

**MULTICOMPONENT ADSORPTION MODELS  
AND THE KINETICS OF DEODOURISATION  
OF COMMERCIAL DPK**

**BY**

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## **DEDICATION**

This work is dedicated to my lovely wife, Mrs. Patience Evbuomwan and my children, Eseosa, Etinosa, Osasuyi, Osasogie and Nosakhare for their co-operation and understanding during the period of this work.

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## ABSTRACT

The Multicomponent adsorption models and kinetics of deodorization of commercial kerosene (DPK) using conventional and non-conventional adsorbents have been investigated. The adsorbents used were bone char, limestone, silica gel and clay. The influence of contact time, adsorbent mass, pH, temperature, and adsorbent particle size on the rate percent aromatic and sulphur removal was evaluated. The experimental results were fitted to the Langmuir, Freundlich, Redlich-Peterson, Radke-Praustniz, and Temkin isotherms to obtain the measured sorption data. The characteristic parameters for each isotherm were determined:

The Kinetic modeling of the process was done using the first-order and second order rate models. Furthermore, the three main thermodynamic parameters namely, enthalpy of adsorption ( $\Delta H$ ), free energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) were investigated, in order to determine what changes can be expected to occur during the sorption process.

Equilibrium studies showed that oxidized bone has the highest adsorption capacity from the list of adsorbent given above. The aromatic and sulphur content of DPK obtained after dearomatisation and desulphurization using oxidized bone and silica gel were 0.74 vol.% and 0.009 wtS, for oxidized bone and 0.65 Vol.% and 0.01 wtS for silica gel respectively. Langmuir and Redlich-Peterson models gave the best fit for the experimental data on the adsorption of sulphur and aromatics. The Pseudo- second-order rate constants for aromatic and sulphur were  $0.0045\text{min}^{-1}$ ,  $0.697\text{min}^{-1}$  for oxidized bone, and  $0.00358\text{min}^{-1}$ ,  $0.672\text{min}^{-1}$  for silica gel. The thermodynamic parameters (entropy, enthalpy and Gibb's free energy) of the system using oxidized bone were -46.35, -1,118 and 5,851 J/gK for aromatics, -34.50, -12,315 and 2,465 J/gK for sulphur. Similarly, when silica gel was used were -48.30, -23,009, 6,832 J/gK for aromatics, -25.10, -11,259

and 2,562 J/gK for sulphur. Experimental results show that the rate of deodourisation of distillate DPK by adsorption techniques is second-order and reversible while the reaction itself is exothermic .

## CHAPTER ONE

### INTRODUCTION

#### 1.1 PREAMBLE

Kerosene is a Canadian discovery, Abraham Gesner, a Nova Scotian Doctor, was searching for a cheaper, brighter lamp oil when he tried distilling New Brunswick coal. The process resulted in burning oils which he called “Kerosene”, and, by 1850 it was lighting up homes in Dartmouth and Halifax, Nova Scotia. When petroleum was discovered a few years later (in Pennsylvania in 1859 and in Ontario in 1860), it soon became the major source for the production of kerosene, the C<sub>9</sub> – C<sub>16</sub> (Concawe, 1995) distillates fraction.

Kerosene, originally developed for heating and lighting, is even more important today as a fuel for jet aircraft. Kerosene, a colorless, thin mineral oil with density between 0.75 and 0.85 grams per cubic centimeter, is a mixture of hydrocarbons, commonly obtained in the fractional distillation of petroleum, as the portion boiling off between 150<sup>0</sup>C and 275<sup>0</sup>C (from [wikipedia](#), the free encyclopedia). Kerosene has been recovered from other substances, notably coal (hence the other name, coal oil), oil shale, and wood. At one time kerosene was the most important refining product because of its use in lamps. Now it is most noted for its use as a carrier in insecticide sprays, solvent vehicle in

oil paints and as a fuel in jet engines. Special properties are required for the application of kerosene as a jet fuel, including high flash point for safe landing, ( $38^{\circ}\text{C}$  for jet A1), low freezing point for high altitude flying ( $-47^{\circ}\text{C}$  for Jet A1) and good water separation characteristics.

The petroleum industry began with the successful drilling of the first commercial oil well in 1839 and the opening of the first refinery twenty two years later to process the crude into kerosene. An oil refinery is an organized and co-ordinated arrangement of manufacturing processes designed to produce physical and chemical changes in crude oil to convert it into everyday products like petrol, diesel, fuel oil, lubrication oil and bitumen. Refining is the processing of one complex mixture to other less complex mixture of hydrocarbons. The safe and orderly processing of crude oil into flammable gases and liquids at high temperatures and pressures requires considerable knowledge and expertise.

Petroleum refining has evolved continuously in response to changing consumer demand for different products. The original requirement was to produce kerosene as a cheaper and better source of light than whale oil. The development of the internal combustion engines led to the production of gasoline and diesel fuels. The evolution of the airplane created a need first for high octane aviation gasoline and then jet fuel, a narrow cut of the

original product, kerosene. Present day refineries produce a variety of products including many required as feedstock for the petrochemical industry.

The first refinery, opened in 1861, produced DPK (kerosene) by simple atmospheric distillation, and its by – product included tar and naphtha. It was soon discovered that high quality lubricating oils could be produced by distillation of long residue under vacuum. However, for the next 30 years, DPK was the product consumers wanted, but significant events changed this situation: (i) the invention of electric light decreased the demand for DPK and (ii) the invention of internal combustion engine created a demand for diesel fuel and gasoline (Naphtha).

## **1.2 BACKGROUND OF STUDY**

Crude oil contains varying amount of aromatic hydrocarbons and sulphur compounds depending on their origin, hence the fractions distilled from a crude will also contain these compounds. Straight run Distillate kerosene (DPK) solvent usually contains 15 – 25% of high boiling aromatic hydrocarbons. Very low aromatic content is needed particularly in the case of kerosene solvents for better odour. Odour is a quality which is of very great importance and will often determine the choice or purchase of any

product. Odour affects not only conditions in workshop etc. where vapours are allowed to escape into the atmosphere, but may also affect the odour of products sold to the customer, for example, paints or polishes. The odour of hydrocarbon solvents depends partly on their chemical compositions and partly on the presence of minute quantities of impurities such as sulphur (which is present as mercaptan, thiophenes or disulphide) and aromatics and it is necessary to remove them by desulphurization and dearomatization.

Kerosene cannot be burnt in the liquid state. It has to be in the form of vapour and mixed with the oxygen in the air in the correct ratio to form a combustible mixture. All petroleum oils including kerosene vapourize to some extent when exposed to the atmosphere. To achieve satisfactory, combustion of DPK (kerosene) used in domestic burners, it is necessary to increase the evaporation rate. This depends on two factors: increasing the surface area of the oil to be burned and increasing its temperature.

The various types of hydrocarbons present in kerosene are paraffins, naphthenes, aromatics and non-hydrocarbons compounds containing sulphur, nitrogen, oxygen and metals. Carbon number of the hydrocarbons present varies from 9 to 16. For the same carbon number paraffins have the least tendency towards smoke formation and aromatics the greatest. Naphthenes are intermediate between the other two. Hence a good quality

kerosene must contain a sufficiently high proportion of paraffinic hydrocarbon relative to aromatics.

Another source (Ramaswamy et al, 1992) states that the average chemical composition by weight is 35% paraffins, 50% Naphthenes and 15% Aromatics. (ERNS) 2003, Kerosene is one of the most commonly spilled petroleum products in the United States.

In recent development, IDEMITSU KOSAN CO. LTD, JAPAN (Nikkei Sangyo Shinbum, 4<sup>th</sup> January, 2002) announced that they have developed desulphurization material which can reduce sulphur content in kerosene to 1/1000. European Union Regulations made in January, (2001), have prohibited the sale of gas oil with more than 0.2% sulphur content. The regulations ban its use above this limit. In most developed countries, the kerosene produced is dearomatized and disulphurised before it is sold. Sulphur specifications are getting more and more stringent. In Asia, countries such as Thailand, Singapore and Hong Kong already have a 0.05% sulphur specification.

The use of process material particularly fullers earth and clay for the deodourization and decolourisation of natural or mineral oils has been a common refinery practice for many years. However, much of the initial work was geared towards decolourisation of liquids, recovery of gases and

the removal of moisture from liquids and gases (Nelson, 1985). The development of silica gel enhanced the application of adsorption for the separation of aromatic hydrocarbons from other refinery products (Unzelman, 1967). Other percolation processes such as in exchange and chromatography were also developed to purify diluents, separate products and recover solvents.

Adsorption is a technique which has been employed in many processes and used to satisfy some of the needs of man. It is a terminology coined from the Latin word “SORBERS” which literally means to suck up. The phenomenon involves a process whereby the adsorbate sticks to the adsorbent surface. (Suzuki, 1993), the adsorbent is usually a solid while the adsorbate could be a liquid or a gas.

Studies carried out by (Udeh, 1996), (Deryio, et al, 197), (Horsley, 1988) have shown that finely divided clay powders, powdered silica and charcoal are able to take up dyes and other substances from solution. This is due to the greater pore space per unit surface area exposed as well as molecular attraction or chemical forces that provide an interface of larger area on the surface of the solid. In adsorption operation, substances are removed or separated from the bulk solution by the ability of certain solids to retain (selectivity) specific substances onto their surfaces. Often the

amount adsorbed is measured as a function of concentration at a given temperature and the result expressed as an adsorption isotherm (Orumwense, 1996).

Production of Multi-component adsorption is one of the most challenging problems in the field of adsorption. Therefore the ability to predict multi-component adsorption from single-component isotherm parameters would be extremely useful. Many models have been proposed and employed for that purpose. However, most of these models were based on either unrealistic assumptions or empirical equations with no apparent definition. Alkamis, (1997) and Wurster et al, (2001) presented the various models used to predict multi-component equilibrium adsorption and applied these methods to bisolute systems.

Kinetic studies are important in determining the time needed to reach equilibrium and examinations into the rates of adsorption which can be used to develop models and an understanding of solutes on adsorbent surface (Horsfall and Spill, 2004).

### **1.3 OBJECTIVES OF STUDY**

The objectives of this work are as follows:

- (a) to develop and formulate appropriate conventional and non-conventional adsorbents for the deodourization of DPK

- (b) to test/compare the effectiveness of our newly developed multicomponent adsorbents.
- (c) To test for the adsorbent having the highest selectivity and best performance in the deodourization of DPK.
- (d) To determine the physico-chemical properties/structural parameters of the adsorbents used in this study.
- (e) To establish the various ways of expressing the equilibrium relationship between the concentration of the solute in the two phases (solid and liquid).
- (f) To determine whether the Freudlich, Langmuir, Redlich Peterson, Temkin and Radke –Prausnitz model fit experimental data over a reasonable range of concentrations.
- (g) To evaluate the kinetic/thermodynamic parameters

#### **1.4 CHARACTER OF THE ODOUR PROBLEM AND OF ITS SOLUTION.**

The need for odourless, non-corrosive and non-toxic kerosene has led to the development of various methods for sulphur and aromatics removal. Sulphur and its compounds like hydrogen sulphide and mercaptans are

known to contribute largely to the unpleasant odour apart from other adverse effects like corrosion which their presence imparts to kerosene.

The essence of the treatment kerosene is to remove the sulphur groups as well as the aromatics. The presence of sulphur compounds in kerosene, such as hydrogen sulphide and mercaptans are dangerous because they may cause corrosion of processing equipment. Sulphur compounds are also undesirable in lighting kerosene, owing to the fact that they promote char formation on the wick. They should be absent when kerosene is used for dry cleaning and in paint manufacture since they may impart bad odour to the clean goods. In paints, particularly those containing white lead as pigment, the colour is spoilt by the formation of lead sulphide. On the other hand, the presence of aromatic compounds in kerosene not only give rise to bad odour but also decrease the flash point of kerosene making it unsafe for normal domestic or industrial use as fuel due to fire risk.

On both performance and toxicological grounds, there has been a growing interest over recent years for solvents that are essentially benzene-free, in some cases, practically aromatic-free solvents are also demanded. Examples of applications where very low benzene content is preferred include oil polyolefin reaction media (mainly for performance reasons), manufacture of paints, in the rubber and printing ink industries.

There are some known expensive industrial process for the deodourization of DPK (kerosene), by sulphur and aromatics removal. These include hydrogenation under pressure in the presence of catalyst and solvent extraction using sulfolane. Multicomponent adsorption with activated carbons/clays is a new approach under serious study which has been found to be economically feasible, cheaper and easier. Adsorption has proved very efficient in removing both sulphur and aromatics from kerosene. However, there is need to search for cost effective multicomponent adsorbents available locally that will lead to the deodourized product starting from a commercial DPK feedstock. In this work, local non-conventional adsorbents will be formulated and used for kinetic studies in odour removal, while conventional silica gel will used as standard (control).

## **1.5 JUSTIFICATION FOR THIS RESEARCH WORK**

There are many reasons why this research is worthwhile and justified.

\* The demand for a relatively cheap but volatile solvent especially in this nation's cosmetic, varnish and aerosol industries has made the deodourization of Nigeria's DPK of increasing significance. This fact has triggered off a lot of studies into the area of kerosene deodourization by various methods in recent years.

\* It has been observed that in order to deodourise DPK, certain aromatics and sulphur had to be removed. This led to the conclusion that the presence of aromatics and sulphur in DPK is responsible for its obnoxious odour. Although the deodourization of mineral oils had sometimes been effected through adsorption, it has not been shown whether or not the laws of multicomponent solid-liquid adsorption were applicable. Most of the earlier experiments have been limited to binary mixtures and mostly those of gases, and insufficient attention has been given to the adsorption of multicomponent mixtures.

\* Activated carbon is one of the most commonly used adsorbents in industry but due to its high cost, thermal disintegration of the structure during regeneration which gives rise to 10-15% losses, the persistence of a grey tinge after treatment, have induced several investigators to search for alternative low cost non-conventional adsorbents.

\* Although hydrotreating of DPK in the presence of Nickel catalyst is still commonly used in industry, this technique requires high technological know-how and expensive equipment, which puts it out of reach of the small and Medium Scale Enterprises (SMEs).

\* This work is focused on the development of efficient adsorbents from a combination of low cost non-conventional limestone/bentonitic clay mixtures coupled with bone char and silica-gel.

\* The use of chars from animal bone aim at furthering research efforts in the internal sourcing of local raw materials for adsorption processes coupled with the need for better management of non-biodegradable solid waste materials.

\* The understanding of adsorption isotherms is important in the solution of a large class of industrial problems. Many of these problems are of current research interest. One particular example is the safe and efficient storage, handling, and transportation of gases. It has been propose that flammable gases could be adsorbed onto a variety of substances prior to transportation, and then released into cylinder after their arrival (Bileo et al, 2001).

\* Finally, this work tries to extend the frontiers of knowledge in the equilibrium behaviour of multicomponent adsorption systems, especially with regard to aromatic and sulphur containing organic solutes.

## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 LITERATURE REVIEW OF WORK ALREADY DONE ON THE SUBJECT MATTER.

Several methods are available for aromatic, sulphur and odour removal. The choice of the obviation (deodourization) process route may be decided by performance, economic and local concentrations. The use of porous material particularly fuller's earth and clay for the refining of mineral oils has been a common refinery practice for many years. However, much of the initial work was geared towards deodourization of liquids, recovery of gases and the removal of moisture from liquids and gases (**Nelson, 1985**). The development of silica gel enhanced the separation of aromatic hydrocarbons from other refinery products (**Unezelman, 1967**). Other percolation processes such as ion exchange and chromatography were also developed to purify diluents and separate products.

It has been observed that in order to deodourise DPK, certain asphaltic or resinous materials, aromatics and even sulphur had to be removed, and that the odour of the oil was greatly improved after such treatments. This lead to the conclusion that the presence of aromatics and sulphur in DPK was responsible for its obnoxious odour (**Friedman, 1913**). Although the

deodourization of mineral oils had some times been effected through adsorption, it was not previously shown whether or not the laws of adsorption were applicable. **Rogers et al (1925)** were the first to carry out a number of deodourization experiments using a number of mineral oils and several adsorbents, and showed that Freundlich's Isotherm applies accurately. **Oduşina, (1988)** a latter work also confirmed that the removal of aromatics and sulphur from kerosene by adsorption on porocel clay can be fairly predicted by the Freundlich Isotherm.

Previous studies carried out by (**Nwadialo, 1988**) (**Onwu, 1978**) and (**Nkanu, 2000**) have shown that small particles sized clays adsorbed more efficiently due to greater pore space per unit surface area exposed. In the study of application of carbonized crude oil sludge in the desulphurization of kerosene **Frank, (2001)** stated that crude oil sludge mixed with saw dust charred and thermally activated can be used as an adsorbent for the removal of sulphur compounds contained in kerosene.

**Quinines et al (1998)** have proposed a method for determining sulphur in distillate cuts which not only obviate any preliminary separation, but also uses packed columns in gas chromatographic separation which features a sulphur-specific detector. Despite its procedural simplicity and

speed, it does not yield a great deal of information concerning the types of sulphur compounds present.

The gas chromatographic investigation of sulphur compounds in high boiling fractions requires the use of elevated temperatures. This in turn leads to column bleed and column degradation.

In the last decade, UOP has developed several new separation processes for the three xylene isomers and ethylbenzene which constitute the 8 carbon ( $C_8$ ) aromatic system that are economically more attractive than conventional techniques. These new processes involve adsorption from the liquid phase on a solid adsorbent. The adsorbent is carefully prepared to accentuate the relative strength of adsorption of the various components of the feed material.

