elements such as H, O, N, and S remain in large amounts along with C after thermal treatment. Hence, yield of activated carbon is expected to decrease as the activation temperature becomes higher. According to Mameri et al. (2000), adsorption capacity also rises with activation time. This can be explained by better pores development as more time is allowed for proper pore development.

Concentration and amount of activating agent solution affects the adsorption capacity of activated carbon. Study by Garcia-Garcia found that microporosity development depends heavily on the activating agent to raw material ratio. Micropore volume increases linearly with the amount of activating agent added up to a certain ratio, which is distinct for different raw material.

2.4.3 Types of Activated Carbons

Three main forms of activated carbon are granular activated carbon, powder activated carbon and pelleted activated carbon. Powder activated carbons (PAC) are pulverized carbons with a size of less than 0.18 mm. Their relative small size results in less diffusional resistance to adsorption and hence higher adsorption rates. They are commonly used in liquid phase application and flue gas treatment. PAC is directly added to the solution, and is separated via filtration subsequently. Granular activated carbons (GAC) are irregular shaped particles with sizes ranging from 0.2 to 5 mm. They are used in both liquid and gas phase applications. Pelleted activated carbons are extruded and cylindrical carbons with diameters from 0.8 to 5 mm. They are mainly used in gas phase application due to their low pressure drop, high mechanical strength and low dust content.

2.4.4 Applications of Activated Carbons

Activated carbons high specific surface area, highly developed porosity and hence large capacity for adsorbing chemicals from liquids or gases make them versatile adsorbents for industrial applications.

2.4.4.1 *Liquid-phase adsorption*

As regards to liquid-phase adsorption, activated carbon is mostly used in water treatment. It is used to remove synthetic organic chemicals such as pesticides, detergents, and natural organic materials such as hydrophilic acids, and proteins. The most popular type of activated carbon for this purpose is granular activated carbon. Besides removals of organics, it also improves taste and odor of water; both are two important parameters of drinking water.

Activated carbon is also important in the removal of color from sugars and purification of various foods and beverages. Sugar solutions contain coloring matter such as caramels which either originate from the raw material or formed during the refining process. Activated carbon also removes colloidal substances by raising their surface tension and decreasing their viscosity. Powdered activated carbon and granular activated carbon are commonly used in sugar industry.

Another use of activated carbons is in the recovery of gold from its ores (Bansal et al., 1988). In this application, a very dilute solution of NaCN and oxygen is used to treat finely ground ore. Gold and other metallic impurities in the ore are oxidized and form cyanide complexes. The gold is then recovered from the cyanide by adsorption on activated carbons.

2.4.4.2 *Gas-phase adsorption*

Application of activated carbon in gas-phase adsorption is mostly in industry solvent recovery. Activated carbon for this application requires high adsorption capacity and

ability to withstand thermal regeneration and resistance to attrition losses due to cyclic processes.

Another use of activated carbon is the prevention of gases contaminants from release to atmosphere. This sees activated carbon used alongside ventilation units to form activated carbon filters. Similar usage of activated carbon is in production of toxic gases protecting mask for military purposes. Activated carbon is impregnated with various metal compound to increase the reactivity and hence adsorption of some toxic chemicals.

Domestic use of activated carbon is seen in hospitals and offices as air purifier. The activated carbon should have high amount of micropores for effective adsorption at low pollutant concentrations (Bansal et al., 1988).

2.4.5 Raw Materials for the Production of Activated Carbons

The main characteristics for a good raw material as precursors of activated carbon preparation are:

1. Potential for obtaining high-quality activated carbon.
2. Presence of minimum inorganic.
3. Volume and cost of the raw material.
4. Storage life of the raw material.
5. Workability of the raw material.

Table 2-4 Past Studies on Preparation of Activated Carbon from Various Raw Material

Researchers	Raw Material Used
Guo and Lua, 2000, 2002	Waste Palm Oil Shells
Tsai et al., 2000	Waste Corn Cob
Lafi, 2000	Acorns and Olive Seeds
Hayashi et al., 2002	Chickpea Husks
Kim at al., 2001	Waste Walnut Shells
Ng et al., 2002	Pecan Shell
Sirichote et al., 2002	Pericarp of Rubber Fruit, Coconut Shells
Rahman and Saad, 2003	Guava Seeds

CHAPTER 3

METHODOLOGY / PROJECT WORK

3.1 RAW MATERIAL

The raw material, waste oil-palm shells are procured from a Tung Hup Palm Oil Mill Sdn. Bhd. The shells are dried at 110°C for 24 hours in oven to reduce the moisture content. They are then grinded and sieved to obtain particle size fraction of 1 – 2 mm prior to carbonization. Sodium hydroxide is used as the activating agent. Table 3.1 and 3.2 show the characteristics of coconut shell.

Table 3-1 Characteristics of raw and carbonized oil-palm shell

Parameters	Raw oil-palm shell	Oil-palm shell charcoal
Solid density (g/cm ³)	1.53	1.63
Apparent density (g/cm ³)	1.47	1.35
Porosity (%)	3.9	7.2
Volatile matter (wt%)	77.6	30.6
Fixed carbon (wt%)	19.8	63.4
Ash (wt%)	2.6	6.0
BET surface area (m ² /g)	1.6	176
Micropore surface area (m ² /g)	0.2	108

Source: Guo *et al*, 2002

temperature) with 100 ml of benzene or n-hexane solutions in sealed beakers. The initial analyte concentration was prepared in the range of 50, 100 and 200ppm for adsorption experiments with different initial benzene concentrations. The final adsorbent concentration was 1.5 g/l unless otherwise stated. The bottles were placed in a temperature-controlled shaker (Yamatake SDC 10 water bath shaker) for proper contact. To ensure equilibrium, bottles for all experiments were left in the shaker for 24 h. After the contact time, an aliquot of the solution was drawn off and preserved in sealed beakers under refrigeration temperature until analyzed by gas chromatography for residual organics in the samples. The procedure is repeated using activated carbon prepared at 400°C and 700°C carbonization temperature to compare the *effect of carbonization temperature*.

The uptake, q , was calculated from the difference between the initial and the final analytes concentration as follows:

$$q = \frac{(C_0 - C_f)V}{M}$$

where q is the uptake (ppm), C_0 is the initial analyte concentration, C_f is the final analyte concentration (ppm), M is the adsorbent dosage (g), and V is the solution volume (ml).

Effect of Initial pH

The effect of solution pH was studied by performing the adsorption experiments at three different pH levels: 3, 6, 9. The solution pH adjustment was achieved by addition of appropriate amounts of either 0.1 M HCl or 0.1 M NaOH solutions.

Effect of Adsorbent Concentration

The effect of adsorbent concentration was examined by conducting adsorption experiments with different concentration (loading ratio): 0.5, 1.5, and 2.5 mg/ml with a fixed initial benzene and n-hexane concentration of 200 ppm.

Effect of Adsorption Temperature

Adsorptions were conducted at 30, 40 and 60°C in order to investigate the effect of adsorption temperature on the adsorption process. 200 ppm benzene solution was used in this study.

CHAPTER 4

RESULTS AND DISCUSSION

Numerous studies (as discussed in Literature Review) have found and proven the seriousness of volatile organic compounds threat to human health. Activated carbon produced from various raw materials has had excellent past track record in metal, dye, and volatile organic compounds removal. In view of the abundance of waste oil-palm shell in Malaysia, activated carbon produced from it would prove to be an excellent alternative in volatile organic compounds removal from aqueous solution. Hence, the production of activated carbon from waste oil-palm shell was proposed and studied. Benzene and n-hexane uptake by the activated carbon were done and the impacts of various adsorption parameters were analyzed.

This chapter has been structured into the following sections to provide a systematic presentation to the readers.

Section 1. Elemental analysis of activated carbon

Section 2: Adsorption Studies

- Effect of carbonization temperature
- Effect of adsorbent concentration
- Effect of initial solution pH
- Effect of adsorption temperature

Section 3: Adsorption Isotherms

4.1 ELEMENTAL ANALYSIS OF ACTIVATED CARBON

Carbon, hydrogen, nitrogen and sulfur content of oil-palm shells after carbonization and after chemical activation were determined using a CHNS analyzer.