The adsorbent exhibits a selective difference between the components that is in general more favourable than liquid phase relative volatilities. This selective advantage is theorized to be due to the more favourable nature of electronic force fields in solids than in a continuous liquid phase. Thus an adsorptive process can be more efficient than fractional distillation **(Deprosset et al, 1980)**.

Also, in the study of the effect of Adsorbent preparation parameters on the selectivity for xylene isomers separation **Miroskaw et al, (1982)**

Choose a binding material and analysed the effect of the binder on sorption capacity. Separation efficiency, mechanical resistance and the effect of thermal treatment on adsorbents' selectivity were determined. On the basis of these studies, a lot of adsorbents were prepared and utilized in pilot plant for the separation of xylene. **Belfort (1979)** has presented the adsorption behaviour of various organic homologs on activated carbon and correlated the molar adsorptive capacity with physiochemical/structural parameters. **Martin (1980)**, has reported the selection procedure of activated carbon for water and wastewater treatment. The adsorption behaviour was established by utilizing continuous flow and column systems.

Oxide adsorbents are often used to separate sulphur compounds and hydrocarbons. Among these, aluminosilicates are the most selective in relation to sulphur compounds and silica gels are the best selective. **Arhmetova (1982)**, studied the Adsorption of Thiophen, and Thiophenol on Alumina and Alumino Silica Gel at 50, 100, 150 and 200<sup>0</sup>C in 1 hour, and compounds containing sulphur atom were adsorbed.

The earliest experiment on multi-component adsorption were basically studies of adsorption of mixtures from solutions, which include cases of decolourization of mineral oils (**Odunsina, 1938**).

In spite of this, information concerning the adsorption of mixtures especially with regard to the reliability of the results and the satisfactory nature of the theoretical interpretations, is far inferior to our knowledge of pure components. Although adsorption techniques are primarily employed to separate mixtures, the present body of knowledge does not satisfy practical needs, and insufficient attention is given to the adsorption of mixtures in the literature (**Poel, et al, 1964**). Even where attempts are made to summarise the present state of knowledge of adsorption of mixtures and to indicate the important semi-empirical relationships and rules, such discussions have been limited to binary mixtures and mostly those of gases.

Attempts will be made here to mention some of the efforts made so far towards the explanation of multi component adsorption from solution. **Adamson, (1967)** considered adsorption from solutions of nonelectrolytes and suggested that logical and necessary division be made according to whether or not the adsorbate is present in dilute solutions. In the first case, treatment is very similar to that for gas adsorption, whereas, in the second case, the role of the solvent itself becomes more explicit.

The complexity of this aspect of adsorption arises from the effects of the competition for adsorption sites on adsorbents between the molecules of the

the components present in solution. **Sinkinson et al, 1926**) noted that in the case of gases, the most easily liquefied gas is mostly readily adsorbed by porous substances. If the difference is sufficiently marked, selective adsorption sets in. **Kipling, (1965)** observed that for preferential adsorption of components from mixtures, multiple layer may occur. However, the selectivity will be vested primarily in the monolayer.

Theoretical predictions presented so far on this topic include the work of **Digiano et al, (1967)** who presented a simplified model for competitive equilibrium adsorption. **Cullinan, (1965)** also proposed a consistent mode of multi component diffusion flux representation and applied to the solution of the general linearised equations of multi component mass transfer. The results not only afforded a basis for uniformity of definitions hereto not available, but also offered a groundwork for the better understanding of the phenomenon of multi component diffusion.

In a paper by **Sircar, (1991)** the role of adsorbent heterogeneity was extensively explored. In it, he developed some simple analytical but thermodynamically consistent correlations between simple and multi component gas adsorption equilibria on the heterogeneous solids using a systematic statistical approach. In an earlier work, he had looked into multi-

component adsorption kinetics (**Sircar, 1989**). Here, it was shown that the adsorbate mass transfer into the adsorbent particle in a packed bed may be controlled by a gas film resistance outside the particles, the resistance to surface diffusion of the adsorbed molecules or a combination of these resistance.

### **2.1.1 Aromatic and Non-aromatic Hydrocarbon Separation:**

Aromatics are partially removed from kerosene and jetfuels to improve smoke point and burning characteristics. This removal is commonly accomplished by hydroprocessing but can also be achieved by liquid extraction with solvents, such as furfural, or by adsorptive separation. Table 2.1 shows the results of a simulated moving – bed pilot plant test using silica gel adsorbent and feedstock components mainly in the  $C_{10} - C_{15}$  range. The extent of extraction does not vary greatly for each of the various species of aromatics present. Silica gel tends to extract all aromatics from nonaromatics (**Broughton) and Hardison, 1962**).

**Table 2.1:** Separation of aromatics from nonaromatics in C<sub>10</sub> – C<sub>15</sub> light cycle oil.

Component	Feed vol%	Extract vol%	Raffinate vol%	Extraction %
Aromatics				
Alylbenzene	17.9	34.3	7.5	76
Tetralins	8.3	14.8	4.2	71
Naphthalene	13.6	30.0	1.6	86
Acronaphthenes	4.4	9.1	0.8	89
Total aromatics	47.6	95.0	14.9	82
Non aromatics	52.4	5.0	85.1	18
<b>Total</b>	100.0	100.0	100.0	100

**Source:** Kirk – Othma (1984)

## 2.2 REVIEW OF DEODOURIZATION PROCESS ROUTE

Several methods are available for odour removal. The choice of the obviation process route may be decided by performance, economic and local consideration. Optimization methods may be used in choosing the process that will give maximum yield at minimum cost and other considerations such as: availability and cost of raw materials, efficiency of process and energy requirements.

The process available for aromatics and sulphur removal can be divided into three major groups:

- (i) The Extraction method e. g Edeleanu process

- (ii) Adsorption method: Adsorption methods use adsorbents like silical gel or activated carbon to remove the sulphur and aromatic contents in the DPK and ;
- (iii) Treatment methods: (a) Hydro treating (b) Acid treatment and (c) Sweetening Processes

### 2.2.1 SOLVENT EXTRACTION PROCESS

#### **Edeleanu Process**

The Edeleanu Process is the oldest liquid extraction process used in the petroleum industry and uses liquid sulphur dioxide as the solvent. At the normal boiling point of sulphur dioxide of  $10^{\circ}\text{C}$ , aromatic and unsaturated hydrocarbons are completely miscible with liquid sulphur dioxide but the paraffinic hydrocarbons are not. Sulphur dioxide treatment also removes cyclic compounds and nitrogen compounds. The Edeleanu process has long been used in the manufacture of premium kerosene , which dissolves the removal of aromatics leading to enhanced burning properties. Straight- run kerosene cut ( $150\text{-}250^{\circ}\text{C}$ ) obtained from Assam crude as such is unsuitable for marketing purposes because of its high aromatic content. Kerosene with high aromatic content burns with a smoky flame. In order , therefore, to produce a superior quality of kerosene which will burn with a stipulated flame height without smoke , the straight- run kerosene is treated with liquid sulphur dioxide to remove its aromatic hydrocarbon content.

This process is also applied to selected naphthas for the recovery of high octane number blending stocks and for the recovery of lacquer diluents. Diesel oils of high diesel index and improved ignition quality can be made from selected gas oils . The operating condition in the liquid sulphur dioxide

extraction process varies from  $-30^{\circ}\text{C}$  for kerosene and other liquid stocks to  $15^{\circ}\text{C}$  or higher for high point material. The high solvent power and selectivity of carbon dioxide permit solvent ratios of the order of 0.5 to 1.5 volumes of solvent per volume of oil.

**Process description-** A simplified flow diagram of the Edeleanu process for treating kerosene is given in fig. 2.1. Straight-run kerosene (feed) is passed through a column filled rock salt (sodium chloride) at about 40-45° C to remove traces of free water. It is then deaerated in vacuum column maintained at a pressure of 0.04atm. If air removal is not done, it will mix up with SO<sub>2</sub> vapor. Air cannot be condensed under the normal operating conditions and it will increase the system pressure considerably, which will be a hindrance to proper SO<sub>2</sub> recovery. Deaerated kerosene is cooled to about 10<sup>0</sup>C and then passed through CaCl<sub>2</sub> drier to remove dissolved water in it. Water content of kerosene from CaCl<sub>2</sub> drier is in the range of 15-20ppm compared to the water content of 40ppm (approximately) in the feed. Dehydrated kerosene is further chilled at about -15<sup>0</sup>C and then sent to a countercurrent extraction column packed with ceramic Rasching rings. In the extractor, kerosene is introduced at the bottom and is extracted with chilled liquid sulphur dioxide (-26<sup>0</sup>C) introduced at the top of the column in the ratio of 1;1 by volume. In the extraction column phase, separation takes place due to difference in specific gravity. The lighter top stream, called raffinate, consists of quality kerosene and small quantity of liquid sulphur dioxide. The heavier bottom stream called extracts consists of bulk liquid dioxide and aromatics. The extract and raffinate streams are then sent to their respective sulphur dioxide recovery systems. These recovery systems consists of a number of fractionating columns operating at different temperatures and pressures. The removal of SO<sub>2</sub> from the extract is achieved in four separate columns which operate at gauge pressures of 13kgf/cm<sup>2</sup> (high), 7 kgf/cm<sup>2</sup> (medium), 0.2kgf/cm<sup>2</sup> (low), and -0.5kgf/cm<sup>2</sup> (vacuum). The recovered sulphur dioxide vapour from the raffinate and extract streams is recirculated after cooling liquefaction. The raffinate and extract streams,

leaving their last column of the solvent recovery system, are water washed and caustic washed to remove and neutralize traces of sulphur and final water washing is carried out for removing caustic. In case of ATF run hypo-washing or heat treatment is given to meet the silver corrosion specification. The extract after caustic/washing is charged to a splitter fractionating column to yield two components viz: light aromatic extract and heavy aromatic extract. Light aromatic extract can be blended in motor spirit/naphtha and heavy aromatic extract can be used as diluent for light diesel fuel oil blends.

**Table 2.2: Typical operating conditions of a Edeleanu process**

Extractor pressure(bottom), kgf/cm <sup>2</sup>	<b>1.5</b>
Extractor temperature. <sup>0</sup> C	
Bottom	-18
Middle	-20
Top	-22
Solvent/feed ratio(vol./vol.)	1

**Table 2.3: Typical yield pattern**

Products	Yield, wt.%	
	ATF run	
Raffinate	58	63
Extract	41	36
Loss	1	1

### 2.2.2 Adsorptive Separation:

Adsorptive process has been used extensively in the removal of aromatics from petroleum fractions especially kerosene. Aromatics are partially removed from kerosene and jet fuels on a commercial basis, as sometimes required to improve smoke point and burning characteristics by adsorptive separation. A stimulated moving bed pilot plant using silical gel feedstock components in the C<sub>10</sub> to C<sub>15</sub> range has been operated with satisfactory results (**Broughten, 1986**).

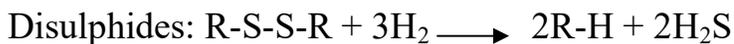
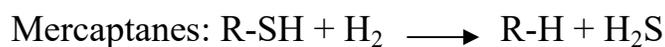
### 2.2.3 Treatments Methods

#### (i) Hydro-Treating:

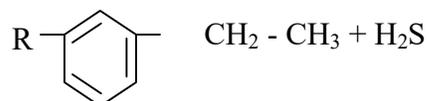
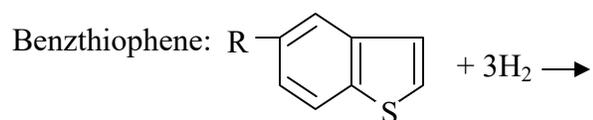
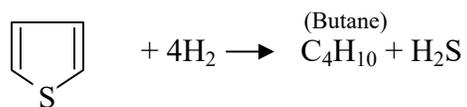
In the case of straight run products, chemical heating methods becomes less attractive since the development of hydrotreating method which became practical as a result of by-product hydrogen from catalytic reforming unit. Hydrotreating is employed industrially to remove sulphur, nitrogen and oxygen in the system at moderate temperature(500-800<sup>0</sup>F) and pressure (20-54 atm) using oxides of cobalt and molybdenum as catalyst. Sulphur, nitrogen and oxygen are removed as hydrogen sulphide, ammonia and water respectively

The following reactions take place in hydrotreating:

#### 1. Desulphurization reactions:

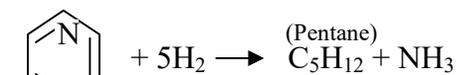


Thiophene:

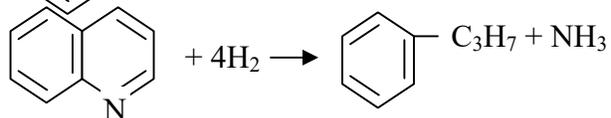


2. The removal of nitrogen:

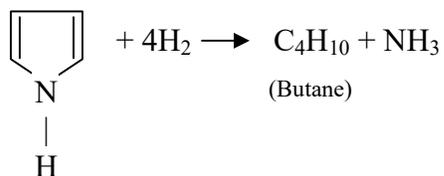
Pyridine



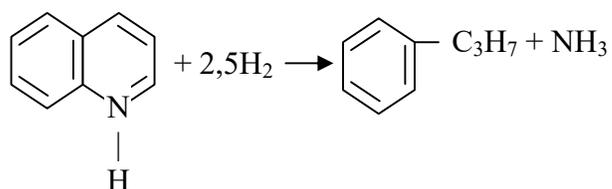
Quinoline



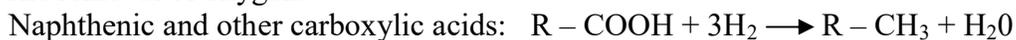
Pyrole



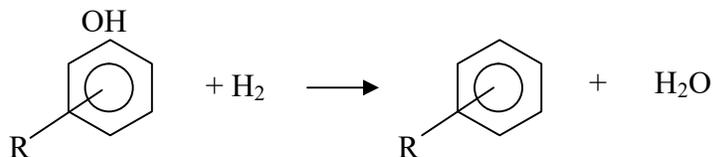
Indole:



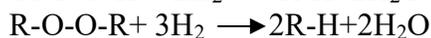
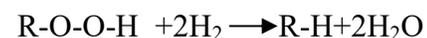
## 3. The removal of oxygen:



Phenoles:



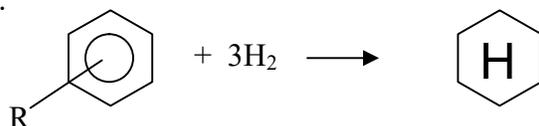
Peroxides:



## 4. The hydrogenation of double bonds:



Aromatics:



In addition to this, hydrocrack reactions also take place to a small extent, although this is not specifically aimed for.

Sulphur in organic sulphur compounds becomes converted to hydrogen sulphide  $\text{H}_2\text{S}$ , the nitrogen of organic nitrogen compounds to ammonia  $\text{NH}_3$ , and the oxygen of organic oxygen compounds to water  $\text{H}_2\text{O}$ . Most of the hydro-carbons formed in these processes have the same number of C atoms as the original heterocompounds. Solely in the case of sulphides, disulphides and some of the peroxides, the process results in two smaller hydrocarbons being formed. Furthermore, monocyclic heterocyclic compounds result in alkylaromatics.

Sulphur-resistant hydrogenation catalysts are used, usually cobalt and molybdenum oxides mixtures in the form of  $\text{M}_2\text{O}_3$  and  $\text{C}_2\text{O}_4\text{M}_2$  (cobalt molybdate) on a carrier material of  $\gamma$ -aluminium oxide. The catalyst

contains 3-4%  $C_O$  and 7-10%  $M_O$ . in the presence of the sulphur compounds in the feedstock, these catalyst oxides becomes converted to sulphides.

Sometimes, a fresh catalyst is first activated by the addition of hydrogen sulphide to the hydrogen, or carbon disulphide to the feedstock.

Molybdenum disulphide  $M_O S_2$  containing a certain proportion of  $C_O$  in the crystal matrix has a particularly good hydrogenation activity. The optimum relationship of  $M_O$ :  $C_O$  is 5.

Apart from the  $C_O M_O$  catalyst,  $Ni M_O$  catalyst is also used on aluminum oxide carriers. Catalyst containing nickel converts the nitrogen compounds quicker than the  $C_O M_O$  catalyst. For his reason, they are preferred for the hydrotreating of feedstocks prior to reforming process, because nitrogen compounds are particularly damaging to the types of catalyst used in reforming. Hydro treating catalyst containing nickel also has an increased activity for the hydrogenation of aromatics to naphthens. However this is undesirable when hydrotreating naphtha fractions, because naphthenes have lower octane number than aromatics. On the other hand, nickel catalysts are desirable in the hydrotreating of middle distillates, particularly kerosene, because aromatics, which are low in hydrogen, have a greater tendency to soot during combustion than the naphthenes.

Hydrotreating a catalyst only need to be regenerated at relatively long intervals because the hydrogen content of the reaction mixture prevents a serious build-up of coke. Only very small amounts of coke are deposited on the catalyst, so that its activity sinks only very slowly. This slow sinking in activity is compensated by increasing the reaction temperature. Edge life's are of the order of months to years. The catalyst is then regenerated in situ by burning off the coke and the high molecular polymers that have become deposited on its surface. In order to do this, first of all superheated steam is

blown through the catalyst bed to remove the hydrocarbon residues. Following this, approximately 2% is added to the steam stream, and the coke and other deposited materials becomes burnt off at reactor temperature of up to 550°C. However, a catalyst whose activity has become reduced by the deposition of heavy metals, in particular vanadium and nickel, cannot be regenerated in this way.

Hydrotreating is used for straight-run fractions from light gasoline to middle distillates and lubricating oil fractions, crack product fractions and sometimes even distillation residues.

**(b) Sulphuric Acid Treatment:**

Sulphuric acid is used to remove aromatics in kerosene and to remove or dissolve resinous materials, asphaltic substances, and sulphur as mercaptans. Acids concentration of 93% is generally used. However, sulphuric acid is highly corrosive and affects process equipment. Also, this process is relatively expensive. Treatment with sulphuric acid results in the sulphonation, oxidation, esterification and polymerization of certain components of mineral oils, some of the products becoming precipitated by or dissolved in the acid. The following reactions take place:

- (i) Aromatics , i-alkanes and thiophenes become sulphonated,
- (ii) Hydrogen sulphide and mercaptans become oxidized,
- (iii) Alkenes become esterified,
- (iv) Dialkenes become polymerized,
- (v) Aspalthenes and petroleum resins becomes precipitated,
- (vi) Sulphides, disulphides and sulphones become dissolved in the acid, and
- (vii) Basic nitrogen compounds become neutralized and dissolved in the acid.

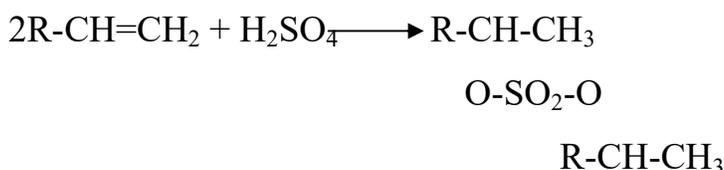
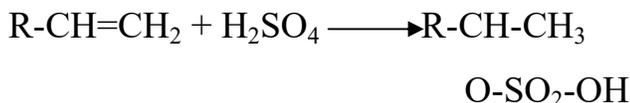
Sulphuric acid also has an oxidizing effect:



Hydrogen sulphide becomes oxidized to sulphur, and mercaptans R-SH to disulphides R-S-S-R, the latter being soluble in sulphuric acid.



Gaseous sulphur dioxide is formed during the reactions. As elementary sulphur is neither soluble in the acid nor in the oil-phase but remains suspended in the raffinate, and if the raffinate is heated it can react to form hydrogen sulphide once more, particularly if naphthenaromatic are present, if any hydrogen sulphide is dissolved in the feedstock it is advantage to remove it prior to acid treatment by means of alkali wash. Together with sulphuric acid, unsaturated hydrocarbons to form alkyl and dialkylesters.



The sulphuric acid monoalkylesters are readily soluble in the acid phase, whereas the dialkylesters are not, and remain in the raffinate. Dialkylesters only form at temperatures above 40<sup>0</sup>C and/ or extended reaction times. For this reason, products high in alkenes should be acid treated at low temperatures.

Under the influence of sulphuric acid, dialkenes polymerize to gum-like materials, which become precipitated. Similarly, precipitated and thus

removable from the products are the colloiddally-dispersed asphaltens and petroleum resins.

A whole row of sulphur compounds-sulphides, disulphides, sulphones, and sulphonic acids- which become formed during acid treatment from aromatics, i-alkenes and thiophenes are soluble in the acid phase, with which they can be removed from the product.

Basic nitrogen compounds are also soluble in the acid phase. However, oxygen compound are not affected by the process.

To summarize, acid treatment results in the removal of most of the sulphur compounds and basic nitrogen compounds, and under particular reaction conditions the aromatic hydrocarbons too. In addition, alkenes and dialkenes can also be removed, and both asphaltenes and petroleum resins becomes precipitated.

Thus, the raffinates produced are low in sulphur and have improved ageing characteristics. The more readily oxidizable components already become oxidized during the treatment and removed from the product. In addition to this, due to their freedom from alkenes, the treated raffinates have a considerably reduced tendency to gum formation.

**(c) Sweetening processes:**

All petroleum products contain sulphur compounds in term of various types of mercaptane. These mercaptances are harmful for the combustion engines and other systems. So it is essential to remove these undesirable sulphur compounds into some acceptable limits as per API limits. Sweetening process may be defined as the removal of sulphur and its compounds such as hydrogen sulphide, mercaptance etc from the petroleum products.

These are various processes for the removal of these mercaptans. However the important and world widely used for these methods are;

i. Hydro desulphurization

ii. Doctor's sweetening process

i. **Hydro desulphurization:**

Hydro-desulphurization of the petroleum product is carried out in a reactor known as hydroheater unit. The reactor having a cobalt and molybdenum based catalyst bed. The process proceeds at a very high temperature (300-320°C) and pressure (30-35 kg/cm<sup>2</sup>) in the presence of hydrogen gas. Due to these severe operating conditions sulphur compounds breaks and recombines with hydrogen gas to form H<sub>2</sub>S (gas). This H<sub>2</sub>S gas is then removed in a series of separator to get sulphur free product i.e the hydrogen sulphide formed maybe removed by scrubbing the hydrogen rich gas, separated from the plant product with an amine or other alkaline absorber liquid and may then be removed for the manufacture of sulphur and sulphuric acid.

**Reaction**



Mercaptans



## ii. Doctor's sweetening processes:

In this process mercaptanes present in the petroleum products are converted into disulphide by treatment with doctor's solution (Sodium Plumbite solution) and sulphur. Lead sulphide is regenerated to sodium plumbite by air blowing the solution.



Doctor sweetening process is carried out at 65<sup>0</sup>C-“20 parts of Doctor's solution are circulated per 100 parts of lead. Feed and doctor solution are contacted for 30 sec before sulphur solution is added and the total mixture is then stirred for 5-15 minutes. Sulphur addition should be controlled as excess sulphur produces polysulphides [ $\text{Pb}(\text{RS})_2 + 2\text{SPbS} + \text{RSSR}$ ] which reduces octane rating of gasoline and lower the burning quality of distillate fuels. Regeneration of doctor's solution is carried out at 80-110<sup>0</sup>C and 1-7 atmospheric pressure.

## 2.3 BASIC REFINERY PROCESSES

Petroleum refining has evolved continuously in response to changing consumer demand for better and different products. The original requirement was to produce kerosene as a cheaper and better source of light than whale oil. The development of the internal combustion engine led to the production of gasoline and diesel fuels. The evolution of the airplane created an initial need for high- octane aviation gasoline than for jet fuel, a sophisticated form

of the original products, kerosene. Present-day refineries produce a variety of products including many required as feedstock for the petrochemical industry.

**Table 2.4 HISTORY OF REFINING**

<b>YEAR</b>	<b>Process</b>	<b>Purpose</b>	<b>By- Product</b>
1862	Atmospheric distillation	Produce kerosene	Naphtha, tar, etc
1870	Vacuum distillation	Lubricants original, then cracking feedstocks(1930s)	Asphalt, residual, coker feedstock
1913	Thermal cracking	Increase gasoline yield	Residual, bunker fuel
1916	Sweetening	Reduce sulphur and odour	Sulphur
1930	Thermal reforming	Improve octane number	Residual
1932	Hydrogenation	Remove sulphur	Sulphur
1932	Coking	Produce gasoline feedstock	Coke
1935	Solvent extraction	Improve lubricant viscosity index	Aromatics
1935	Cat, polymerization	Improve gasoline yield and octane number	Petrochemical, feedstocks

1937	Catalytic cracking	Higher octane gasoline	Petrochemical, feedstocks
1939	Visbreaking	Reduce viscosity	Increased distillate, tar
1940	Alkylation	Increase gasoline octane and yield	High octane aviation gasoline
1940	Isomerization	Produce alkylation feedstock	Naphtha
1942	Fluid catalytic cracking	Increase gasoline yield and octane	Petrochemical feedstocks
1950	Deasphalting	Increase cracking feedstock	Asphalt
1952	Catalytic reforming	Convert low quality naphtha	Aromatics
1954	Hydrodisulphurization	Remove sulphur	Sulphur
1956	Inhibitor sweetening	Remove mercaptan	Disulphides
1957	Catalytic isomerization	Convert to molecules with higher octane number	Alkylation feedstocks
1960	Hydrocracking	Improve quality reduce sulphur	Alkylation feedstocks
1974	Catalytic dewaxing	Improve pour point	Wax
1975	Residual hydrocracking	Improve gasoline yield from residual	Heavy residuals

### 2.3.1: The Refining Process

Every refinery begins the separation of crude oil into different fractions by distillation. The fractions are further treated to convert them into mixtures of more useful saleable products by various methods such as cracking, reforming, alkylation, polymerization and isomerization. These mixtures of new compounds are then separated using methods such as fractionation and solvent extraction. Impurities are removed by various methods, e.g. dehydrate, desalting, sulphur removal and hydrotreating.. Refinery processes have developed in response to changing market demands for certain products. With the advent of the internal combustion engine, the main task of refineries became the production of petrol. The quantities of petrol available from distillation alone was insufficient to satisfy consumer demand. Refineries began to look for ways to produce more than better quality petrol. Two types of processes have been developed:

- (a) Breaking down large, heavy hydrocarbon molecules.
- (b) Reshaping or rebuilding hydrocarbon molecules

#### **Distillation(Fractionation)**

Because crude is a mixture of hydrocarbons with different boiling temperatures, it can be separated by distillation into groups of hydrocarbons that boil between two specified boiling points. Two types of distillation are performed: Atmospheric and Vacuum.

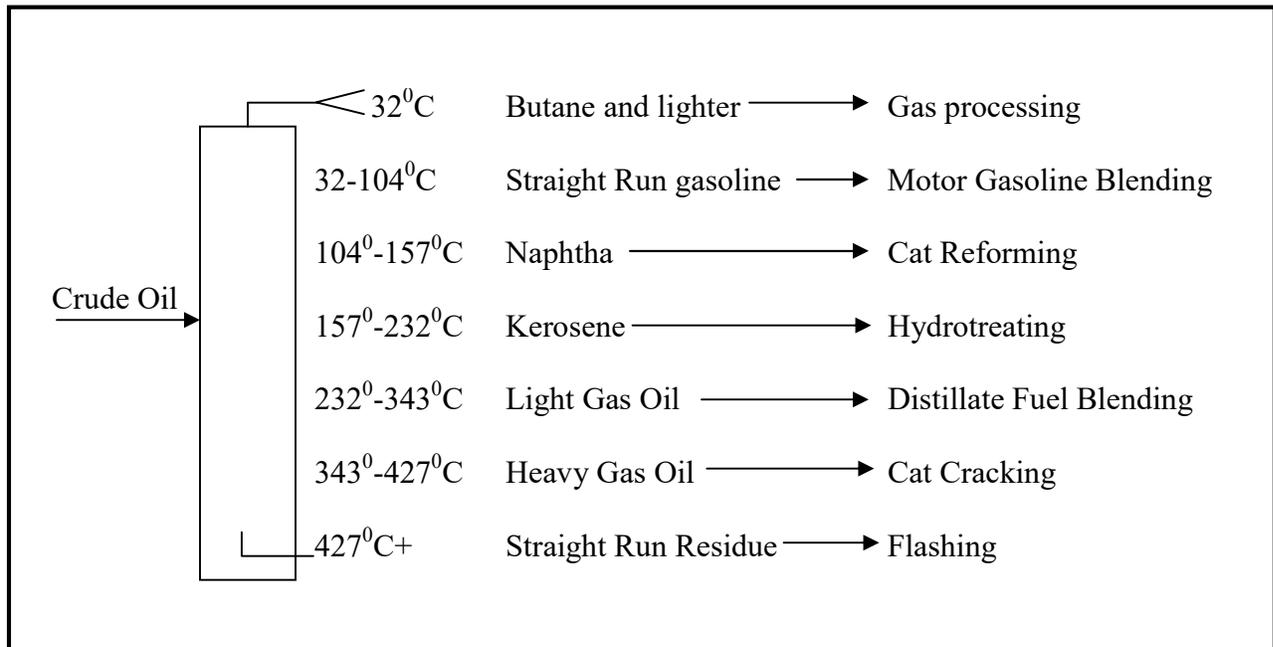
Atmospheric distillation takes place in a distillation column or at a near atmospheric pressure. The crude oil is heated to 350-400<sup>0</sup>C and the vapour and liquid are piped into the distillation column. The liquid falls to the bottom and the vapour rises, passing through a series of perforated trays(sieve trays). Heavier hydrocarbons condense more quickly and settle on lower trays and lighter hydrocarbons remain as a vapour longer and condense on higher trays. Liquid fractions are drawn from the trays and removed. In this way the light gases, methane, propane and butane pass out to the top of the column. Petrol is formed in the top trays, kerosene and gas oils in the middle, and fuel oils at the bottom. Residue drawn off the bottom may be burned as fuel, processed into lubricating oils, waxes and bitumen or used as feedstock for cracking such as coke and gas.

To recover additional heavy distillates from this residue, it may be piped to a second distillation column where the process is repeated under vacuum, called vacuum distillation. This allows heavy hydrocarbons with boiling points of 450<sup>0</sup>C and higher to be separated without them partly cracking into unwanted products as coke and gas.

The heavy distillates recovered by vacuum distillation can be converted into lubricating oils by a variety of processes. The most common of these is called solvent extraction. In one version of this process the heavy distillate is washed with a liquid which does not dissolve in it but which dissolves( and so extracts), the non- lubricating components out of it. Another version uses a liquid which does not dissolve in it but which causes the non- lubricating oils components to precipitate(as an extract) from it. Other processes exist which removes

impurities by adsorption onto a highly porous solid or which remove any waxes that may be present by causing to crystallize and precipitate out

**Table 2.5 Distilling Crude and Product Disposition**



## 2.4 DEFINITION AND CHARACTERISTICS OF AN ADSORBENT

An adsorbent is any substance having the ability concentrate significant quantities of other substances on its surface. An adsorbent is also the separating agent used to express the difference between molecules in a mixture. The separating agent is a solid surface on which the accumulation occurs.

The characteristics of adsorbents are as follows:

1. An adsorbent should not swell, soften or disintegrate in ordinary water
2. An adsorbent should have a high surface area
3. An adsorbent should not be toxic
4. An adsorbent should adsorb liquid, vapour and gasses without any change or form or properties

5. An adsorbent should have resistance to shock and abrasion
6. An adsorbent should be chemically inert to most gases and vapour.

#### **2.4.1 Advantages of Non- conventional adsorbents over Conventional adsorbents**

1. Non- conventional adsorbents are relatively cheaper compound to conventional ones and are easily available resulting in savings in cost.
2. Since the cost of these adsorbents is relatively low, they can be used once and discarded.
3. These non-conventional adsorbents can be disposed of safely

### **2.5 HISTORY OF BONE CHAR**

One of the earliest forms of black tinting material known to man was the charred bones of animals remaining in their early cooking fires. As far back as 2650 BC, bone char was used to paint the interior walls of Perneb's tomb in Egypt. During the 18<sup>th</sup> dynasty at Thebes, bone char was ground with a gum to create the first type of paints.

Through the ages, bone char found many diverse avenues for use. Hypocrites used bone char as a medicinal epilepsy, anthrax, gangrenous ulcers and mouthwash. Its medicinal value continued through the 1790s and many types of activated charcoal are still used for purification of pharmaceuticals today.

However, during the late 1790s a new business emerged. Charcoal was discovered as a means to clarify sugar liquors in the production of crytalized sugar. Louis Constant received a patent in 1812 for this purpose. In the year prior to this, M. Figuier, a Montpellier pharmacist, found that

bone char or bone black, worked better in decolorizing wines and vinegars. Considering Mr. Figuier's discovery, Mr. Payen and sons, and Mr. Pluvinet introduced bone charcoal to the sugar industry. This began a new era for bone charcoal, and a surprisingly new industry for a developing country, called United States.

As settlers followed the trail west to establish homesteads and farms in the Great American Heartland, they found the prairies littered with bones of the slaughtered buffalo or American Bison. Most settlers found the bones to be a nuisance, clearing them from their land, stock piling them and then destroying them. This is until fertilizer plants back East expressed interest in them. Bone gathering and selling began first in the Plains area around 1884, and grew into a thriving industry. Four hundred trainloads per year of bones were shipped back east. The average price for one ton of dried bones was \$10.00. This allowed many settlers to pick bones at their leisure to increase the family income. Because picking bones was not a strenuous chore, even the children participated in gathering bones to supplement the family's income.

### **2.5.1 PRODUCTION OF BONE CHAR PROCESS**

Bone char, also known as bone black or animal charcoal, is a granular black material produced by calcinating animal bones. This process is also known as destructive distillation of animal bones in the absence of oxygen. Thus, animal bones are carefully selected and prepared for calcinations. Only fresh, hard bones free from extraneous material can be used. This is accomplished by boiling or rendering the bones to remove fat and oily hermetically sealed retorts in kilns. The process operates at temperatures up to 1000<sup>0</sup>C and carbonization time is around 12 hours. The subsequent

pigment is created by crushing the bone char and screening it into various sizes, which range from 0.3 to 44 microns. These intermediary products are then custom blended to create a wide variety of shades which are suitable for many different applications.

The manufactured bone char is a unique adsorbent pigment composed principally of carbon and hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] the latter being the inorganic constituent of natural bone. The carbon content of the bone charcoal is derived from the complete carbonization of the naturally occurring organic content of the raw material (bone) and is around 10% by weight of the finished product. During the manufacturing process, a micro-porous structure of wide pore size distribution is formed within both the carbon and the hydroxyapatite components. Unlike many other charcoal and activated carbons, this porosity is achieved totally by thermal means without the use of any other chemical additives. Each of the two components of bone charcoal, the carbon and the hydroxyapatite, play a distinct role in the adsorption process. The carbon surface adsorbs weakly anionic molecules while the hydroxyapatite adsorbs strongly charged molecules together with many inorganic ions. The total surface area of bone charcoal is approximately  $100\text{m}^2/\text{g}$  of which around 50% is attributable to the carbon content. The product also exhibits a unique buffering capacity, thus maintaining alkalinity of the adsorbate.