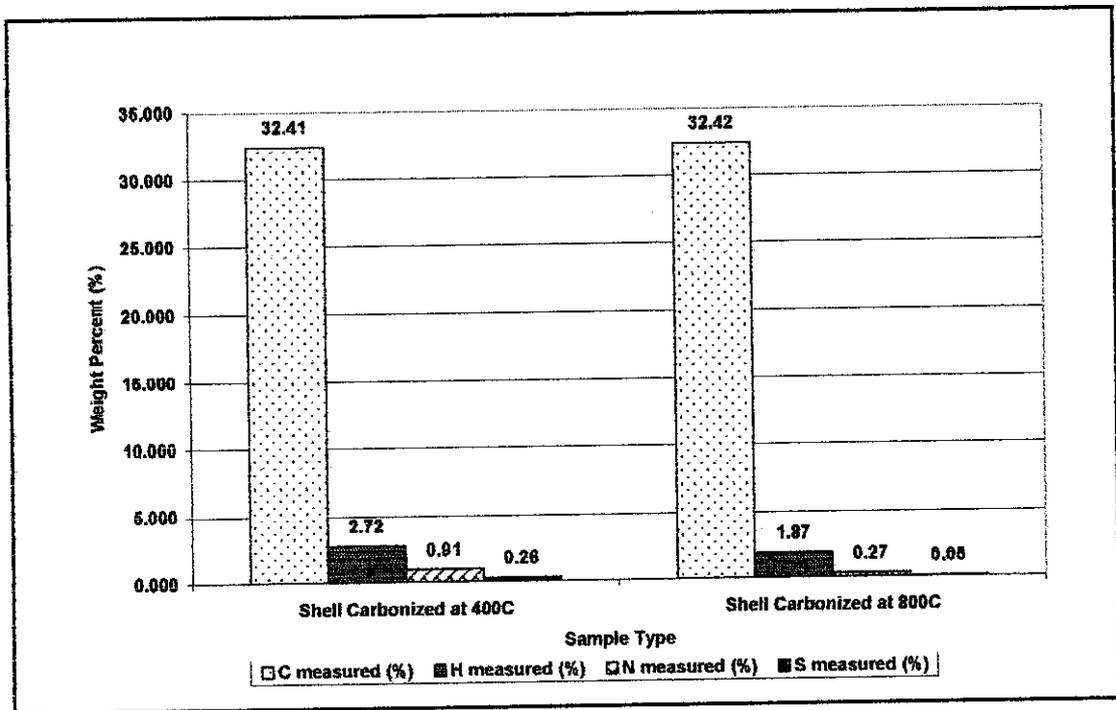


Figure 4-1 CHNS content of charcoals at various carbonization temperature.

Figure 4-1 shows that the carbon content of shells carbonized at 400°C is 32.41% while that carbonized at 800°C is 32.42%. This indicates that with higher carbonization temperature, the removal of volatile matter is better. The amount of H, N and S measured in shells carbonized at 800°C are found to be lower than that found in shells carbonized at 400°C. At both carbonization temperatures, volatile matter is removed and thus reduces the total weight of sample, which in turn causes carbon remained to become higher in weight percent.

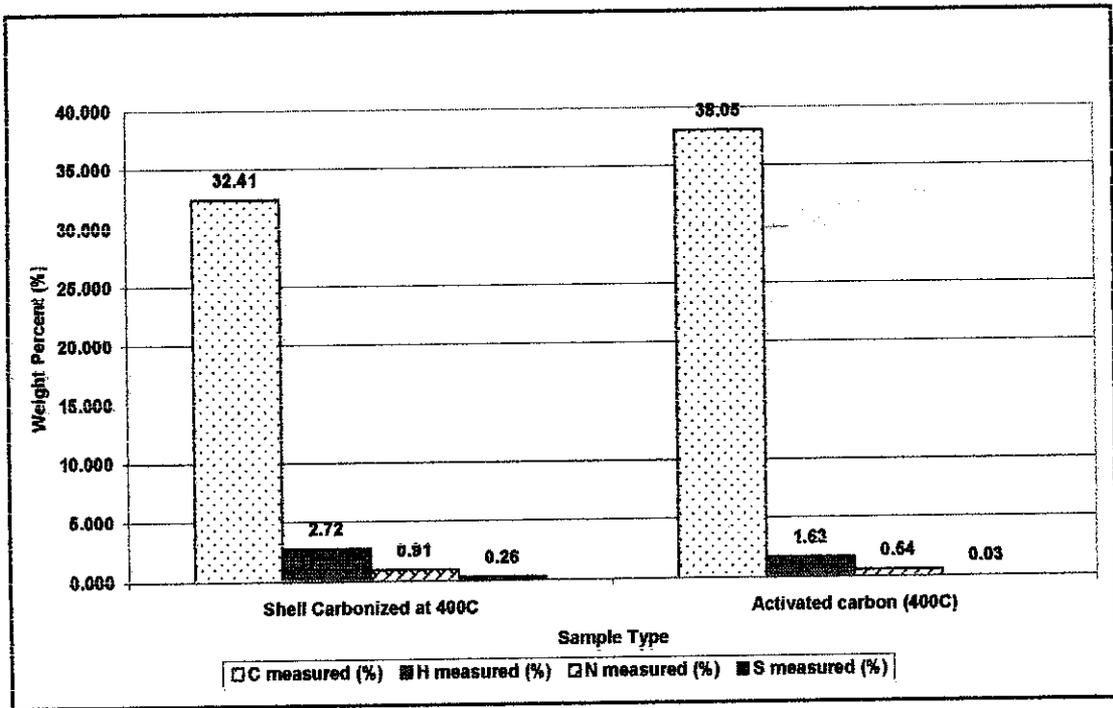


Figure 4-2 CHNS content comparison between shells before and after chemical activation (carbonized at 400°C).

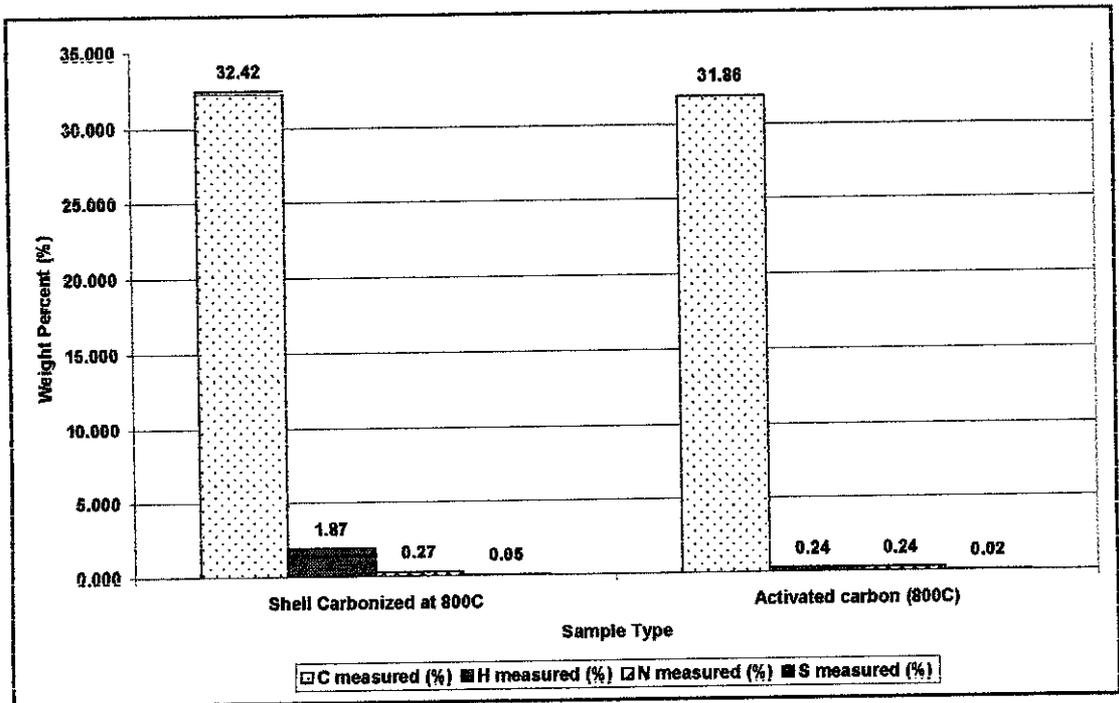


Figure 4-3 CHNS content comparison between shells before and after chemical activation (carbonized at 800°C).

Results shown in Figure 4-2 and 4-3 demonstrate that the carbon weight % in samples increases after chemical activation and other elements, i.e. hydrogen, nitrogen, and sulfur are further reduced. This observation is inline with literature (A. Garcia –Garcia) which states that the yield of carbon is increased through chemical activation.

Figure 4-1, 4-2, and 4-3 only show the weight percent of the four elements in the samples analyzed but offer no indication on the distribution of pores, surface area, and hence do not provide direct relation to the adsorption performance of the activated carbon produced. Further more, CHNS analyzer only takes a very small portion of each sample, i.e. 2 mg in each analysis. Oil-palm shells are not homogeneous, which means that the elements composition is not the same in every granule of shells. Hence, 2 mg of sample is too tiny to give a good presentation of the overall content of a sample type. This error is however reduced by taking 2 mg from 2 quadrants drawn across a piece of paper on which the shells are spread as evenly as possible.

4.2 ADSORPTION STUDY

4.2.1 Effect of Carbonization Temperature

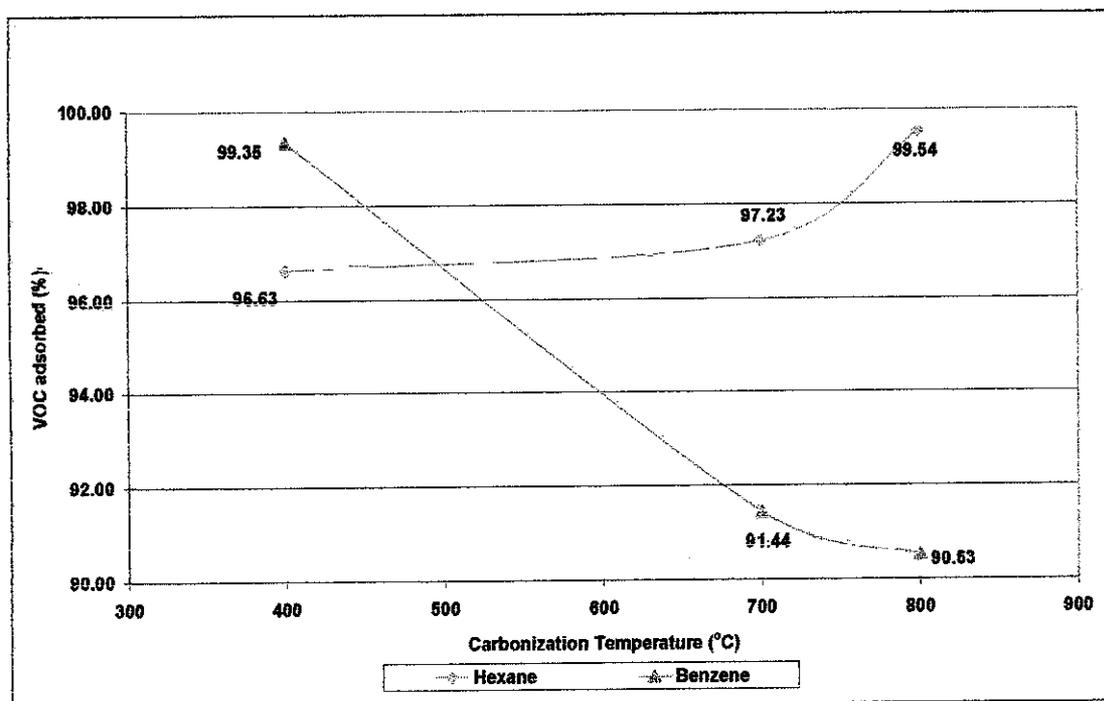


Figure 4-4 Effect of carbonization temperature on the removal of benzene and n-hexane.

In order to study the effect of carbonization temperature on benzene and n-hexane removal, three batches of activated carbons, produced at carbonization temperatures of 400°C, 700°C and 800°C were contacted with a fixed initial benzene and n-hexane concentration of 200ppm. Figure 4-4 is plotted using results from sample A1, B1, C1, A2, B2, and C2 (refer Appendix I). Adsorbent concentration is fixed at 1.5 g/l while adsorption temperature is constant at 30°C. From Figure 4-4, it can be observed that for n-hexane adsorption, as the carbonization temperature increases, the percentage adsorbed also increases. However, adsorption of benzene shows opposite trend.

The adsorptive capacity of activated carbon is related to the specific pore surface area. Generally, the higher the pore surface area of the activated carbon, the larger is

its adsorptive capacity. Hence, the effect of carbonization temperature on the adsorption of benzene and n-hexane is discussed from the aspect of percentage of burn-off or weight-loss after carbonization.

From Table 4-3, it can be seen that as carbonization temperature is increased, the percent burn-off increases, and hence the increase in BET surface area, and surface area based on Langmuir and Dubinin-Raduskevich equations. Similar findings were reported by D. Lozano et al. (2002) and A. Ahmadpour et al. (1997). These reports explain the better n-hexane uptake when carbonization temperature of activated carbon is higher.

Apart from that, J. Guo et al. (2002) reported that increasing the carbonization temperature from 500°C to 900°C increased the solid density and decreased the apparent densities, resulting in the development of porosity. Daud et al., 2002 and Vilaplana-Ortego et al., 2002 observed that micropore volume increases almost linearly with the increase in burn-off. Hence, it can be concluded that as carbonization temperature is increased, the percent burn-off increases, which results in the increase of micropore volume in activated carbon that is responsible for the better adsorption capacity of n-hexane, as shown in Figure 4-4.

At lower carbonization temperature, activated carbon produced possesses more mesopores as compared to those produced at higher carbonization temperature as the micropores have not been fully developed. Analysis by Daud et al., 2002 based on cumulative pore volume indicates that mesopores volume almost linearly decreased upon increasing the carbonization temperature on the macropore volume. This also means that mesopores volume is higher when the carbonization temperature is lower. In view of that, the deterioration in benzene adsorption with increase of carbonization temperature suggests that micropore volume is not useful for benzene uptake by activated carbon. The benzene curve in Figure 4-4 deduces that mesopore and macropore could be more important in the adsorption of benzene from aqueous media. The discrepancies between the benzene and n-hexane curves also indicate that the molecular size of solutes has a significant role in the adsorption process, which was also observed in the study by F. Banat et al. (2003).

Table 4-1 Surface Area of Activated Carbon Produced from Waste Palm Oil Shell at Various Burn - offs and Activation Temperature by Daud et al., 2002

Carbonization Temperature (°C)	Burn - off (%)	S_{BET}^a (m²g⁻¹)	S_{Lang}^b (m²g⁻¹)	S_{DR}^c (m²g⁻¹)
800	36.2	533	794	790
	37.6	561	834	829
	49.4	797	1187	1179
	58.5	954	1425	1413
	63.9	1022	1530	1514
850	35.2	516	768	763
	43.4	593	1030	1025
	51.9	839	1250	1248
	57.3	935	1395	1348
	77.4	1400	2129	2019
900	38.8	544	810	806
	49.4	783	1168	1162
	64.2	1111	1666	1652
	70.4	1232	1862	1977

^a Surface area based on BET equation

^b Surface area based on Langmuir Equation

^c Surface area based on Dubinin-Raduskevich Equation

4.2.2 Effect of Adsorbent Concentration

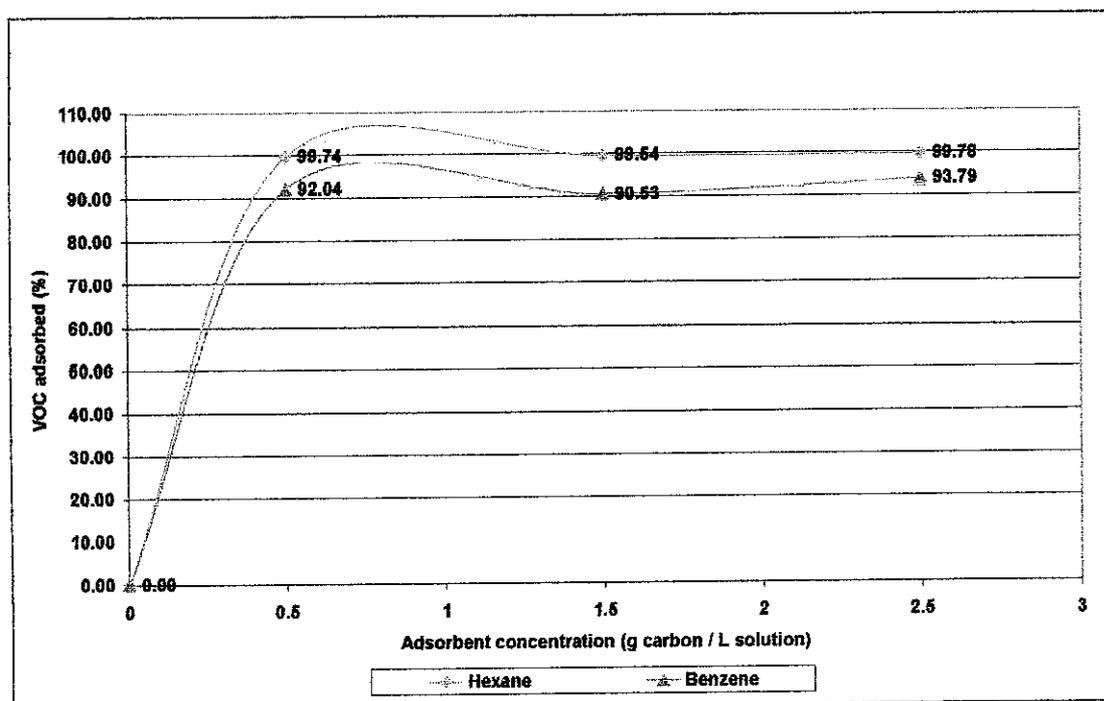


Figure 4-5 Effect of activated carbon concentration on the removal of benzene and n-hexane.