## **2.5.2 PROPERTIES OF BONE CHAR**

- (a) A well-burned char has a firm physical structure, high porosity and white ash upon ignition.
- (b) It is non-toxic material

- (c) Bone char has also a high adsorptive capacity for lead, mercury and arsenic
- (d) Low vehicle adsorption and heat stability

Bone char is classified as non-hazardous and does not contain aromatic hydrocarbons, which are considered to be carcinogenic. Because of this, bone char can be used for food grade applications, which meet the food chemical codex.

Other properties of bone char are its low vehicle adsorption and heat stability.

### 2.5.3 COMPOSITION / SPECIFICATION

Through the calcining process crushed bone is stripped clean leaving carbon and tricalcium phosphate.

Carbon content	-	9 – 11%
Acid soluble Ash	-	3% max
Tricalcium phosphate	-	70 – 76% max
Calcium carbonate	-	7 – 9%
Calcium sulfate	-	0.1 – 0.2%
Total surface area	-	100m <sup>2</sup> /g
Carbon surface area	-	50m <sup>2</sup> /g
Iron	-	<0.3%
Pore size distribution	-	7.5 – 60,000nm
Pore volume	-	0.225cm <sup>2</sup> /g
Moisture (as packed)	-	5% max
Bulk density	-	40 ibs/ft <sup>3</sup>
Typical mesh size available	-	4 x 6 / 20 x 60

## 2.6 LIMESTONE

Limestone is a rock containing chiefly calcium carbonate and variable quantities of magnesium carbonate. Production of limestone in the United State (1970) is approximately 630 million tons/yr. Limestone is classified as highcalcium ( $\text{CaCO}_3$  containing 5% or less  $\text{MgCO}_3$ ); dolomitic ( $\text{CaCO}_3$ ); and magnesium (predominantly  $\text{CaCO}_3$  but containing 5-35%  $\text{MgCO}_3$ ). High calcium limestone occurs as two minerals, calcite and aragonite. The former is the ordinary stable form, having a specific gravity of 2.71, Mohs' hardness of 3.0, and rhomboheral crystal structure. Aragonite is  $\text{CaCO}_3$  precipitated from salty water either by inorganic processes or by the formation of marine shells. Aragonite is relatively unstable, slowly transforming to calcite. Aragonite has a specific gravity of 2.93 and Mohs' hardness 3.5-4.0, and crystallizes in the orthorhombic form. Dolomite is a chemical compound, not a physical mixture, resulting from contact of Mg-bearing waters with calcite. Dolomite has a specific gravity of 2.8-2.9, Mohs' hardness of 3.5-4.0, and a rhombohedral crystal structure. All limestone evolve  $\text{CO}_2$  and bubble in dilute HCl, providing a simple means of mineral identification. Dolomite reacts only in hot dilute HCl, while calcite will decompose in cold dilute HCl.

Limestone vary greatly in colour and texture. Texture ranges from dense and hard limestone, e.g. marble or travertine, which can be sawed and polished for use as decoratine stone, to soft, friable forms e.g. chalk and marl. Chalks is an extremely fine-grained white limestone, while marl is an impure deposition product containing clay and sand. Texture, hardness, and porosity appear to be functions of degree of cementation and consolidation during formation of these materials. Colour variation is due to impurities. Impurities may be deleterious, e.g. sulfur and phosphorus in stone for

metallurgical processes, or harmless or beneficial, e.g. argillaceous impurities in Portland cement rock.

Over 90% of all limestone is quarried the balance is mined underground. Although limestone occurs widely, good chemical and metallurgical grade limestone is scarce in many areas. Along the coast, oyster-or clamshells are dredged as a source of  $\text{CaCO}_3$ . Limestone normally is processed through a series of crushing, screening and grinding operations. Because of transportation costs, the proximity of limestone sources to users is essential.

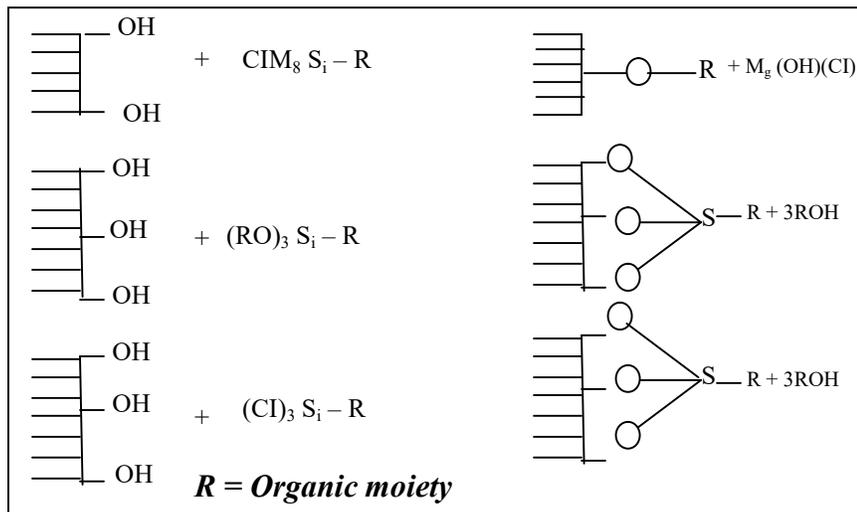
The major use of limestone is in construction (asphalt filler, road stone, riprap and bituminous aggregate), representing about 60% of total consumption. Portland cement consumes about 15%, lime manufacture about 5%, agricultural liming about 5%, and use as a blast-furnace flux in iron production about 5%. Other applications include ground carbonate fillers for paint, paper, plastics and adhesives; incorporation in animal feeds ; as a fertilizer filler; in glass and refractories manufacture; and for acid neutralization. Limestone is the source of the cheapest alkali for the chemical industry and a leading candidate for control of  $\text{SO}_2$  pollution from industrial combustion processes. Lime also is used to neutralize acidic mine waters.

## **2.7 SILICA GEL**

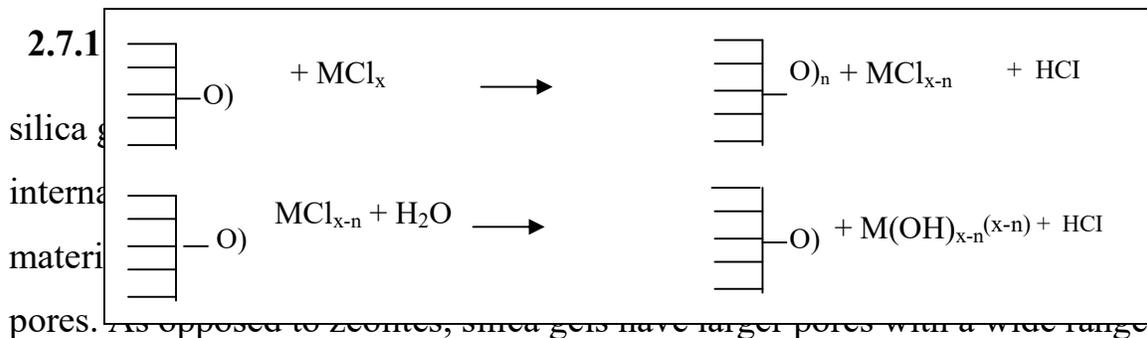
The silica gel can be considered a condensation product of silicic acid,  $(\text{Si}(\text{OH})_4)$ . Its structure consists of tetrahedral units of  $\text{SiO}_4$ , United by siloxane (Si-O-Si) in its interior, constituting in a material forms amorphous characteristics, besides hard and porous, forming particles with irregular forms that can be triturated and selected. The commercial type silica

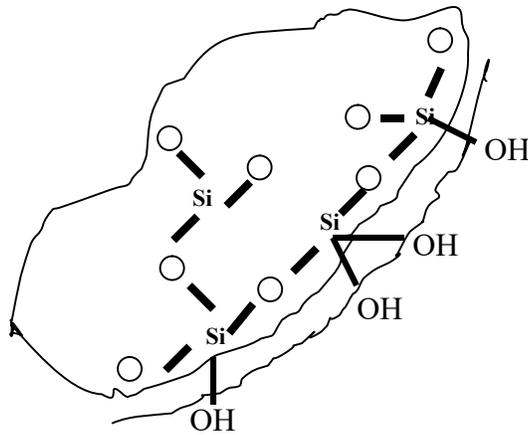
presents a specific area of 300 to 800 m<sup>2</sup> g<sup>-1</sup>, with pores diameters of 20 to 150 Å, containing impurities such as ions sodium, calcium, aluminum, Fe (III), and Ti (IV) in the order of 0.01-0.05%. The silica surface under normal conditions is covered with hydroxyl groups (silanol groups: Si-OH) that exercise important functions in adsorption processes, while the interior of the solid presents connection type siloxanes. Several studies evaluated the concentration maximum of silanol groups on the silica gel surface after activation at 150°C as being 8.0-13.0 moles.nm<sup>-2</sup>, corresponding to 4.5-8.0 groups.nm<sup>-2</sup>, depending on the silica type. Currently it is accepted that the estimated number of OH groups per nm<sup>-2</sup>, accessible in the silica surface, is between 4 and 5. The inorganic adsorbent most used as support is the silica gel, due mostly to its chemical behaviour determined by reactivity of the silanol groups present in the chemical reactions with other organic or inorganic groups, modifying entirely the original silica gel properties. The functionalization is a modification process of porous adsorbent surfaces, via chemical bonding with other organic or inorganic groups, involving, therefore, a reaction between a support and an adequate modifying agent. This procedure supplies to the silica surface specific properties, allowing several applications.

Silica gel surface can be modified by two distinct processes: organofunctionalization where the modifying agent is an organic group, and inorganofunctionalization, in which the group anchored on the surface can be an organometallic composite or a metallic oxide. Fig. 2.2 and 2.3 show in a schematic fashion the reactions that take place in the organo-and inorganofunctionalization.



**Fig. 2.2:** Schematic of organic functionalization reactions on silica gel surface.





**Fig. 2.4 Pore size of silical gel**

It is possible to adjust the prize range in the manufacturing process: - Silica gels synthesized with an average pore size of about  $20 \text{ \AA}$  are known as narrow pore silica gels - Silica gels with an average pore size of about  $110 \text{ \AA}$  and beyond are called wide pore silica gels. Silica gels maintain their structure when activated. Activation frees the large internal surface area and pore volume, enabling physical adsorption and capillary condensation.

Silica gel is extremely pure by industrial standards due to the absence of noticeable concentrations of metallic compounds like aluminium, iron or heavy metals. Therefore pure silica gel is much less active as a catalyst than other adsorbents like zeolites or aluminas, thus unwanted reactions like cracking reactions in hydrocarbon streams and resulting coke formation can be minimized.

### **2.7.2 Adsorption on Silica Gels**

Like zeolites, silica gel functions on the basis of physisorption. Adsorption occurs due to van der Waals interactions and capillary condensation at high humidities. The adsorption force is less than for zeolites, resulting in a lower adsorption capacity at low concentrations of adsorbates.

On the other hand, at higher concentrations of adsorbents, the adsorption capacity is higher than for zeolites, due to the higher internal pore volume. Certain grades of silica can adsorb up to 1.2 times their own weight of water.

### **2.7.3 Chemical Formula / Properties**

#### **SiO<sub>2</sub> (Silica Gel)**

- Trade name / synonym: silica gel
- Molecular weight: 60.08
- Boiling point: 2230°C
- Melting point: 1610°C

Silica gel is form of silicon dioxide, SiO<sub>2</sub>, the material that occurs in nature as sand. The difference between silica gel and sand is that sand is a crystalline, non-porous form, whereas silica gel is non-crystalline and highly porous. Silica gel is synthetically manufactured from the chemical reaction between sodium silicate and sulfuric acid.

Silica gel is an amorphous adsorptive substance with stable chemical properties and has a highly complicated porous structure. It is odorless, tasteless, and non-toxic, and offers an excellent capacity for physical and chemical dehumidification because of good absorbability, chemical stability, wide surface area and higher mechanical strength. Therefore silica gel is

used for packing food, pharmaceuticals, goods for export and precision instruments. Silica gel is easy to handle and silica gel saturated with moisture can be regenerated to afford new moisture protection by simply reheating under specified condition.

#### **2.7.4 Application**

Silica gel is used in various fields of our daily life as high adsorbent on high safety. Silica gel has excellent adsorption capacities at low relative humidity for keeping materials dry. Current uses of desiccant include the following: pharmaceutical stoppers, laboratory desiccators, diagnostic and medical equipment, transformer tank breathers, drying flower packaging during transportation and storage, gas drying and refining as well as protection of the electronic and telecommunications equipment photographic and optical equipment, engines, clothing and leather good, food (especially dried seaweed). Other uses of silica gel are aromatics, gas absorbent, and hydrogel, and so on.

### **2.8 CLAYS**

Clays, as they occur in nature, are rocks that may be consolidated or unconsolidated. They are technologically useful as a result of their distinctive properties, some of which include:

**a) Plasticity** – This signifies the property of the clay when wetted and permits deformation by application of relatively slight pressure and retention of the deformed shape after release of the pressure they are composed of extremely fine crystals or particles, often colloidal in size and usually platy in shape, of clay minerals with or without other rock or mineral particles.

To geologists, clay are sediments or sedimentary rock particle with diameters of  $3.9\mu\text{m}$  or less. Soil scientists define clays as disperse system of the colloidal products of weathering in which secondary mineral particles of dimensions smaller than  $2\mu\text{m}$  predominate. Clays, as defined by ceramists are earthy or stony mineral aggregates, plastic when sufficiently pulverized and wetted, rigid when dry, and vitreous when fired at a sufficiently high temperature. Chemically, the clay minerals, mostly phyllosicated, are hydrous silicates of Al, Mg, Fe and other less abundant elements.

The very fine clay particles give correspondingly large specific – surface areas that are physically supportive and chemically surface – reactive. Many clay mineral crystals carry an excess negative electric charge owing to internal substitution by lower valent cations. This increase internal reactivity in chemical combination and in ion exchange. The ability of clays to accommodate certain organic substances has been known for a very long time; this constitutes the basis of the wide use of clays for decolourizing edible oils and clarifying alcoholic beverages (**Grim, R.E., 1962; Siddiqui, M.K.H., 1968**). The fulling process, that is, the removal of grease from raw wool by means of an aqueous slurry of crude clays is traceable to Biblical times.

### **2.8.1 CLAY MINERAL STRUCTURES**

Details of the structures of clay minerals, together with their identification have been carried out by x-ray diffraction studies. **Hadding, A. (1923) and Rinne, F. (1924)**, were the first to apply x-ray diffraction analyses to the study of clays. By 1940, the crystallinity and structures of the main groups of layers silicates related to clay mineral had been established.

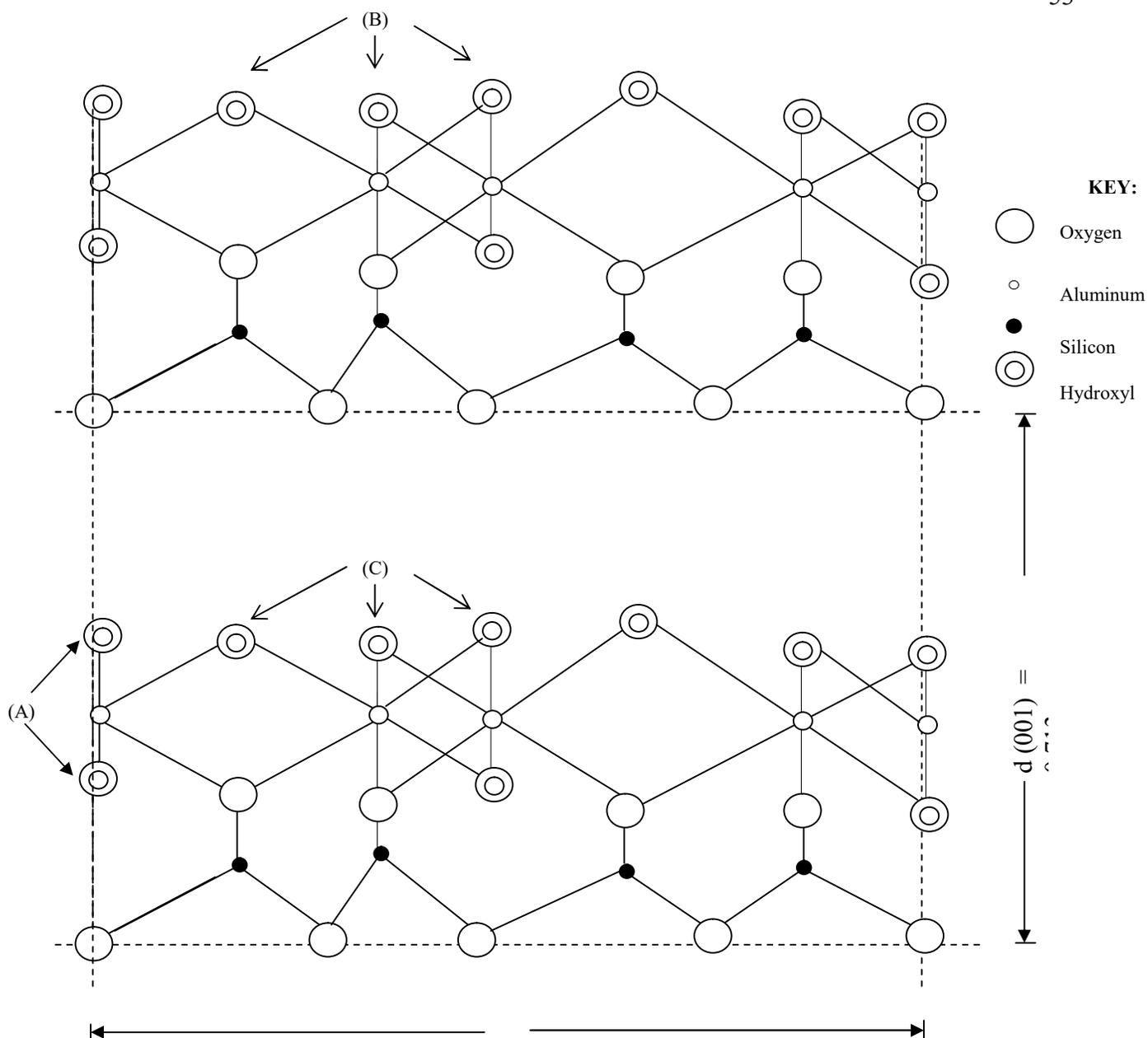
As the name suggests, the layer silicates or phyllosilicates are essentially made up of layers formed by condensation of sheets of linked Si (0, OH)<sub>4</sub> tetrahedra with those of linked M<sub>2-3</sub>(OH)<sub>6</sub> octahedra where M is either a divalent or a trivalent cation, condensation in a 1:1 proportion gives rise to the two-sheet or dimorphic minerals with a general layer formula,

M<sub>2-3</sub>Si<sub>2</sub>O<sub>5</sub> (OH)<sub>4</sub>, of which kaolinite is perhaps, the best known example. The three-sheet or trimorphic clays are formed by a 2:1 condensation, the octahedral sheet being sandwiched between two sheets of inward-pointing tetrahedral (the mica-type layer structure) giving a layer formula of M<sub>2-3</sub>Si<sub>4</sub>O<sub>10</sub> (OH)<sub>2</sub>. Four- sheet or tetramorphic units alternate with M(OH)<sub>2-3</sub> sheets of octahedrally coordinated M<sup>2+</sup> or M<sup>3+</sup> ions, exemplified by chlorite.