The influence of activated carbon concentration on benzene and n-hexane removal is studied by at three adsorbent concentrations: 0.5 g/l, 1.5 g/l, and 2.5 g/l. 200 ppm VOC solutions were used in this study. Figure 4-5 is plotted using results from sample D1, E1, C1, D2, E2, and C2. Adsorption temperature is held constant at 30°C and activated carbon used were carbonized at 800°C. Initial pH of benzene and n-hexane solutions is made constant at 9.

The effect of adsorbent concentration on the uptake of benzene and n-hexane is shown in Figure 4-5. Generally, the uptake of both VOC is seen to increase with increase in amount of the adsorbent material. However, the increase is very small, in the vicinity of less than 2 weight %. This is largely due to the fact that the adsorbent concentration of 0.5 g/l is already sufficient for the adsorption of both 200ppm benzene and n-hexane.

The high VOC removal at 0.5 g/l adsorbent concentration suggests that the activated carbon produced in this study is very suitable for benzene and n-hexane adsorption. Hence, it can be concluded that small amount of adsorbents is sufficient for efficient VOC removal. In the study by V. K. Gupta (2003) on basic dye removal using adsorbents (activated carbon and activated slag) converted from waste carbon slurries and blast furnace slag, substantial increase of adsorption occurred when adsorbent concentration was increased from 0.5 g/l to 1.5 g/l.

It can be hypothesized that increasing the adsorbent concentration at a fixed benzene and n-hexane concentration provides more available adsorption sites for the VOC and thus increases the extent of VOC removal.

Table 4-2 Effect of amount of activated carbon and activated slag on the rate of uptake of basic red (V. K. Gupta, 2003)

Adsorbents	Amount of adsorbent (g/l)	Amount adsorbed (mol)
Activated carbon	0.5	0.7×10^{-5}
	1.0	1.5×10^{-5}
	1.5	2.5×10^{-5}
Activated slag	0.5	3.1×10^{-5}
	1.0	5.0×10^{-5}
	1.5	5.5×10^{-5}

4.2.3 Effect of Initial Solution pH

The effect of the initial pH of solution on the uptake of benzene and n-hexane by activated carbon was studied at three pH levels: 3, 6, 9. 200 ppm VOC solutions were used. Figure 4-6 is plotted using results from sample F1, G1, C1, F2, G2, and C2. Adsorbent concentration and adsorption temperature are fixed at 1.5 g/l and 30°C respectively.

As depicted in Figure 4-6, the changes in initial solution pH do not change the adsorption of benzene and n-hexane substantially. In other word, the adsorption of benzene and n-hexane are not pH dependent. This can be related to the non-polar nature of both adsorbates which cause them to exist as molecule form in water.

Consequently, increasing or decreasing the pH (presence of excess OH^- or H^+ ions in water) do not result in competition for the negatively charged activated carbon adsorption sites, as can be seen in other studies discussed below.

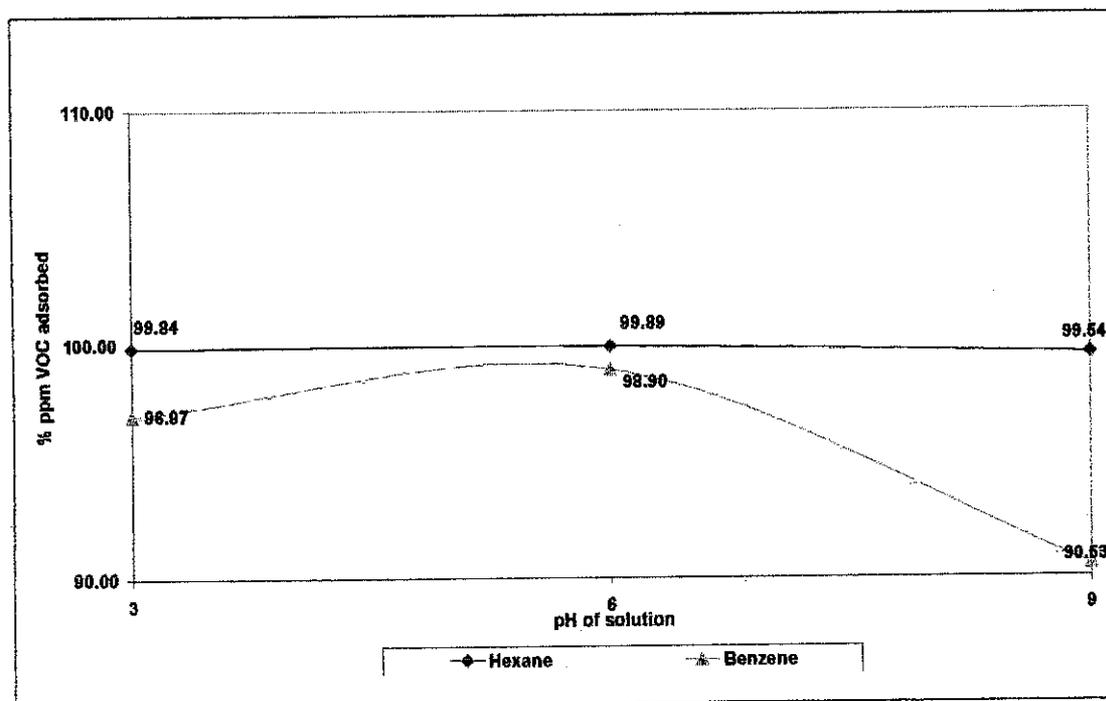


Figure 4-6 Effect of pH on the removal of benzene and n-hexane.

Separate studies by Namasivayam C. (2001), Kannan (2001) and F. Banat et al. (2003) found that high pH favored methylene blue removal. The low uptake of methylene blue under acidic conditions was related to the presence of excess H^+ ions competing with the dye cation MB^+ for the adsorption sites. On the other hand, V.K Gupta et al. (2003) found that adsorption of another dye, basic red is better at acidic condition (pH 2) when using activated carbon as adsorbent. At lower pH, positive charge density was more on the dye molecule and this accounts for higher uptake on the negatively charged surface of activated carbon. The same study also showed that when activated slag was used as adsorbent for basic red removal, the adsorption is better at basic condition (pH 10). According to V. K. Gupta, the opposite trend of adsorption using activated slag was a result of the positively charged adsorbent in acidic medium. Since the dye molecules are positively charged, the repellent of the

same charge between the molecules and adsorbent surface caused the low dye removal. These studies show that pH is an influential factor on adsorption when the adsorbate is cation or anion. They also highlights that the same pH would have different effect on the adsorption of the same adsorbate if the adsorbents are different in terms of their surface charge.

4.2.4 Effect of Adsorption Temperature

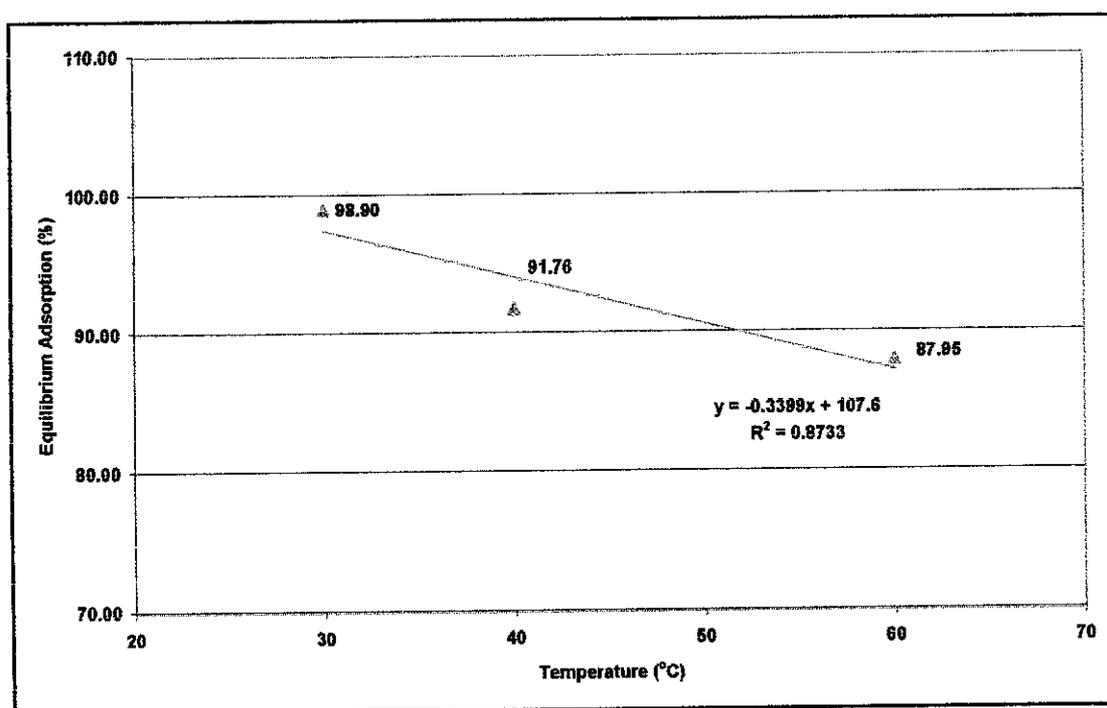


Figure 4-7 Effect of adsorption temperature on the removal of benzene.