There is scope in these structures for isomorphous replacement, that is, for substitution of Si<sup>4+</sup> and/or M<sup>2+/3+</sup> for cations of similar size but different (usually lower) valency. As a result of this isomorphous substitution, the structure of many phyllosilicates is negatively charged. This positive charge deficiency may, to some extent, be compensated by internal substitution but for most part, electrical neutrality is maintained by sorption of extraneous cations which may or may not be exchangeable. This amount as well as the site of isomorphous replacement influence the surface and colloidal properties of the layer silicates, since they determine the surface density of charge and the cation-silicate layer attraction.

For kaolin (a 1:1 type mineral) each layer occupies a thickness of ~ 0.72nm, a value equal to the basal [d(001)] spacing. As depicted in Fig.2.5, the kaolinite layer is electrically neutral but in reality it carries a small negative charge due to a small amount of isomorphous replacement. **(Schofield, R.K. et al, 1953; Robertson, R.H.S. et al, 1954; Quirk, J.P., 1960)**. This permanent as opposed to the pH-dependent – negative charge

(**Schofield, R.K. 1949**) is responsible for the small but measurable ( $< 0.1 \text{ mol kg}^{-1}$ , monovalent cations) exchange capacity of kaolinite samples under acid conditions. **Hofmann et al (1961)** proposed that the exchange sites are located on only the tetrahedral surface of the kaolinite crystal. The superposition of oxygen and hydroxyl planes of successive layers within a single kaolinite crystal gives rise to pairing of O and OH ions and interlayer O ...HO H-bond formation. The forces arising from H-bonding and those due to non-specific van der Waals interaction holding adjacent layers together, must be overcome if interlayer sorption (intercalation) of extraneous species is to occur. For the reason, penetration of the kaolinite interlayers by organic compounds is difficult to achieve and adsorption is generally confined to the external crystal surfaces. The edges of the kaolinite crystals are of particular importance as they contain unsatisfied valencies (broken bonds) which occupy an appreciable proportion (10-20%) of the total crystal area [ $(15-40) \times 10^3 \text{m}^2 \text{kg}^{-1}$ ] (**Cashen, G.H., 1959**). In montmorillonite type mineral (2:1 type) only 2-3% of the total (external crystal and interlayer) area of  $760 \times 10^3 \text{m}^2 \text{kg}^{-1}$  is apportioned to the crystal edges (**Greene-Kelly, R., 1964**). The influence of the crystal edges on the pH-dependent charge and sorption of anion (**Edward, D.G. et al, 1962**) is much more in



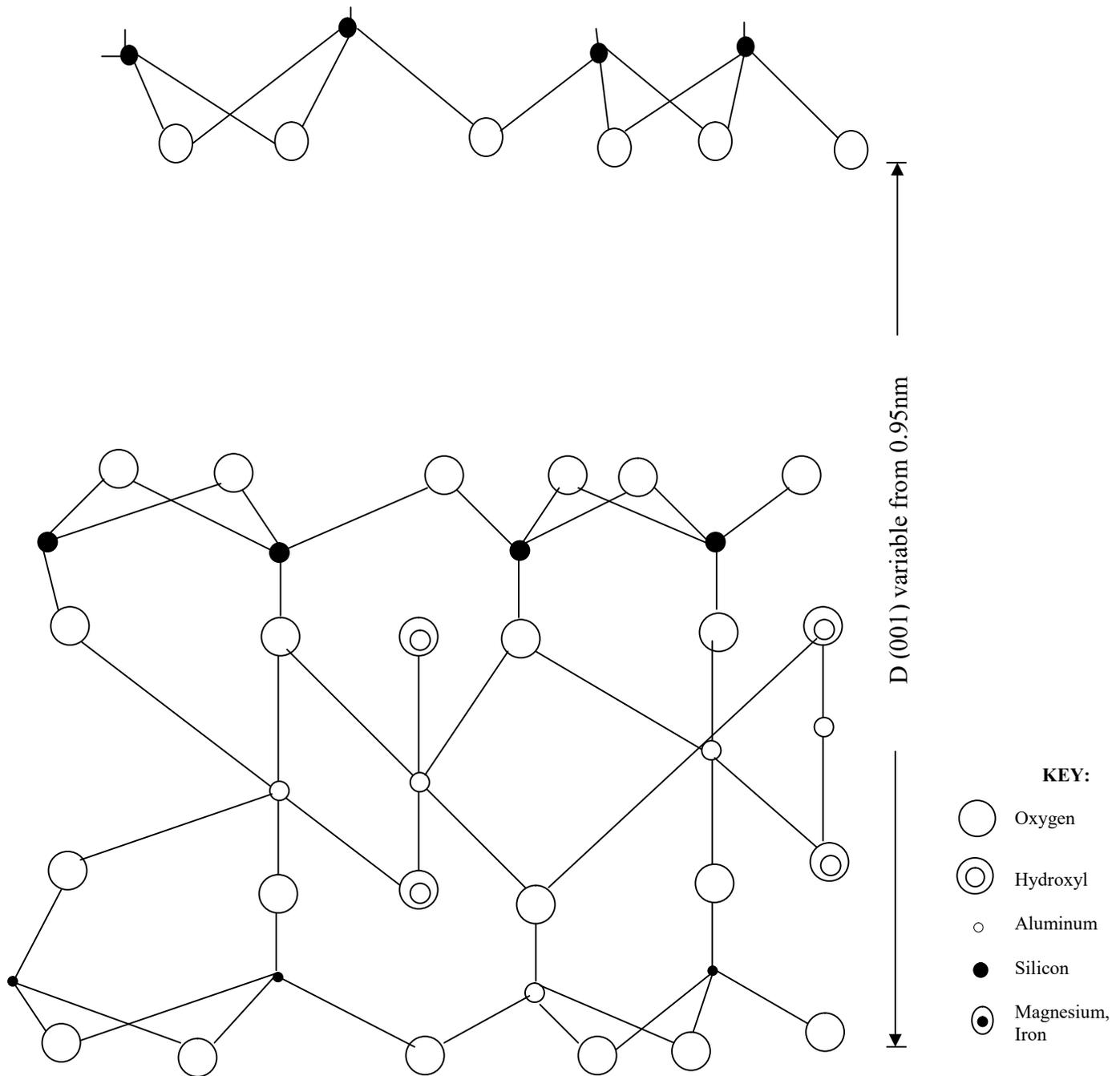
*Fig. 2.5: Structure of Kaolinite clay sample from Brindley, G.W. (1961)*

evidence with Kaolinite than with montmorillonite type minerals.

Halloysite, regarded as being composed of Kaolinite layers between which a single layer of water molecules is interposed, is capable of intercalating a variety of organic liquids by replacement of the interlayer water

**(MacEwan, D.M.C., 1948).** Intercalation is easier here than in Kaolinite because the layer consists of an open 'hexagonal' network of oxygen ions carrying negative charges whereas the other side may be linked to an  $\alpha$  – hydroxide surface and is positively charged. Because of the amphoteric nature of halloysite layers, for an organic compound (e.g. methanol) capable of being intercalated, montmorillonite tends to form a double – layer complex, but only a single layer is adsorbed in the halloysite interlayers. **MacEwan, D.M.C (1948)** rationalized these observations by proposing that the negatively charged oxygen surfaces of opposing montmorillonite layers tend to orient polar molecules and so individually adsorb a monolayer of the organic compound.

Figure 2.6 shows the generally accepted structure of montmorillonite. The choice of montmorillonite as a sorbent of organic compound is dictated by its large surface area ( $760 \times 10^3 \text{ m}^2\text{kg}^{-1}$ ), its high cation exchange capacity ( $\sim 1 \text{ mol kg}^{-1}$  monovalent cations) which is largely independent of salt concentration and pH, exchange cations water layers



***Fig. 2.6: The Hofmann-Endell-Wilm-Marshall-Maegde frau-Hendricks structure of montmorillonite clay sample.***

the relative ease by which it forms an interlayer complex with a wide range of organic with a wide range of organic molecules (Gram, R.E., 1953; McEwan, D.M.C., 1961; Weiss, A., 1963; Greenland, J.D., 1965). An added advantage is that changes in basal spacing accompanying interlayer sorption

may readily be followed by x-ray diffraction. The d (001) spacing of montmorillonite can thus vary over a wide range (0.95nm – 1.9nm).

Since uncharged polar organic molecules are adsorbed essentially by replacement of interlayer water, the behaviour of such molecules is likewise strongly influenced by the exchangeable cation. At low water contents, cation-dipole interactions are of paramount importance in their effect on the adsorption of polar organic species by clay minerals (Mortland, M.M., 1970).

## 2.8.2 ORIGIN OF CLAY

Clay is a product of geological weathering of the earth's surface. As mountains and hills (which are composed essentially of igneous rocks) are worn away by water and wind, the resulting debris (ground finer by the action of water / wind) is finally laid down according to their particle sizes in still estuaries or delta. Later these beds of disintegrated rocks, from which most soluble matter have been removed any, by gradual geological upheaval be elevated to dry land, where they exist as clay.

Chemically, rocks are composed of minerals which have definite composition. The basic minerals in igneous rocks are shown below.

<b>Mineral</b>		<b>% Composition</b>
Feldspar	-	59.5
Ferro –magnesium group	-	16.8
Quartz	-	12.0
Biotite	-	3.0
Titanium Mineral	-	1.5
All others	-	6.4

As shown above, only five minerals account for over 90% of the bulk of the earth's crust. Feldspar is the most common mineral (60%) and contains alumina and silica combined with one or more other oxides of an alkaline in nature. Commonly occurring feldspar are:

Orthoclase	-	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$
Albite	-	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$
Anorthite	-	$CaO \cdot Al_2O_3 \cdot 2SiO_2$

When feldspar is disintegrated by geological weathering, the alkaline part, namely the sodium, potash and lime being relatively soluble is carried off by water. This leaves alumina ( $Al_2O_3$ ) and silica which later become hydrated (or chemically combined) after long exposure, as shown below

$$K_2O \cdot Al_2O_3 \cdot 6SiO_2 + x H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 \cdot xH_2O + (SiO_2) + 3SiO_3$$

The chemical formular of clay  $Al_2O_3 \cdot 2 SiO_2 \cdot 2H_2O$ , gives only the molecule of alumina is associated with 2 molecules of silica and water respectively. The formular also over looks the complex array of impurities always present in actual sample. Chemically therefore, clay minerals can be defined as hydrous aluminum silicate with magnesium or iron proxying wholly or in part for aluminum and with alkali of alkaline metal present as essential constituent in some of them.

### 2.8.3 CLAY MINERAL NOMENCLATURE

Most of the names given to clay mineral are derived from locations of initial discovery. Examples include: montmorillonite clay named after montomorillon town in France, Kaolin from Chinese word 'Kauling' meaning hill ridges, Nontronite from Nontron town in France. Illite from Illinois, USA (%), Bentonite from Fort Benton in Wyoming, USA, Beldellite from Beidell in Colarado USA etc.

Towns or location derived – nomenclature presented problems to clay users and indications were that millions of clay type existed. However, with the development of x-ray diffraction, differential thermal analysis, coupled with infra-red spectroscopy, the structure of fine-grained clay can now be elucidated. Structural elucidation helps in assigning single name to a group of mineral sourced in different locations. Nowadays, the name montmorillonite (for example) is used both as a group name for all clay minerals with expanding lattice (e.g. Nontromite, illite, Berdellite) as well as a specific mineral name.

#### **2.8.4 CLAY MINERAL CLASSIFICATION**

At present, there is still considerable difference of opinion regarding the basis for satisfactory classification. The different classification suggested includes:

- (a) That crystalline clay mineral be divided into chain – and – layer structures and that the layer structure be divided into 2:1 and 1:1 families with the names trimorphic and dimorphic applied to them respectively
- (b) This is based on the shape and expandable or non-expandable character of the 2:1 and 1:1 layer silicates. The examples characteristics were emphasized because of the ease which they can be determined.
- (c) This is based on the relative position of the tetrahedral silicate and octahedral aluminate in the sample. Thus clays are designated as 1:1, 2:1, 1:2:1 etc.
- (d) This approach relates to the relative amount of exchangeable cations in the tetrahedral and octahedral position.
- (e) The classification based on layer charges as determined by associated international Pour l' Etude des Argiles (AIPEA) conference in 1963 is now

used for layered silicates (Phyllosilicate). This is the nearest approach to solving problem of classification. Under this approach, there exist layer charge of zero (e.g. Kaollin), 2:1 with layer charge of -1 (e.g. Montmorillonite), etc.

### **2.8.5 CHARACTERIZATION OF CLAY**

Structural elucidation of clay mineral using x-ray diffraction technique, Infra red spectroscopy, electron microscopy, etc. have helped immensely in clay characterization and classification. Supplementary characterization aimed at quality control and specifications are often necessary. These properties include ion-exchange capacity, moisture, surface area, density, etc.

### **2.8.6 ION-EXCHANGE AND SORPTION**

Clay minerals have the property of sorbing certain anions and cations and retaining them in an exchangeable state. However, more information is available regarding cation exchange than anion exchange. In clay minerals, the commonest exchangeable cations are  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$  in about that order of general relative abundance. The cation – exchange capacity is important in the utilization of clay mineral in plant food (in soil), alkali exchange in geological weathering, concentration of sodium in ocean, etc.

Normally, the exchangeable ions are held around the outside of the silica – alumina clay structure. Experimentally, methylene blue is the commonest solvent used in determining exchange capacity of clay mineral. The change in colour of a standard methylene blue permits a determination of the amount of the organic molecule adsorbed, from which cation-

exchange capacity value (expressed as ml equivalent per 100g of solvent) is determined. The value of cation exchange is dependent on particle size, crystallinity, time of treatment and concentration of clay. These factors controlling exchange capacity values often make the accurate determination very difficult – consequently, no high degree of accuracy can be claimed.

### **2.8.7 MOISTURE CONTENT**

Water molecules are held either as primary water (on surface of clay mineral), secondary water (in the inter layer of the crystalline region) or as tertiary water (chemical combination where it exist as integral part of its structure). The amount of this water affect the property and therefore performance of given clay mineral.

The primary water require little energy for its removal (drying at only little above room temperature), whereas a temperature of at least 100<sup>0</sup>C is needed at remove secondary water. Tertiary water removal results in modification of the clay mineral structure.

Moisture content determination involved eliminating the primary and secondary water content through heating at elevated temperature (100-110<sup>0</sup>C). The difference in weight gives the moisture content. However, for unprocessed clay (which is not pure clay mineral) loss in weight is not necessarily due entirely to loss of moisture. It may be due to loss of carbon dioxide from carbonate and to loss of volatile contents present in non-clay mineral component. Also divalent ion and / or manganese are present, their oxidation would tend to cause an increase in weight and thereby introduce apparent water loss. Variation in the specific characteristics of the clay minerals viz: grain size, crystallinity, nature of adsorbed ions, etc. affect dehydration results.

### **2.8.8 SURFACE AREA**

Surface area is one of the major features of clay affecting its numerous applications. Many methods have been employed in determining the surface area of clay mineral with each giving different result for same mineral. Such methods include static calorimeter, flow calorimeter, gaseous adsorption and adsorption from solution / solvent. All these adsorbed or the amount of heat evolved to give a mono layer coverage of a sheet on to a powder surface. Both the static calorimeter and gaseous (nitrogen) adsorption method are tedious and require skilled operation and drastic condition for degassing of powder. The flow calorimeter though useful is explosive. On the other hand, the method based on adsorption from solution is simple and does not involve much instrumentation – since it involves selecting a particular solvent whose area absorption per unit molecule is known. Commonly used solvents include methylene blue and Ethylene glycol.

### **2.8.9 SPECIFIC GRAVITY**

Determination of the specific gravity of clay mineral is made by aggregation of the fine particles using a liquid. The measurement is inherently difficult because of the likelihood of in-complete penetration of the liquid into the interstices of the aggregate mass. Furthermore, there is the possibility of a chemical or physical changes during the measurement as a consequence of adsorption of the liquid or an exchange reaction between the liquid and the clay material. It is therefore, particularly difficult to measure the density of the clay mineral in their natural state with their adsorbed water, which sometimes forms an integral part of their structure.

In case of clay mineral which are subject to isomorphous substitution within the lattice e.g. montmorillonite, the density varies from one specimen to another. For such clays, there is a range of characteristic density rather than a single value.

### 2.8.10 pH

The pH of clay samples essentially measures the critical acid or alkali range. This is, the pH at which solubility of the given clay is maximum, which in essence determines the limitation of acid treatment.

Solubility characteristics are important in preparation of clay for decolourizing oil, binding refractories, fixation of certain mineral in soil.

### 2.8.11 POROSITY

Many solid and powder materials both natural (stones, soils, minerals, etc) and manufactured (catalysts, cement, pharmaceuticals, metal oxides, ceramics, carbons, zeolites, etc) contain a certain void volume of empty space. This is distributed within the solid mass in the form of pores, cavities and cracks of various shapes and sizes. The ratio between the pore volume and the total or bulk volume in a porous material is called porosity. Mathematically, porosity is expressed as;

$$\emptyset = \frac{V_P}{V_B}$$

where;

$\emptyset$  = porosity (%)

$V_P$  = pore volume

$V_B$  = Bulk volume

The type and nature of porosity in natural materials depend on their formation (for instance, rocks can be of igneous, sedimentary or metamorphic origin) while in man-made materials depend on their manufacturing and generally it can be controlled. Porosity strongly determines important physical properties of materials such as durability, mechanical strength, permeability, adsorption properties, etc. The knowledge of pore structure is an important step in characterizing materials, and predicting their behaviour.

The characterization of solids in terms of porosity consists in determining the following parameters.

**Pore size:** Pore dimensions cover a very wide range, pores are classified according to three groups depending on the access size:

Micropores: less than 2nm diameter

Mesopores: between 2 and 50nm diameter

Macropores: larger than 50nm diameter

**Pore volume measurement:** The pore volume of adsorbent sample may be determined gravimetrically by totally saturating a sample with a liquid of known density and noting the weight increase.

**Pore size distribution:** It is generally represented as the relative abundance of the pore volume.

**Percentage porosity:** The percentage porosity is represented by ratio between the pore volume and the bulk volume multiplied by 100.

**Tortuosity:** The pores in the adsorbent are not straight and cylindrical rather they are a series of tortuous, interconnecting paths of varying cross-sectional areas. The inverse of porosity is called tortuosity.

### 2.8.12 PROPERTIES OF CLAY

1. Ability to hold certain cation and anion (ion exchange) which are readily exchangeable for cations and anions is most significant e.g. in soil, the retention and availability of potash added in fertilizers depends on certain cation exchange between the potash salt and clay mineral in the soil.
2. Ability to hold water. This water is of two types;
  - (i) Low temperature water which can be driven off by heating to  $143.6 - 212^{\circ}\text{F}$  ( $62 - 100^{\circ}\text{C}$ ). This is the water in pores, on the surface and around the edges of minerals composing the mineral.
  - (ii) OH structure water: Clays are dehydrated by heating. This loss of water (adsorbed, interlayer or structure 'OH' water) held clay minerals. Heating also causes clay structure to change which at high temperature new mineral phases are formed. This structural modification are particularly important in the firing of clay mineral.
3. Ability to react with organic mineral. Clay with high adsorbing capacity are used in decolouring oils, while others provide catalyst in cracking of organic compounds.

#### **Heat effect on Major Components of Fuller's Earth**

(A) **KAOLINITE:** Is a white, very fine, non abrasive (hardness 2 – 2.5 on mohs scale) and chemically inert in most uses. Kaoline does not swell in  $\text{H}_2\text{O}$ . It swells only by using intercalation compounds such as hydrazine, urea and aluminum acetate. Dehydration of Kaoline is complete at  $550^{\circ}$  it recrystallises to form mullite. It contains 30%  $\text{Al}_2\text{O}_3$ . It's use is in plant, ceramic, plastics, paper and in petroleum refining as a catalyst when treated with  $\text{H}_2\text{SO}_4$  and calcinated. Calcinated Kaoline is used as a source of Al. and silica to produce zeolite, which are used in molecular sieves.

**(B) BENTONITE**

Bentonite composed mainly of clay mineral Montmorillonite when montmorillonite is dehydrated, the interlayer water is lost at a relatively low temperature 212 – 390<sup>0</sup>F (100 – 200<sup>0</sup>C). The loss of 'OH' water begins gradually at about 840 - 930<sup>0</sup>F (450 – 500<sup>0</sup>C), ending at 1110 – 1290<sup>0</sup>F (600 – 750<sup>0</sup>C). The temperature vary with type and amount of structural substitution. The structure of montmorillonite usually persists to temperatures of the order of 1470<sup>0</sup>F – 1600<sup>0</sup>F (800 – 900<sup>0</sup>C). On further heating, a variety of phases form such as mulite, cristobalite, and cordierite depending on the composition and structure prior to fusion at 1830 – 2700<sup>0</sup>F (1000 – 1500<sup>0</sup>C)<sup>4</sup>.

Bentonite swells to form thixotropic gelatinous substance in contact with water. They are of two types;

- (i) The swelling bentonites which have a higher sodium content and shows considerable swelling about 15 times its volume. The swelling is irreversible.
- (ii) The non-swelling bentonite which have a higher calcium or magnesium content and swells only slightly when wetted and do not form stable aqueous dispersion.

Bentonite is used in drilling muds and as a catalyst in petroleum industry, as bonding agent in foundries and taconite pellet, and as adsorbent in many industries. They also contain some illite, chlorite and Kaolinite.

**(C) ATTAPULGITE**

Is a hydrated magnesium alumina-silicate with a needle like shape. This gives it its unusual properties. Each individual needle is exceedingly

small about 1 micro I length and  $\frac{1}{100th}$  micro across. They are used as adsorbent beds for petroleum, floor adsorbent, carriers for agricultural chemicals, catalyst agent in paints etc.

**Table 2.6 REVIEW OF WORK ON CONVENTIONAL AND NON-CONVENTIONAL ADSORBENTS**

<b>S/ No.</b>	<b>Authors</b>	<b>Adsorbate</b>	<b>Adsorbent</b>	<b>Variables Studied</b>	<b>Remarks</b>
1	Sekar and Murthy(1998)	Distillery spent wash	Powdered activated carbon	Initial conc., adsorbent dosage	Removal of 18% is noted and when spent wash was pretreated with polyelectrolyte as a flocculating agent, the colour was increased to 99%
2	Yeh and	Synthetic	Powdered	Effect of	95-98% of

	Thomas(1995)	dye wastewater of disperse-red-60	activated carbon (PAC)	contact time, conc. of PAC	COD removal for 25-200ppm and 88-98% for various particle sizes. Freundlich, Langmuir, Dziubek and Kowals adsorption isotherms fit well. Film-pore double resistance diffusion model describes the mass transfer External film mass transfer coefficient increases with decrease in particle size.
3	Yeh and Adrian	Disperse-red-60	Powdered activated	Contact time,	Decrease in particle size

	Thomas(1995)		carbon, activated alumina, molecular sieve & diatomite	adsorbent dosage, particle size	gave only a minor improvement for activated alumina; finer molecular sieve materials reduce the dosage requirement by half. Performance of adsorbents are as PAC> activated alumina> molecular sieve.
4	Mahesh et al. (1998)	Catechol	Granular activated carbon (industrial grade; laboratory grade)	Initial concentration, PH, adsorbent, dosage, particle size	Equilibrium studies that IGGAC has the maximum adsorption capacity. Diffusion studies

					showed that initial part of the adsorption is attributed to external mass transfer effects followed by intraparticle diffusion
5	Kapadia et al. (2000)	Petrochemical effluent (Raw)	Fly ash (coal)	Initial concentration adsorbent dosage, contact time.	Adsorption dose of 3-3.5% shows significant color removal. Contact period of 30-40 minutes gives optimum removal.
6	Kapadia et al (2000)	Petrochemical effluent (Raw)	Powdered activated carbon, granular activated carbon, carbon soot,	Bed height, particle size	Batch studies show that flyash also reduces suspended solids ammonical

			fly ash		nitrogen, COD, and nitrophenol apart from color. Efficiencies of adsorbents in decreasing order of PAC>carbon soot>GAC>fly ash.
7	Mall and Upadhyay (1998)	Malachite green, methylene blue	Fly ash 1&2	Initial concentration adsorbent dosage, contact time, bed height	Maximum color removal was attained with fly ash containing high carbon content.
8	Sharma et al (1999)	Malachite green	Bagasse pith, orange peel, sawdust, eichornia, shoot &	Effect of initial dye conc., initial adsorbent dosage &	PH studies shows that there exists some chemical interaction between

			root	PH	adsorbent and adsorbate. Efficiency in decreasing order Eichornia root>Eichornia shoot>sawdust >Bagasse
9	Nassar and Geundi(1991)	Astrazone blue,maxillon red, talon blue	Activated carbon, natural clay, bagasse pith, maize cob.	Initial concentration, adsorbent dosage	Activated carbon has maximum adsorption capacity. Cost analysis showed that natural clay,bagasse pith and maize cob were economically attractive than activated carbon.
10	Balasubra	Cr(iv)	Lignite	Adsorbent	Kinetic studies

	manium et al(1998)			dosage	showed the applicability of Lagergren model. The datas tend to follow first order rate kinetics.
11	Annadurai G.(1998)	Direct scarlet B.	Chitin	pH adsorbent dosage, particle size,temp	Diffusion studies showed adsorption mechanism involves an initial rapid uptake of dye due to surface adsorption followed by intraparticle diffusion.
12	Sankar et al (1999)	Direct Red 31, acid black 1 and blue 16	Rice bran based, activated carbon	Contact time,initial concentration,temp., particle	Maximum removal is seen at acidic pH and 20-30 degree C.The

				size	enthalpy value show that adsorption is a physical phenomena
13	Nassr and Magdy(1999)	Basic red 22	Natural clay	Initial concentration, adsorbent dosage, air flow rate. Mode of contact: fixed bed	Mass transfer study showed that external mass transfer is the only rate- controlling step
14	McKay and Ho(1998)	Astrazone Blue	Carbonized wood	Initial conc., agitation speed	Mass transfer study showed that external mass transfer is the only rate- controlling step
15	McKay and Allen(1980)	Telon Blue (Acid)	Peat	Initial conc., pH, adsorbent dose	Temperature has the most pronounced effect on mass

				contact time, agitation speed	transfer
16	McKay and Ho(1998)	Astrazone (BG)	Peat	Initial conc., adsorbent dosage	Pseudo-second order mechanism has been explained
17	Annadurai and Krishnan (1997)	Verofix red	Chitosan	Initial conc., pH, adsorbent dosage, temperature	Equilibrium data tend to follow Freundlich, Langmuir and Redlich-Peterson isotherms. Desorption studies showed that adsorption is a chemical phenomena
19	Das and Patnaik(2001)	Raw paper mill effluent	Blast furnace dust and slag	Initial COD conc., pH,	COD removal efficiency of BFD is

				temp., adsorbent dosage	significantly better than basic slag
20	McKay(198 2)	Deorlene Yellow, Teflon blue	Activated carbon	Bed height, particle size	Column studies show the applicability of BDST
21	McKay(198 2)	Deorlene Yellow, Teflon blue, Victoria blue	Activated carbon	Initial conc., PH, particle size, adsorbent dosage	Batch study shows that addition of salt in the form of sodium sulphate increase the rate of adsorption
22	McKay(198 3)	Deorlene Yellow, Teflon blue, Victoria blue, disperse blue	Activated carbon	Adsorbent particle size, initial conc.	Diffusion study show that intraparticle diffusion is not a rate controlling step
24	McKay(198	Teflon blue,	Activated	Initial	Homogenous

	4)	deorlene yellow	carbon	conc.	solid phase diffusion coefficient has been estimated using two- film resistance mass transfer
25	Allien et al (1989)	Maxilon Red, Astrazone yellow	Lignite	Initial conc	Equilibrium data tend to follow Freundlich, Langmuir and Redlich- Peterson isotherms. The equilibrium isotherm deviates from the theory.
26	Kapadia et al(2002)	Copper (Synthetic)	Fly ash	Initial conc., pH, adsorbent dosage	Maximum efficiency was at the pH of 6.0. The fly ash treatment raises the pH of effluent

27	De (2001)	Cadmium (Synthetic)	Coal fly ash	Bed height, initial conc., pH.	100% removal is seen at lower initial conc. of 3mg/l.
28	Rao et al (2001)	Copper and Lead (synthetic)	Bagasse, fly ash	Particle size, adsorbent dosage, initial conc., pH	Adsorption capacity decrease in the order fly ash, bagasse, PAC for removal of lead ions under optimum conditions
29	Rai et al (2000)	Magenta	Rice husk fly ash (Boiler feed)	Initial conc.	When compared to other adsorbents, Chitin has the maximum adsorbent potential, Nickel shows more preference for

					adsorption sites of chitin than zinc.

Reference : <http://www.eco.com/editorial/040201.html>

## 2.9 PROPERTIES / QUALITY OF KEROSENE

### 2.9.1 Smoke Point

The maximum flame height in millimeters (mm) at which the oil without smoking when tested in a standard wick-fed lamp under specified conditions is termed the smoke point.

Smoke point is important because it determines the degree of illumination possible from a given kerosene in a wick-fed lamp. Smoke point is related to the hydrocarbon composition of kerosene – it is highest with paraffins, considerably lower with naphthenes and very much lower with aromatics. The smoke point is also an indication of the tendency to smoke when the flame is smaller than the maximum stipulated size. Smoking under such conditions is usually caused by an inadequate supply of air or by a sudden draught.

Excise / customs requirements stipulate a minimum flame height of 18 mm mainly to distinguish it from HSD. The Indian customs method for testing smoke point tends to give somewhat lower readings than the standard IP method.

### **2.9.2 Burning Test: Char Value**

It is important that kerosene should burn freely and steadily for reasonable periods without attention to the appliance and with no diminution of flame. Burning tests have been developed to assess these properties.

The burning test is carried out for 24 hours in a standard lamp with a flame conforming to a specified size and shape. At the end of the test the consumption of kerosene and the amount of char formed on the wicks are measured, while a qualitative assessment is made of the appearance and colour of any bloom which may have been formed on the chimney. The char value is expressed as milligrams of dry char per kilogram of kerosene consumed.

### **2.9.3 Volatility**

The nature of the distillation range is of significance with regard to burning characteristics, such as warming up time and initial flame size, etc. and it is customary to place suitable limits on volatility. An abnormally high final boiling point can indicate contamination with higher boiling constituents.

### **2.9.4 Colour**

Colour in itself has no bearing on burning quality, but its measurement is useful in checking consistency of supplies and contamination.

### **2.9.5 Sulphur**

Only slight amounts of sulphur compounds remain in kerosene after refining which removes most of the undesirable products. Hydrogen

sulphide and mercaptans are removed so as to render the kerosene marketable from the point of view of odour.

Free or corrosive sulphur in appreciable amount could corrode metallic components of an appliance, e.g. pressure burner vapourising tubes which operate at high temperatures. The usual test applied in this connection is the copper corrosion test. The total sulphur content of kerosene should be low because oxides of sulphur formed during combustion should not be present to harmful extent in the atmosphere. This is particularly important in respect of indoor burning appliances which are not provided with the flue. Also, as mentioned earlier a higher sulphur content can contribute to the formation of lamp chimney deposits.

#### **2.9.6 Flash point**

In the interest of safety, legislation has been introduced in most countries fixing minimum flash point limits to prevent the inclusion of highly inflammable volatile fractions in kerosene distillates. According to controller of explosives classification it falls in the category of class B petroleum products. Its flash point (Abel) is stipulated as Min. 35 deg C in the IS specification.

#### **2.9.7 Specific Gravity**

As with colour, specific gravity has no relation to burning quality, but it is a useful aid for quantity reckoning and identity.

#### **2.9.8 Cloud Point**

This test is an indication of the temperature at which the wick may become coated with particles, thus, lowering the burning qualities of the oil.

### 2.9.9 Aniline Point

Aniline point of an oil is the lowest temperature at which the oil is completely miscible with an equal volume of aniline.

### 2.9.10 Doctor Test

This test is intended to quantitatively detect mercaptans in kerosene and similar petroleum products. In this process, mercaptans present in the petroleum are converted into disulphide solution.

### 2.9.11 Physical and Chemical Properties of Kerosene

**Chemical Family:** Mixed hydrocarbons / petroleum hydrocarbons/  
petroleum hydrocarbon distillate

**Molecular Formular:** Complex mixture of C<sub>9</sub> – C<sub>16</sub> hydrocarbons

Structural Formula: Complex mixture

**Appearance and Odour:** Water-white to pale yellow, mobile, oily, liquid with characteristic, mild petroleum odour. Combustible liquid and vapour. May accumulate static charge by flow or agitation. Liquid can float on water and may travel to distant locations and / or spread fire. Causes skin irritation. Aspiration hazard. Swallowing or vomiting of the liquid may result in aspiration into the lungs.

**Physical Hazards:** Flammable liquid and vapor. Keep away from heat, sparks, flames, static electricity or other sources of ignition.