The removal of benzene is studied at 30, 40 and 60°C and is presented in Figure 4-7. Figure 4-7 is plotted using results from sample G2, VI, and VII. Adsorbent concentration, pH of benzene solution, and carbonization temperature are fixed at 1.5 g/l, pH 9 and 800°C respectively.

The influence of temperature on equilibrium adsorption can be examined thermodynamically by using van't Hoff equation (V. L. Snoeyink et al., 1996)

$$\log K_2 - \log K_1 = -\left(\frac{\Delta H^0}{R}\right)(T_2^{-1} - T_1^{-1}) \quad (1)$$

where K_1 and K_2 are equilibrium constants at T_1 and T_2 , respectively, T is the absolute temperature (K), ΔH^0 the standard enthalpy at equilibrium (kJ.mol), and R the gas constant (8.314×10^{-3} kJ/mol K).

Equation (1) explains the relationship between equilibrium constant and temperature under the assumption that ΔH^0 is constant in the temperature range concerned. The ΔH^0 for the adsorption of benzene can be considered to be constant in the temperature range for the present study as it has been known to be nearly constant in a wide range of temperature for most physicochemical reactions (P. W. Atkins, 1990).

The adsorption equilibrium constant, K , is defined as the weight ratio of adsorbate adsorbed onto the activated carbon compared to that remaining in solution at equilibrium state (J. -W. Kim et al., 2001). With K defined, ΔH^0 can be calculated based upon experimental results. Also, thermodynamic parameters for adsorption, such as ΔG^0 and ΔS^0 can be obtained from the following relations:

$$\Delta G^0 = -RT \log K \quad (2)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (3)$$

The estimated thermodynamic parameters and equilibrium constants at each temperature are summarized in Table 4-3. The negative value of ΔH^0 thermodynamically substantiates that the adsorption of benzene on the produced activated carbon to be exothermic. Even though the values are small, ΔG^0 are calculated to be positive for the entire temperature range. This result probably means that the adsorption of benzene is not a thermodynamically spontaneous phenomenon, that is, benzene molecules adsorb on activated carbon mainly due to the physical process of diffusion. ΔS^0 are estimated to be very small in the experimental

conditions, therefore, the entropic change occurring from adsorption is thought to be negligible.

Table 4-3 Equilibrium constant and thermodynamic parameters for the adsorption of benzene on activated carbon

Adsorption Temperature (°C)	Concentration Detected (ppm)	Concentration adsorbed (ppm)	K (ppm adsorbed/ppm detected or remained)	ΔG^0 (kJ/mol)	ΔS^0 (kJ/mol K)	ΔH^0 (kJ/mol)
30	2.204	197.796	2.204	-11.334	-0.506	-164.7
40	16.480	183.520	11.136	-6.275	-0.506	
60	24.096	175.904	7.300	-5.506	-0.478	

4.3 ADSORPTION ISOTHERMS

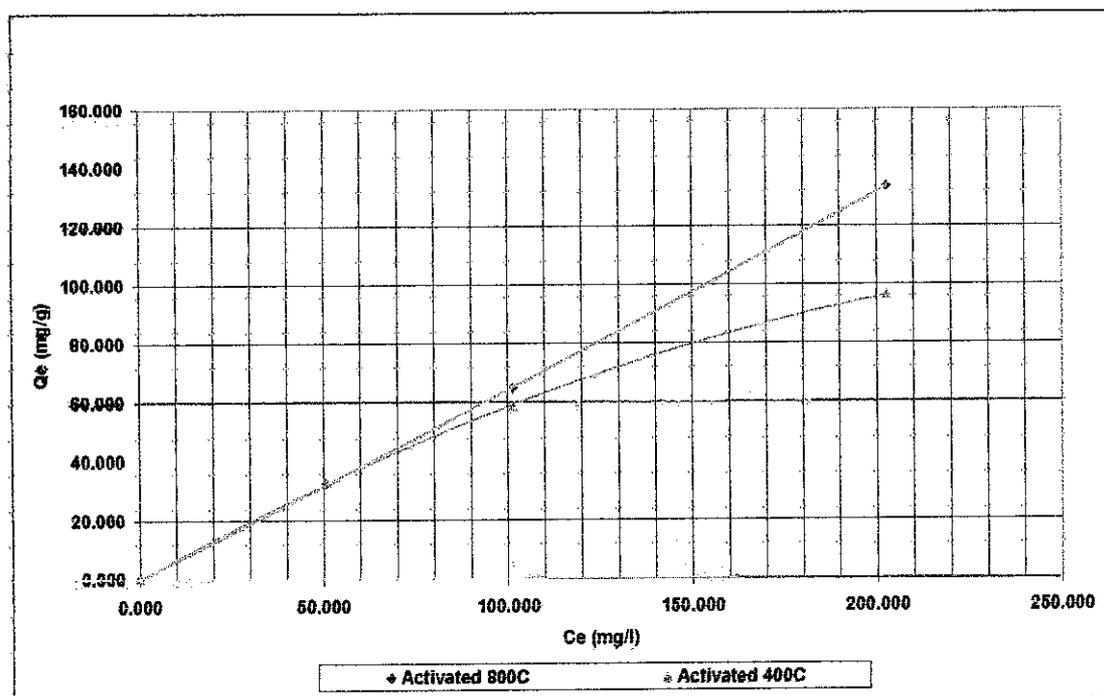


Figure 4-8 Adsorption isotherm of benzene on activated carbon produced at different carbonization temperatures.

The isotherms for adsorption of benzene on activated carbon produced at 400°C and 800°C carbonization temperatures are shown in Figure 4-8. Figure 4-8 is plotted using results from sample I, II, G2, III, IV, and V. pH of solutions were fixed at 6, adsorbent concentration at 1.5g/l, and adsorption temperature at 30°C.

The solid curves in Figure 4-8 represent least-square fitting of the data. Uptake is seen to increase with increasing benzene initial concentration. At low concentration, uptake between the two set of activated carbons are close but still the data trend suggests a continuous increase with increasing benzene concentration. Figure 4-9 suggests that the optimum choice between carbonization temperature in preparing activated carbon lies on the initial benzene concentration. For concentration lower than 60 mg/l, both set of activated carbons are seen to have similar adsorption capacity. Hence, 400°C carbonization temperature is sufficient to produce a good activated carbon for adsorption of benzene which is lower than 60 mg/l

concentration. However, to adsorb benzene at higher concentrations, 800°C is the optimal carbonization temperature.

The data for the adsorption of benzene on activated carbon were fitted to Freundlich and Langmuir isotherms. The linear forms of Freundlich and Langmuir models are represented by the equations

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

$$\frac{1}{q_e} = \left(\frac{1}{Q^0 b} \right) \left(\frac{1}{C_e} \right) + \frac{1}{Q^0} \quad (5)$$

where q_e is the amount of benzene adsorbed per unit weight of carbon (mg/g), C_e is the concentration of benzene in solution at equilibrium, K_F and $1/n$ are Freundlich characteristic constants, Q^0 (mg/g) and b (mg/l)⁻¹ are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

The constants K_F and $1/n$ can be evaluated from the intercept and the slope of the linear plot of the experimental data of $\log q_e$ versus $\log C_e$ (Figure 4-11) respectively. Q^0 and b can also be evaluated in similar manner from linear plot of experimental data of $1/q_e$ versus $1/C_e$ (Figure 4-10).

Figure 4-9 shows a linear relationship of $1/q_e$ versus $1/C_e$ for the adsorption of benzene, suggesting on the applicability of the Langmuir model. The validity of Langmuir model suggests that the surface of the pores of the adsorbent is homogeneous ($\Delta H_{ads} = \text{constant}$) and that the forces of interaction between adsorbed molecules are negligible. The maximum adsorption capacity, Q^0 , presented in Table 4-4 indicates that activated carbon produced at 800°C is a superior adsorbent over that produced at 400°C. This observation is inline with that seen in the *Effect of carbonization temperatures* discussed. The importance of carbonization in micropore development is again demonstrated. Similar findings were also reported by Juang and Tseng (2000) who found that increasing the carbonization temperature of plum kernels produces carbons with higher adsorptive capacity towards methylene blue.

Lafi (2001) also observed a similar behavior for the carbonization temperature effect on the methylene blue adsorption by activated carbons prepared from acorns and olive seeds.

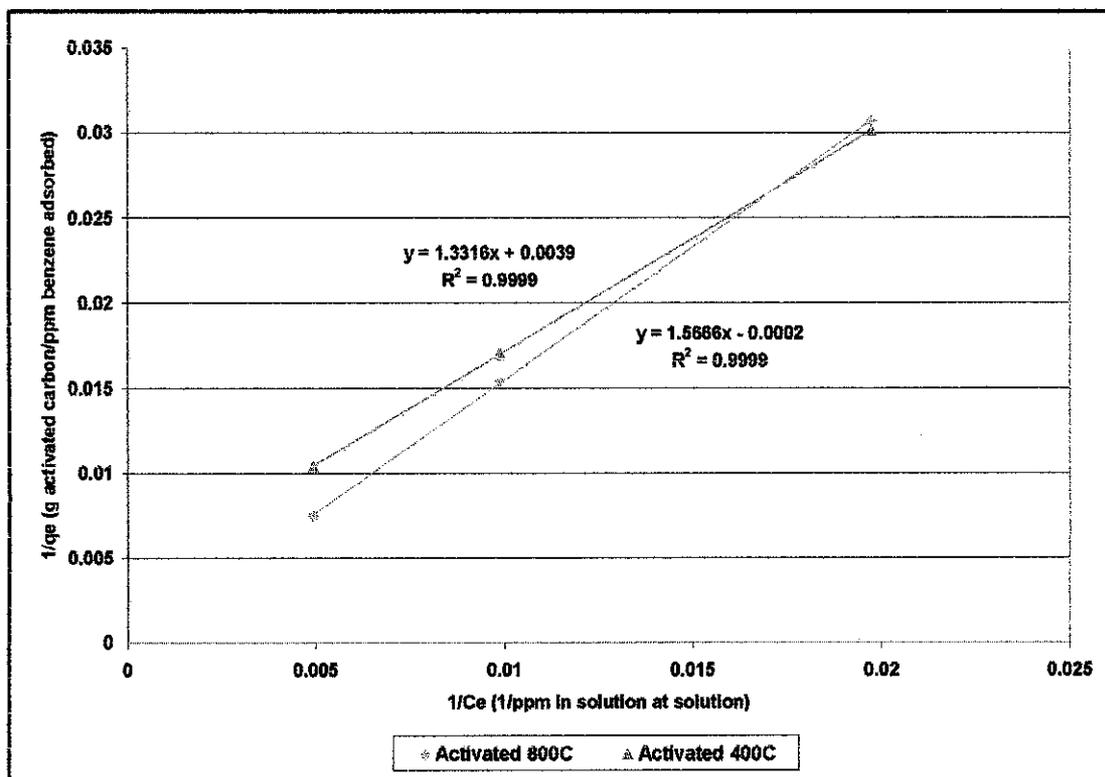


Figure 4-9 Langmuir isotherm for adsorption of benzene.

Table 4-4 Freundlich and Langmuir parameters for benzene adsorption on activated carbon

Carbonization Temperature (°C)	Freundlich parameters			Langmuir parameters		
	K_F (mg/g)	N	R^2	Q^u (mg/g)	$b \times 10^4$ (mg/l) ⁻¹	R^2
400	1.6466	1.3019	0.9986	256.41	29.288	0.9994
800	0.59676	0.983	0.9998	3333.33	1.9529	0.9999

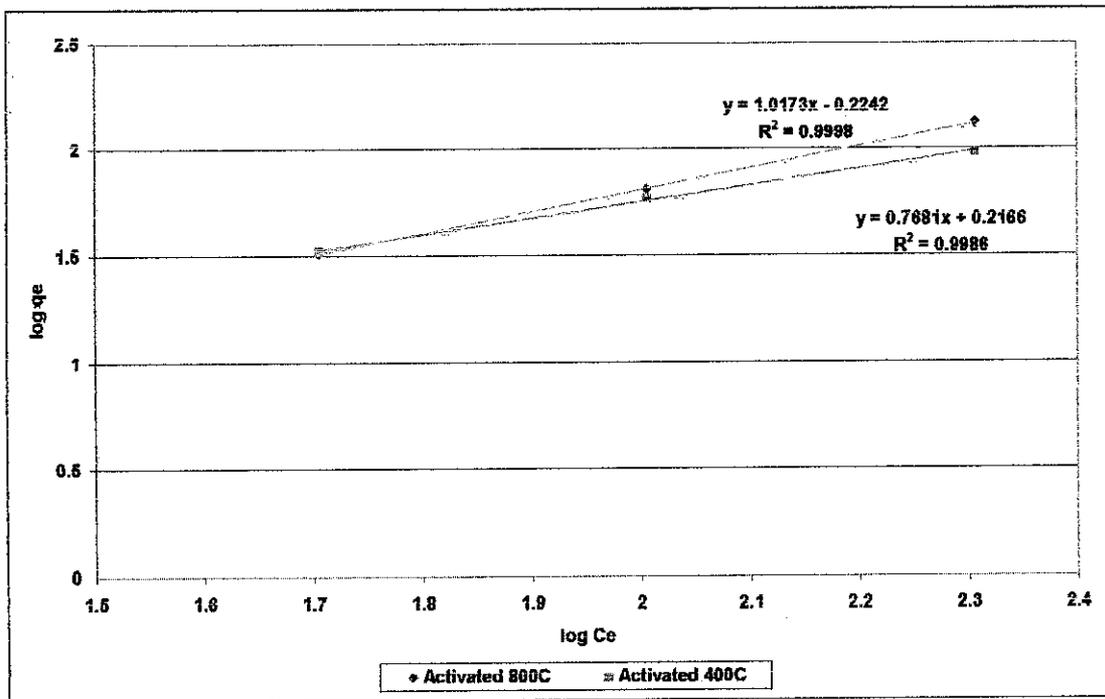


Figure 4-10 Freundlich isotherm for adsorption of benzene

The value of K_F obtained from Figure 4-10 is used as a relative measure of adsorption capacity while $1/n$ and b are related to enthalpy and intensity of adsorption. Result obtained from Figure 4-10 show the applicability of Freundlich model over a range of benzene concentration (50ppm to 200ppm). The validity of Freundlich model suggests that the activated carbon produced has heterogeneous surface with a nonuniform distribution of the heat of adsorption over the surface, as discussed by Brunauer (1943).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Granular activated carbon was successfully produced from waste oil-pal shells through carbonization and chemical activation. Main objectives of the study to analyze the effects of adsorption parameters on the removal of benzene and n-hexane from aqueous medium have been achieved

The studies presented revealed that activated carbon developed from waste oil-palm shells can be used as low-cost adsorbents for benzene and n-hexane removal.

From three sets of activated carbon, each produced at 400°C, 700°C and 800°C respectively; increasing the carbonization temperature is found to aid the adsorption of n-hexane but has opposite effect on the adsorption of benzene. Adsorption of n-hexane was best when activated carbon produced at 800°C was used. On the other hand, adsorption of benzene was best when activated carbon produced at 400°C was used.

By varying the adsorbent concentration at 0.5g/l, 1.5g/l and 2.5g/l, it is found that increasing the adsorbent concentration increases the extent of benzene and n-hexane removal. Nevertheless, it is found that as little as 0.5 g/l adsorbent concentration is sufficient to remove most of benzene and n-hexane from 200ppm solution.

Effect of pH was studied by varying the benzene and n-hexane solutions pH at 3, 6 and 9. Changes in initial benzene and n-hexane solutions pH were found to have no effect on the extent of adsorption. In practical sense, this means that the activated

carbon produced can adsorb benzene and n-hexane effectively from wastewater of any pH.

Study on adsorption temperature of 30, 40 and 60°C found that adsorption of benzene decreased as adsorption temperature was increased. Adsorption of benzene by activated carbon was found to be exothermic in nature. Optimal adsorption temperature was found to be at 30°C, which is very close to room temperature in Malaysia. The fact that no additional energy is needed to increase benzene adsorption makes the use of waste oil-palm shell-based activated carbon an attractive alternative in VOC removal from wastewater.

Adsorption data could be fitted into both Freundlich and Langmuir models. The applicability of Langmuir model suggests monolayer adsorption but with Freundlich model also fitted well, a certain amount of heterogeneity due to porosity is also expected on the activated carbon produced.