**Molecular Weight:** Approximately 128-198 (mean molecular weight: 175)

**Relative Density (Specific Gravity):** 0.798 at 15.6 deg C (water = 1)

**Solubility in water:** Insoluble

**Solubility in other liquids:** Probably soluble in all proportions in other petroleum solvents

**Vapour Pressure:** Approximately 0.5 kPa (3.75 mm Hg) at 20 deg C

**Saturation Vapour concentration:** 4935 ppm (0.49%) at 20 deg C  
(calculated)

**Evaporation rate:** Approximately 0.01 (butyl acetate = 1)

**Boiling point:** Range 150-275 deg C; 150 – 290 deg C (302 – 554 deg F)

**Coefficient of Oil/water distribution (Partition coefficient: Log P (oct):**  
3.3-6+

**Viscosity Kinematic:** 1.1-2.5mm<sup>2</sup>/s (1.1-2-5 centistokes) at 20 deg C Note:  
Unless otherwise stated, values are determine at 120<sup>0</sup>C (68<sup>0</sup>F) and 760mm  
Hg (1 atm)

**Flash point:** 100-134<sup>0</sup>F / 38-57<sup>0</sup>C (TCC)

**Flammable / Explosive limits (%):** LEL: 0.7 / UEL: 7.0

**Auto ignition Temperature:** 410<sup>0</sup>F / 210<sup>0</sup>C

**Physical State:** Liquid

**Odour:** Characteristic petroleum

**Odour Threshold:** 0.03 ppm (0.0002 mg/L) (16% detection); 0.3 ppm  
(0.002 mg/L) (83% detection); 0.09 ppm (0.0006 mg/L) (probable odour  
threshold); 3 ppm (0.02 mg/L) 100% detection).

**Vapour Pressure (mm Hg):** 0.40

**Vapour Density (air = 1):** >4.5

**Specific gravity:** 0.775-0.840

**Percent Volatile:** 98-100 @ 545<sup>0</sup>F

**Evaporation Rate (nBuAc=1):** <1

**Boiling Point / Range:** 300-572<sup>0</sup>F / 149-300<sup>0</sup>C

**Freezing / melting point:** <-40<sup>0</sup>F / <-40<sup>0</sup>C

**Freezing / Melting point:** 50

**Bulk Density:** 6.73 Ibs/gal

**Reactivity:** 0 (Least)

**Percent volatile:** 60%

**Incapability:** Avoid strong oxidizers such as chloride and oxygen, strong acids or bases, amines.

**Hazardous decomposition products:** Combustion produces carbon monoxides, carbon dioxide and hydrocarbons.

**Table 2.7: PROPERTIES OF NIGERIA KEROSENE  
STRAIGHT – RUN DISTILLATE KEROSENE (175 – 250<sup>0</sup>C)  
BONNY LIGHT**

<b>PROPERTIES</b>	<b>LEVEL</b>
API Gravity	39.35
SP. Gr. At 15/15	0.828max
Sulphur % wt	0.13
Smoke point (mm)	19.4
Aromatics % vol.	17
Flash point ( <sup>0</sup> C)	45 minimum
KVOP	11.52
Distillation profile	Level
IBP ( <sup>0</sup> C)	160
10% V ( <sup>0</sup> C)	193
30%V ( <sup>0</sup> C)	205
50%V ( <sup>0</sup> C)	215
70% V ( <sup>0</sup> C)	226
90% V ( <sup>0</sup> C)	240
FBP	255

*Source: NNPC Refinery, PH*

**Table 2.8: TYPICAL PROPERTIES OF PETROLEUM  
HYDROCARBON SOLVENT (KEROSENE)**

	<b>PRODUCT</b>	<b>KEROSENE ODOURLESS</b>	<b>KEROSENE DISTILLATE</b>	<b>KEROSENE AROMATIC</b>
1	Normal boiling range (°C)	190 – 250	160 – 230	200 – 265
2	Flash point (°C)	69	43	78
3	SP. Gr at 15.6/15.6°C	0.780	0.791	0.893
4	Aromatic, % vol.	0.5	16	84
5	K.B. Number	28	36	71
6	Aniline pt (°C)	79	57	31
7	Viscosity at 25°C (cp)	1.60	1.11	1.77

*Source: G.D. Hobson (1994)*

**TABLE 2.9: STANDARD, PREMIUM AND ODOURLESS KEROSENE PRODUCTS SPECIFICATIONS**

Properties		Test methods		Specification limits		
	Odourless Kerosene	Regular kerosene	Premium kerosene (Dyed)	Odourless kerosene	Regular kerosene	Premium kerosene (Dyed)
Density @ 15C	ASTM D4052	ASTM D4052	ASTM D4052		0.820 Max.	0.820 Max.
Appearance @ 15C	VISUAL	VISUAL	VISUAL	Clear & bright	Clear & bright	Clear & bright
Colour Saybolt	ASTM D156	N/A	N/A	+20 min.	N/A	N/A
Odour	N/A	N/A	N/A	Merchantable	N/A	N/A
Distillation	ASTM D83	ASTM D86	ASTM D86	-	-	-
IBP C	-	-	-	-	-	175 (Typical)
50% C	-	-	-	240 max.	N/A	N/A
90% C	-	-	-	210 min.	N/A	N/A
FBP C	-	-	-	280 max.	N/A	280 max
Residue	-	-	-	-	-	-
% Vol.	-	-	-	N/A	2.0 min.	N/A
Flash Point	(PMCC) C IP 34	(Abel) C IP 170	(Abel) C IP 170	75 min.	20 min.	43.0 min.
Smoke Point mm.	N/A	IP 57	IP 57	N/A	20 min.	25 min.

Sulphur content % Wt.	IP 336	IP 336	IP 336	0.01 max.	0.2 max	0.04 max
Copper corr. 3hrs: 100 C	ASTM D130	ASTM 130	ASTM D130	1 max.	1 max.	1 max
Aromatics % Vol.	HPLC	N/A	N/A	1.0 max	N/A	N/A
Kauri Butanol value	ASTM D1133	N/A	N/A	-	-	-
Doctor Test	IP 30	IP 30	IP 30	Negative	Negative	Negative
24hr Burning test mg/kg	N/A	N/A	IP 10	-	-	10 max.

**Source:** file://A:\STANDARD,PREMIUM%20AND%20ODOURLESS%20KEROSENE,%20p... 2/10/05

## CHAPTER THREE

### THEORETICAL PRINCIPLES

#### 3.1 ADSORPTION

The use of solids for removing substances from either gaseous or liquid solutions has been widely used since biblical times. This process, as adsorption, involves nothing more than the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. From the early days of using bone char for decolourization of activated carbon for removing nerve gases from the battlefield, to today's thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation.

Adsorption phenomena are operative in most natural physical, biological, and chemical systems and adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters.

The process of adsorption involved separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption, a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a 'solution'. The term sorption is a general expression encompassing both processes.

Physical adsorption is caused mainly by Van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which

compose the adsorbent surface. Thus adsorbents are characterized first by surface properties such as surface area and polarity.

A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. The size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents. Especially materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence turned for a particular separation.

Surface polarity corresponds to affinity with polar substances such as water or alcohols. Polar adsorbents are thus called 'hydrophillic' and aluminosilicates such as zeolites, porous alumina, silica gel or silica-alumina are examples of adsorbents of this type. On the other hand, non polar adsorbents are generally 'hydrophobic'. Carbonaceous adsorbents, polymer adsorbents and silicalite are typical non polar adsorbents. These adsorbents have more affinity with oil or hydrocarbons than water.

### **3.1.1 Types of Adsorption**

There are two basic types of adsorption namely:

- 1. Physical Adsorption:** Physical adsorption is non-specific and somewhat similar to the process of condensation. The forces attracting the fluid molecules to the solid surface are relatively weak with the energy of activation being no more than 1 kca/gmol. The heat evolved during the adsorption process is of the order 0.5 to 5.0 kcal/gmol. The amount of physical adsorption decreases rapidly as the temperature is increased and it

is generally very small above the critical temperatures of the adsorbed components. Physical adsorption is not highly dependent on the irregularities in the nature of the surface, but is usually directly proportional to the amount of surface. However, the extent of adsorption is not limited to a monomolecular layer on the solid surface especially near the condensation temperature.

Determination of physical properties of solid catalyst can be done by physical adsorption and it answers the questions of surface area and pore size distribution in porous catalyst by measurement.

At higher temperatures (above 200°C), the activation energy is available to make or break chemical bonds, and if such a mechanism prevails, we have;

## **2. Chemisorption**

This type of adsorption is specific and involves forces much stronger than physical adsorption. There are two types – activated and non-activated.

Activated chemisorption means that the rate varies with temperature according to a finite activation energy in the Arrhenius equation. However, in some systems chemisorption occurs very rapidly, suggesting an activation energy near zero. This is termed non-activated chemisorption.

A substance is able to adsorb molecules of a second substance at its surface if the attractive forces (physical or chemical) between the molecules of different substances are larger than the attractive forces between the molecules within the second substance.

### 3.1.2 Other Factors that affects Chemisorption are:

- (a) The chemical composition of the adsorbent
- (b) The prevailing condition of the surface area of the adsorbent and other physical characters.
- (c) Nature of the adsorbent
- (d) Temperature
- (e) Pressure

Table 3.1: Distinction between Physical and Chemical Adsorption

S/N	PARAMETER	PHYSICAL	ADSORPTION (CHEMICAL)
1	Adsorbent	All solid	Some solids
2	Adsorbate	All gases below critical temperature	Some chemically reactive gases
3	Temperature range	Low temperature	Generally high temperature
4	Heat of adsorption	Low ( $\approx \Delta H$ cond.)	High; order of heat of reaction
5	Rate activation energy	Very rapid, low E	Non-activated, low E, activated, high E
6	Coverage	Multiplayer possible	Monolayer
7	Reversibility	High reversibility	Often irreversible
8	Importance	For determination of surface area and pore size	For determination of active center area and elucidation of surface reaction kinetics
9	Bonding forces	Weak	Strong
10	Specificity	Non-specific	Highly specific

### 3.2 FACTORS AFFECTING ADSORPTION

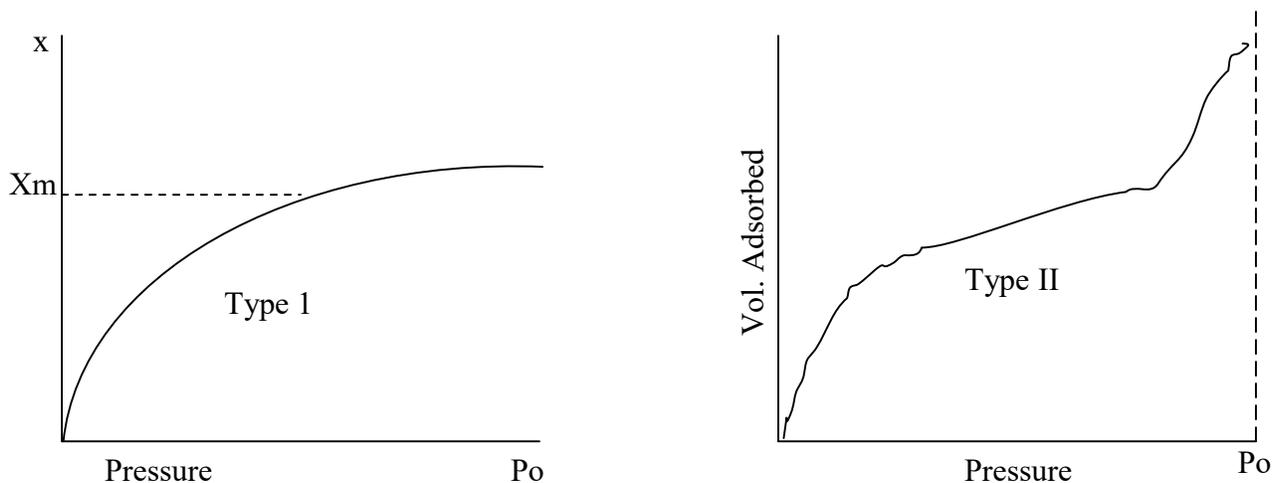
1. **Temperature:** The lower the temperature, the faster the adsorption rate, high temperature lowers adsorption rate.
2. **Molecular Structure:** The larger the molecules, the more sorbable,. Because of the more chemically stable bond are formed which makes desorption difficult. Branched molecules adsorb more than their saturated or linear counter part.
3. **Surface area:** The smaller the particles size, of the absorbent, the greater the surface area and high surface area favours adsorption.
4. **pH Effect:** This is the acid – base concentration effect of the adsorbent on adsorption process. The effect of pH is dependent on the chemical composition of the system. For instance, the oxalates are adsorbed by activated carbon from acid and not from an alkaline solution because of the strong interaction between hydrogen or hydrogen ions and the molecules of many solutes in the adsorbing properties of activated carbon.

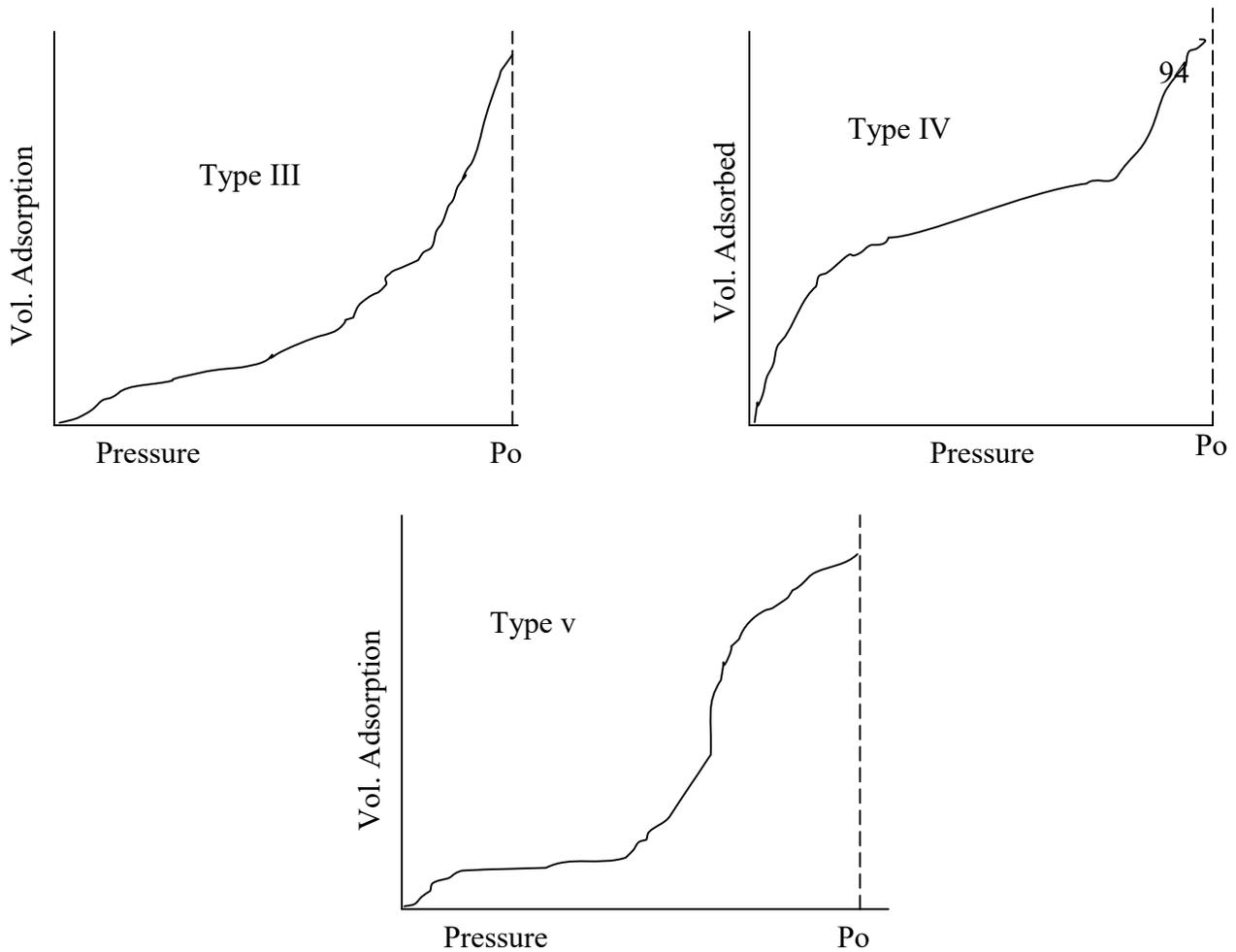
When a mineral acid is presents, weak organic acids adsorb better. This is due to the ever increasing ionization of the weak acid which consequently increases the number of molecules in the non-ionized and more adsorbable form.

### 3.3 ADSORPTION ISOTHERMS

The relationship between the mass of material adsorbed at equilibrium per unit mass of the adsorbent and the concentration of the adsorbate at a given temperature is called an adsorption isotherm.

The nature of the adsorption isotherm mainly depends on the interaction between the adsorbed gas or solute and a well defined adsorbent as well as their concentration and the pressure / temperature conditions under which the process takes place. All other conditions being equal, knowledge of the quantity adsorbed together with its associated equilibrium concentration or pressure enables the adsorption isotherm to be specified. Generally, an adsorption isotherm shows the variation of the rate or amount of adsorption of a substance with concentration or pressure.





**Fig. 3.1: The various types of adsorption isotherm**

**Type I Isotherm:** All the above isotherm curves possibly occur in the case of physisorption except type 1, which occur in the case of chemisorption where adsorption does not proceed beyond the formation of a monolayer. Such type of isotherm is obtained when oxygen is adsorbed on carbon black at  $-183^{\circ}\text{C}$ . The volume of gas adsorbed per given quantity of adsorbent increases relatively, rapidly and then the increase become much more slowly. As the surface becomes covered with gas molecules, at a point desorption begins to occur.