Findings of this study strongly suggest that the production of granular activated carbons from waste oil-palm shells for benzene and n-hexane removal from wastewater is viable.

5.2 RECOMMENDATIONS

The present study has been carried out according to the objectives which were set by taking into account the time constraint of the study duration. However, further improvements can be done for the purpose of expansion and continuation of the present study. The suggested future works are:

- The characterization of produced activated carbon should be done in view of its importance to the adsorption capacity of the adsorbent. Thermogravimetric analyzer (TGA), AUTOSORB-I and BET equipment could be used to determine the fixed carbon content and most importantly, the total surface area available in the activated carbon.

- Study on the effect of adsorption time on the adsorption characteristics of the produced activated carbon could be done to evaluate the equilibrium adsorption time for benzene and n-hexane adsorption by the activated carbon
- Similar study could be done on the adsorption of other volatile organic compounds to observe the versatility of the activated carbon produced.

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APPENDICES

APPENDIX I: LIST OF SAMPLES USED AND THEIR DESCRIPTIONS

Samples were systematically prepared so that every objective of this study is achieved with minimal quantity of samples. Table below shows the code and description of each sample prepared and tested.

No	Sample Codes	Descriptions					
		VOC type (H=n-hexane, B=benzene)	Initial VOC Solution Concentration (ppm)	Temperature at which activated carbon is carbonized (°C)	Initial pH of VOC solution	Adsorbent concentration (g/L)	Adsorption temperature (°C)
1	A1	H	200	400	9	1.5	30
2	B1	H	200	700	9	1.5	30
3	C1	H	200	800	9	1.5	30
4	D1	H	200	800	9	0.5	30
5	E1	H	200	800	9	2.5	30
6	F1	H	200	800	3	1.5	30
7	G1	H	200	800	6	1.5	30
8	A2	B	200	400	9	1.5	30
9	B2	B	200	700	9	1.5	30
10	C2	B	200	800	9	1.5	30
11	D2	B	200	800	9	0.5	30
12	E2	B	200	800	9	2.5	30
13	F2	B	200	800	3	1.5	30
14	G2	B	200	800	6	1.5	30
15	I	B	50	800	6	1.5	30
16	II	B	100	800	6	1.5	30
17	III	B	50	400	6	1.5	30
18	IV	B	100	400	6	1.5	30
19	V	B	200	400	6	1.5	30
20	VI	B	200	800	6	1.5	40
21	VII	B	200	800	6	1.5	60

**APPENDIX II: RESULTS TABULATED FOR CHNS AND ADSORPTION
EXPERIMENT RESULTS**

List of samples tested for VOC adsorbed and Their Descriptions

No	Sample Codes	GC Sample IDs	GC Data Filenames	VOC type (H=n-hexane, B=benzene)	Initial VOC Solution Concentration (ppm)	Descriptions Temperature at which activated carbon is carbonized (°C)	Initial pH of VOC solution	Adsorbent concentration (g/L)	Adsorption temperature (°C)	Remark
1	A1	hexane a1	EE-HEX.D02	H	200	400	9	1.5	30	
2	B1	hexane a2	EE-HEX.D03	H	200	700	9	1.5	30	
3	C1	hexane c1	EE-HEX.D04	H	200	800	9	1.5	30	
4	D1	hexane d1	EE-HEX.D05	H	200	800	9	0.5	30	
5	E1	hexane e1	EE-HEX.D06	H	200	800	9	2.5	30	
6	F1	hexane f1	EE-HEX.D07	H	200	800	3	1.5	30	
7	G1	hexane g1	EE-HEX.D08	H	200	800	6	1.5	30	
8	A2	benzene a2	EE-BEN.D01	B	200	400	9	1.5	30	
9	B2	benzene b2	EE-BEN.D04	B	200	700	9	1.5	30	
10	C2	benzene c2	EE-BEN.D05	B	200	800	9	1.5	30	
11	D2	benzene d2	EE-BEN.D06	B	200	800	9	0.5	30	
12	E2	benzene e2	EE-BEN.D07	B	200	800	9	2.5	30	
13	F2	benzene f2	EE-BEN.D08	B	200	800	3	1.5	30	
14a	G2	benzene g2	EE-BEN.D09	B	200	800	6	1.5	30	
14b	G2	benzene g2.2	EE-BEN.D10	B	200	800	6	1.5	30	
15	I	ben I	EE-BEN.D12	B	50	800	6	1.5	30	
16	II	ben II	EE-BEN.D15	B	100	800	6	1.5	30	
17	III	ben III	EE-BEN.D13	B	50	400	6	1.5	30	
18	IV	ben IV	EE-BEN.D16	B	100	400	6	1.5	30	
19	V	ben V	EE-BEN.D17	B	200	400	6	1.5	30	
20	VI	ben VI	EE-BEN.D18	B	200	800	6	1.5	40	
21	VII	ben VII	EE-BEN.D19	B	200	800	6	1.5	60	
										This G2 sample is tested with GC twice.

Standard Solutions Tested

Solution Description	GC Sample IDs	GC Data Filenames
Standard 200ppm Hexane	std hexane 200ppm	EE-HEX.D01
Standard 200ppm Benzene	benzene std 200ppm 2	EE-BEN.D03
Standard 50ppm Benzene	std hexane 200ppm	EE-BEN.D11
Standard 100ppm sample	ben 100ppm sample	EE-BEN.D14

Effect of Temperature (Constant: pH 9, 1.5 g/L)

Sample	Temperature (°C)	Concentration detected (ppm)	Concentration adsorbed (ppm)	Percent Adsorbed (%)	ppm adsorbed
1	400	6.733	193.267	96.63	193.267
1	700	5.532	194.468	97.23	194.468
1	800	0.929	199.071	99.54	199.071

Effect of Loading Ratio (Constant: pH 9, 800C)

Sample	Loading Ratio (g carbon/L solution)	Concentration detected (ppm)	Concentration adsorbed (ppm)	Percent Adsorbed (%)	ppm adsorbed
	0	200.000	0.000	0.00	0.000
1	0.5	0.530	199.470	99.74	199.470
1	1.5	0.929	199.071	99.54	199.071
1	2.5	0.431	199.569	99.78	199.569

Effect of pH (Constant: 1.5g/L, 800C)

Sample	pH	Concentration detected (ppm)	Concentration adsorbed (ppm)	Percent Adsorbed (%)	ppm adsorbed
1	3	0.323	199.677	99.84	199.677
1	6	0.225	199.775	99.89	199.775
1	9	0.929	199.071	99.54	199.071

Effect of Temperature (Constant: pH 9, 1.5 g/L)

Sample	Temperature (°C)	Concentration detected (ppm)	Concentration adsorbed (ppm)	Percent Adsorbed (%)	ppm adsorbed
2	400	1.300	198.700	99.35	198.700
2	700	17.117	182.883	91.44	182.883
2	800	18.940	181.060	90.53	181.060

Effect of Loading Ratio (Constant: pH 9, 800C)

Sample	Loading Ratio (g carbon/L solution)	Concentration detected (ppm)	Concentration adsorbed (ppm)	Percent Adsorbed (%)	ppm adsorbed
	0	200.000	0.000	0.00	0.000
D2	0.5	15.925	184.075	92.04	184.075
C2	1.5	18.940	181.060	90.53	181.060
E2	2.5	12.425	187.575	93.79	187.575

Effect of pH (Constant: 1.5g/L, 800C)

Sample	pH	Concentration detected (ppm)	Concentration adsorbed (ppm)	Percent Adsorbed (%)	ppm adsorbed
F2	3	6.053	193.947	96.97	193.947
G2	6	2.204	197.796	98.90	197.796
C2	9	18.940	181.060	90.53	181.060

For G2:

Sample	G2 (2nd)	average
1.632	1.776	2.204

Sample	C measured (%)	H measured (%)	N measured (%)	S measured (%)
1	0.047	-0.004	0.067	0.051
2	0.050	-0.010	0.023	0.065
3	0.037	0.000	-0.023	0.030
4	0.043	0.030	-0.047	0.032
5	0.038	0.024	-0.053	0.012
6	0.030	0.035	-0.062	0.006
7	0.022	0.027	-0.071	0.022
8	0.030	0.020	-0.081	0.029
9	0.015	0.002	-0.091	0.011
10	0.019	-0.032	-0.084	0.010
Average	0.033	0.009	-0.042	0.027

Parathion (Before calibration)

Sample	C measured (%)	H measured (%)	N measured (%)	S measured (%)
1	51.59	5.257	19.42	11.38
2	48.69	5.136	19.22	10.49
3	49.45	5.276	19.45	11.83
Average	49.91	5.223	19.36	11.23
Real	51.78	5.070	20.13	11.52
Deviation (%)	0.036	-0.030	0.038	0.025

Parathion (After calibration)

Sample	C measured (%)	H measured (%)	N measured (%)	S measured (%)
1	53.52	5.103	20.19	11.67
2	50.51	4.985	19.98	10.76
3	51.30	5.122	20.22	12.14
Average	51.78	5.070	20.13	11.52
Real	51.78	5.070	20.13	11.52
Deviation (%)	0.000	0.000	0.000	0.000

Actual Samples

Sample	Description	C measured (%)	H measured (%)	N measured (%)	S measured (%)
1	Shell Carbonized at 400C	33.020	2.717	1.003	0.413
2	Shell Carbonized at 400C	31.790	2.727	0.819	0.109
	Average	32.405	2.722	0.911	0.261
3	Shell Carbonized at 800C	41.660	1.989	0.322	0.059
4	Shell Carbonized at 800C	23.180	1.756	0.213	0.041
	Average	32.420	1.873	0.268	0.050
5	Activated carbon (400C)	50.520	3.054	0.884	0.033
6	Activated carbon (400C)	25.580	0.201	0.190	0.018
	Average	38.050	1.628	0.537	0.026
7	Activated carbon (800C)	30.440	0.210	0.210	0.025
8	Activated carbon (800C)	33.280	0.275	0.275	0.017
	Average	31.860	0.243	0.243	0.021

Constant: Carbon ratio 1.5 g/l
 pH 6
 Benzene
 Adsorption temperature 30C

FOR CARBON CARBONIZED AT 80JC

Initial Concentration (ppm)	Concentration Detected (ppm)	Concentration adsorbed (mg/L)	Percent Adsorbed (%)	qe (mg benzene adsorbed/g solid)	Ce (mg benzene/L solution)	1/qe	1/Ce	log qe	log Ce
				0.000	0.000				
50	829	48.171	96.34	32.551	50.681	0.030721258	0.01973126	1.512561	1.704845
100	4.06	95.94C	95.94	64.830	101.360	0.015424992	0.009865825	1.811775	2.005867
200	2.632	197.363	98.68	133.368	202.720	0.007498043	0.004932912	2.125052	2.306897

I
 II
 G2

FOR CARBON CARBONIZED AT 40JC

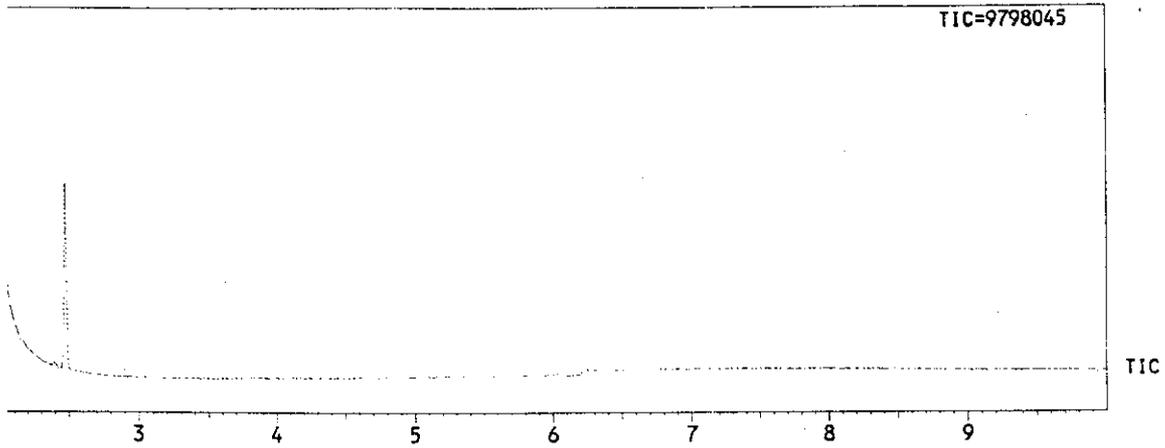
Initial Concentration (ppm)	Concentration Detected (ppm)	Concentration adsorbed (mg/L)	Percent Adsorbed (%)	qe (mg benzene adsorbed/g solid)	Ce (mg benzene/L solution)	1/qe	1/Ce	log qe	log Ce
				0.000	0.000				
50	0.863	49.137	98.27	33.204	50.681	0.030117299	0.01973126	1.521184	1.704845
100	13.414	86.586	86.59	58.509	101.360	0.017091374	0.009865825	1.767223	2.005867
200	57.486	142.514	71.26	96.301	202.720	0.010384059	0.004932912	1.963633	2.306897

III
 IV
 V

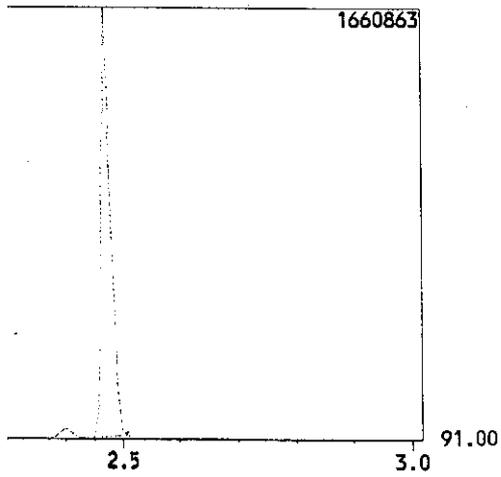
**APPENDIX III: SAMPLE RESULT PRINTOUTS FROM GCMS
EQUIPMENT**

ample : hexane a1
D : hexane a1
ype : Unknown
ethod File Name : EE-HEX.MET

** Chromatogram ***



** Quantitation ***

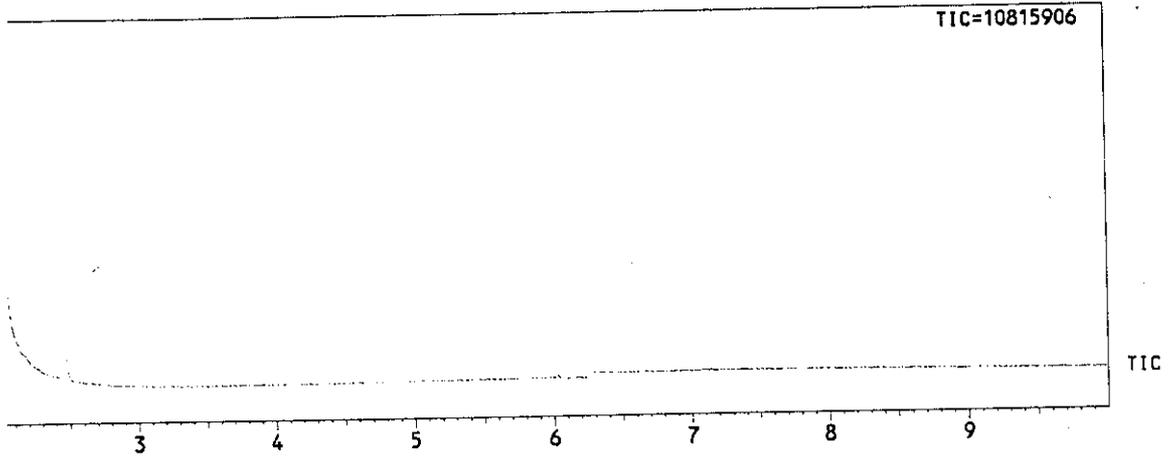


ID : 1 M/Z : 91.00
Type : Target
Name : toluene

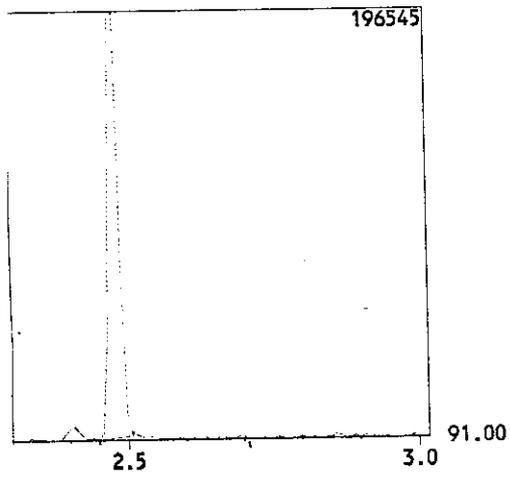
Time : 2.471
Area : 1887303
Conc. : 6.733

Sample : hexane c1
Sample : hexane c1
Sample : Unknown
Method File Name : EE-HEX.MET

*** Chromatogram ***



*** Quantitation ***



ID : 1 M/Z : 91.00
Type : Target
Name : toluene
Time : 2.475
Area : 260524
Conc. : 0.929