**Type II Isotherm:** This type of isotherm can be explained by postulating the formation of multilayer after the completion of the monolayer, this is to be expected especially as the gas pressure is increased, since the Van-der Waal forces of the gas molecule in the first layer will tend to hold a second layer, and so on. In some cases, actual condensation of the gas (desorption) may occur in the small pores and capillaries of the adsorbent even at pressures below  $P_0$ . Typical example of this type of isotherm is obtained when water vapour is adsorbed by carbon black at  $30^{\circ}\text{C}$ .

**Type III Isotherm:** This occurs when the amount of gas adsorbed increases without limitation as its relative saturation approaches unity. The convex structure is caused by heat of adsorption of the first layer being less than heat of condensation due to molecular interaction in a monolayer. Such adsorption isotherm occur when bromine is adsorbed on silica gel at  $79^{\circ}\text{C}$ .

**Type IV and V:** In the case of type IV isotherm, it is like that of type II and that of type V is the same class with III but in the case were actual condensation of gas occurs in the pores and capillaries of the adsorbent, type IV and V are predominantly excepted. Example of type IV is the adsorption of benzene on ferric oxide gel at  $50^{\circ}\text{C}$  while an example of type V is the adsorption of water vapour on activated charcoal at  $100^{\circ}\text{C}$ .

Although no single combination of adsorbent and adsorbate that shows all types of behaviour, but there is a tendency for the isotherms to change gradually from type I to type V as the temperature is lowered or highered.

Various equation often used to describe experimental isotherm called isotherm equations, which are derived and developed by various researchers

such Freundlich, Brunauer, Emmett, Teller, Temkin Langmuir, Redlich Peterson and others.

### 3.4 ADSORPTION ISOTHERM MODELS (MONOLAYER FORMATION)

For kinetic development, derivations may be carried out by using a measure of the amount of adsorbed material either the fraction of the surface covered or the concentration of the gas adsorbed on the surface.

It is assumed that at the establishment of equilibrium, a fraction ( $\theta$ ) of the surface of a mono-molecule layer is covered by adsorbed molecules; and  $(1 - \theta)$  is the fraction of the total surface not covered. The rate of adsorption will then be proportional to the concentration ( $C$ ) of the molecules in the gas phase or in solution and also to the fraction of the surface that is bare. The assumption being that adsorption can occur only when molecules strike the bare surface.

$$\text{The rate of adsorption } R_a = K_a (C) (I - \theta) \dots\dots\dots 3.1$$

Where  $K_a$  is the proportionality constant relating to the adsorption process. The rate of desorption is proportional only to the number of molecules attached to the surface, which in turn is proportional to the fraction of the surface covered.

$$R_d = K_d (\theta) \dots\dots\dots 3.2$$

At equilibrium therefore, the rate of adsorption and desorption are the same and hence;

$$K_a (C) (I - \theta) = K_d \theta \dots\dots\dots 3.3$$

$$\frac{\theta}{I - \theta} = \frac{K_a}{K_d} (C) \dots\dots\dots 3.4$$

Since the ratio  $\frac{K_a}{K_d}$  is the equilibrium constant and can be rewritten as

K, equation (3.4) reduces to

$$\frac{\theta}{1-\theta} = K(C)$$

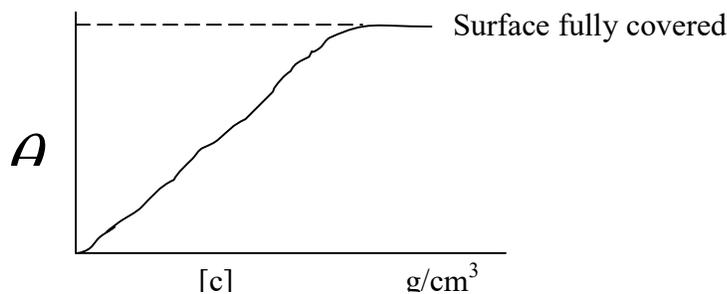
$$\theta = K(C) - K(C)\theta$$

$$\theta(1+K(C)) = K(C)$$

$$\theta = \frac{K(C)}{1+K(C)} \dots\dots\dots 3.5$$

Equation (3.5) is the Langmuir adsorption isotherm

When a graph of  $\theta$  is plotted against (C) the nature of it is illustrated below.



**Fig. 3.2:** A plot of fraction of surface covered  $\theta$ , against concentration of substance in the gas phase or in solution (C) for a substance that obeys Langmuir adsorption isotherm.

At sufficiently low concentration, i.e. (C)  $\ll 1$ , the equation reduces to

$$\theta = K(C) \dots\dots\dots 3.6$$

Also, at sufficiently high concentration (i.e.)  $C \gg 1$  equation becomes

$$\theta = 1 \text{ since } K(C) \gg 1 \dots\dots\dots 3.7$$

indicating that the surface is saturated.

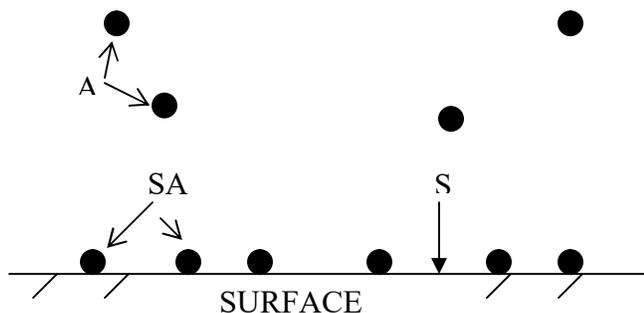
In terms of pressure, Langmuir, also provide a model for the adsorption process, particularly for the chemisorption process. This model led him to a simple but all important theoretical derivation of an adsorption isotherm. The chemisorption process is pictured as leading ultimately to a monomolecular film on the surface of the adsorbent and the derived adsorption isotherm results from an investigation of the equilibrium that is set up between the fluid phase and the partially formed monolayer. When the fluid is at a pressure  $P$ , the fraction of the surface that is covered is represented by  $\theta$ . The equilibrium state can be interpreted in terms of the dynamic equilibrium that results from an equal rate of evaporation of the adsorbed material and rate of condensation of the liquid phase molecules. The Langmuir theory suggests that the rate of evaporation can be taken to be proportional to the fraction of the surface covered and can therefore be written as  $K_1\theta$  where  $K_1$  is some proportionality constant. This simple proportionality assumption depends on the extent of coverage and may impose limitations to the simple assumption of an evaporation rate proportionality to  $K_1\theta$ . The rate of condensation furthermore, is taken to be proportional both to the gas pressure  $P$ , which according to the kinetic molecular theory determines the number of molecular collisions per unit area per unit time, and the fraction of the surface not readily covered by

adsorbed molecules (i.e.) to  $(1 - \theta)$ . It is assumed that only collisions with this exposed surface can lead to adsorption of a molecule of the surface.

### 3.5 DERIVATION OF THE LANGMUIR ISOTHERM

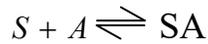
For molecules in contact with a solid surface at a fixed temperature, the Langmuir Isotherm, developed by Irving Langmuir in 1916, describes the partitioning between gas phase and adsorbed species as a function of applied pressure. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on four hypotheses:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal
2. Adsorbed molecules do not interact
3. All adsorption takes place through the same mechanism.
4. At the maximum adsorption only a mono-layer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.



### 3.5.1 Thermodynamic Derivation

The adsorption process between gas phase molecules, A, vacant surface sites, S, and occupied surface sites, SA, can be represented by the equation;



Assuming that there a fixed number of surface sites present on the surface.

An equilibrium constant, K, can be written:

$$K = \frac{[SA]}{[S][A]}$$

$\theta$  = fraction of surface sites occupied ( $0 < \theta < 1$ )

Note that;

- [SA] is proportional to the surface coverage of adsorbed molecules, or proportional to  $\theta$
- [S] is proportional to the number of vacant sites,  $(1 - \theta)$
- [A] is proportional to the pressure of gas, P

Thus it is possible to define the equilibrium constant, b:

$$b = \frac{\theta}{(1-\theta)P}$$

Rearranging gives the expression for surface coverage:

$$\theta = \frac{bP}{1+bP}$$

### 3.5.2 Kinetic Derivation

The rate of adsorption will be proportional to the pressure of the gas and the number of vacant sites for adsorption. If the total of sites on the surface is N, then the rate of change of the surface coverage due to adsorption is:

$$\frac{d\theta}{dt} = K_a PN(1 - \theta)$$

$$\frac{d\theta}{dt} = -K_d N\theta$$

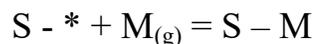
In these equations,  $k_a$  and  $k_d$  are the rate constants for adsorption and desorption respectively, and  $p$  is the pressure of the adsorbate gas. At equilibrium, the coverage is independent of time and thus the adsorption and desorption rates are equal. The solution to this condition gives us a relation for  $\theta$ :

$$\theta = \frac{bP}{1+bP}$$

where  $b = k_a/k_d$ .

### 3.5.3 Langmuir Isotherm – derivation from equilibrium

We may derive the Langmuir isotherm by treating the adsorption process as we would any other equilibrium process – except in this case the equilibrium is between the gas phase molecules (M), together with vacant surface sites, and the species adsorbed on the surface. Thus, for a non-dissociative (molecular) adsorption process we consider the adsorption to be represented by the following chemical equation.



where:  $S - *$ , represented a vacant surface site.

Note: In writing this equation we are making an inherent assumption that there are a fixed number of localized surface sites present on the surface. This is the first major assumption of Langmuir isotherm.

We may now define an equilibrium constant (K) in terms of the concentrations of “reactants” and “products”.

$$K = \frac{[S-M]}{[S-*][M]}$$

We may also note that:

- $[S - M]$  is proportional to the surface coverage of adsorbed molecules, i.e. proportional to  $\theta$
- $[S - *]$  is proportional to the number of vacant sites, i.e. proportional to  $(1 - \theta)$
- $[M]$  is proportional to the pressure,  $P$ .

Hence, it is also possible to define another equilibrium constant,  $b$ , as given below.

$$b = \frac{\theta}{(1 - \theta)P}$$

Rearrangement then gives the following expression for the surface coverage.

$$\theta = \frac{bP}{1 + bP}$$

which is the usual form of expressing the Langmuir Isotherm.

As with all chemical reactions, the equilibrium constant,  $b$ , is both temperature – dependent and related to the Gibbs free energy and hence to the enthalpy change for the process.

Note:  $b$  is only a constant (independent of  $\theta$ ) if the enthalpy of adsorption is independent of coverage – this is the second major assumption of the Langmuir Isotherm.

### 3.6 THE FREUNDLICH ADSORPTION ISOTHERM

Adsorption from solution generally follows the same principles laid down for the adsorption of gasses and is subjected to the same factors. Adsorption of solutes unlike that of gases involves the establishment of equilibrium between the amount adsorbed on the surface and the concentration of the substance in solution. The variation of the extent of

adsorption with concentration of the solute is usually represented by the Freundlich equation which works better with adsorption in solution than that in a gas.

The Freundlich adsorption isotherm equation is an empirical one. Though the equation is simple and convenient it does not always produce experimental data over a wide range of pressure though it has been widely used as an empirical equation, for quantitative purposes it seems not to have a particular theoretical foundation. But it can be derived by assuming a certain distribution function for sites having different change in free energy ( $\Delta G^0$ ) value.

The system of this assumption is as follows:

Adsorption solvent = adsorbed solute

In solution + solvent.

The isotherm is completely an empirical attempt in order to fit experimental data and is used to describe the adsorption of solute from solution as well as in the gas phase adsorptions. Freundlich found that if the concentration of solute at equilibrium,  $C_e$ , was raised to the power  $1/n$ , the amount of solute sorbed being  $q_e$ , then  $C_e^{1/n} q_e$  was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for nonideal sorption and is expressed by the following equation:

$$q_e = KC_e^{1/n} \dots\dots\dots 3.8$$

$$q_e = x/m$$

$x$  = amount of solute adsorbed(mg or g )

$m$  = mass of adsorbent(mg or g )

Where  $k$  and  $n$  are constants to be determined empirically

$C_e$  = Concentration of solute remaining in solution after adsorption is complete at equilibrium.

$x/m$  = Mass of substance adsorbed per unit mass of adsorbent.

Taking logarithm of both sides of equation (3.8) we have;

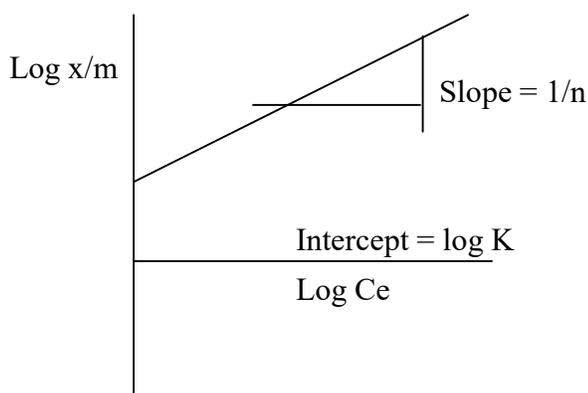
$$\text{Log } x/m = \text{log } k + 1/n \text{ log } C_e \dots\dots\dots 3.9$$

For the gas phase adsorption where pressure is considered in place of concentration, the equation (3.9) will become;

$$x/m = kp^{1/n} \dots\dots\dots 3.10$$

Where  $p$  = pressure.

A plot of  $\text{log } x/m$  against  $\text{log } C_e$  will yield a straight line with  $1/n$  and  $\text{log } k$  as slope and intercept respectively.



### 3.7 REDLICH – PETERSON ISOTHERM

The Redlich-Peterson isotherm (Redlich and Peterson, 1959) contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. The Langmuir equation is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute on the adsorbent surface, that energy of adsorption is constant and that there is no

transmigration of adsorbate in the plane of the surface. The rate of sorption to the surface should be proportional to a driving force which times an area. The driving force is the concentration in the solution, and the area is the amount of bare surface. If the fraction of covered surface is  $\theta$ , the rate per unit of surface is;

$$r_a = K_a C(1-\theta) \dots\dots\dots 3.11$$

The desorption from the surface is proportional to the amount of surface covered;

$$r_d = K_d \theta \text{-----} 3.12$$

where  $K_a$  and  $K_d$  are rate constants,  $r_a$  is sorption area,  $r_d$  is desorption rate,  $C$  is concentration in the solution, and  $\theta$  is fraction of the surface covered.

At equilibrium, the rates are equal, and

$$\theta = \frac{K_a C_e}{K_d + K_a C_e} \text{-----} 3.13$$

and

$$K_a = \frac{K_d}{K_e}$$

since  $q_e$  is proportional to  $\theta$

$$\theta = \frac{q_e}{q_m}$$

The saturated monolayer sorption capacity,  $q_m$  can be obtained. When  $\theta$  approached 1, then  $q_e = q_m$

The saturated monolayer isotherm can be represented as

$$q_e = \frac{q_m k_a C_e}{1 + K_a C_e} \text{-----} 3.15$$

The above equation can be rearranged to the following linear form

$$C_e/q_e = 1/K_a q_m + C_e/q_m \text{-----} 3.16$$

The above can also be written in the form

$$q_e = \frac{bq_m C_e}{1 + bC_e} \text{-----3.17}$$

where  $q_m$  is the maximum capacity and  $b$  is a constant related to the affinity of the binding sites.

The empirical freundlich model based on sorption on to a heterogeneous surface is given by

$$q_e = K_f C_e^{1/n} \text{-----3.18}$$

The three-parameter Freundlich – Langmuir model was developed to improve the fitness found by the Freundlich or Langmuir model. The model is given by;

$$q_e = \frac{bq_m C_e^{1/n}}{1 + b C_e^{1/n}} \text{-----3.19}$$

where  $b$ ,  $q_m$  and  $n$  are the Freundlich Langmuir parameters.

The three – parameter Redlich-Peterson model is therefore expressed as;

$$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^\beta} \text{-----3.20}$$

$q_e$  is proportional to  $\theta$

It can also be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \text{----- 3.21}$$

It has three isotherm constants, namely,  $A$ ,  $B$ , and  $g$ , ( $0 < g < 1$ ), which characterize the isotherm. Its limiting behaviour is summarized:

Where  $g = 1$

$$q_e = \frac{AC_e}{1 + BC_e} \text{----- 3.22}$$

i.e. the Langmuir form results,

where  $g = 0$

$$q_e = \frac{AC_e}{1+B} \text{-----} 3.23$$

i.e. the Henry's law form results,

equation (3.21) can be converted to a linear form by taking logarithms;

$$\ln\left(\frac{AC_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B) \text{-----} 3.24$$

### 3.8 TEMKIN ISOTHERM

The Temkin isotherm describes the characteristics adsorption potential of the adsorbents by the adsorbates. It is given by the relationship;

$$\theta = K_p^{\frac{1}{m}} \text{-----} 3.25$$

where  $K$  is a constant and  $m$  is number greater than unity. It can be shown that the heat of adsorption  $\Delta H_{ad}$  decreased with  $\log \theta$

$$\Delta H_{ad} = \Delta H_{ad}^0 (1 - \alpha \theta) \text{-----} 3.26$$

This behaviour of  $\Delta H_{ad}$  leads to the Temkin equation.

$$\theta = \frac{RT}{\Delta H_{ad}^0 \alpha} \ln(A_0 P) \text{-----} 3.27$$

where  $\alpha$  and  $A_0$  are constants for a given system at constant Temperature.

$$\theta = \frac{v}{V_m} = \frac{1}{a} \ln(A_0 P) \text{-----} 3.28$$

$$\text{where } a = \Delta H_{ad}^0 \frac{d}{RT}$$

$V$  = volume of the adsorbed gas

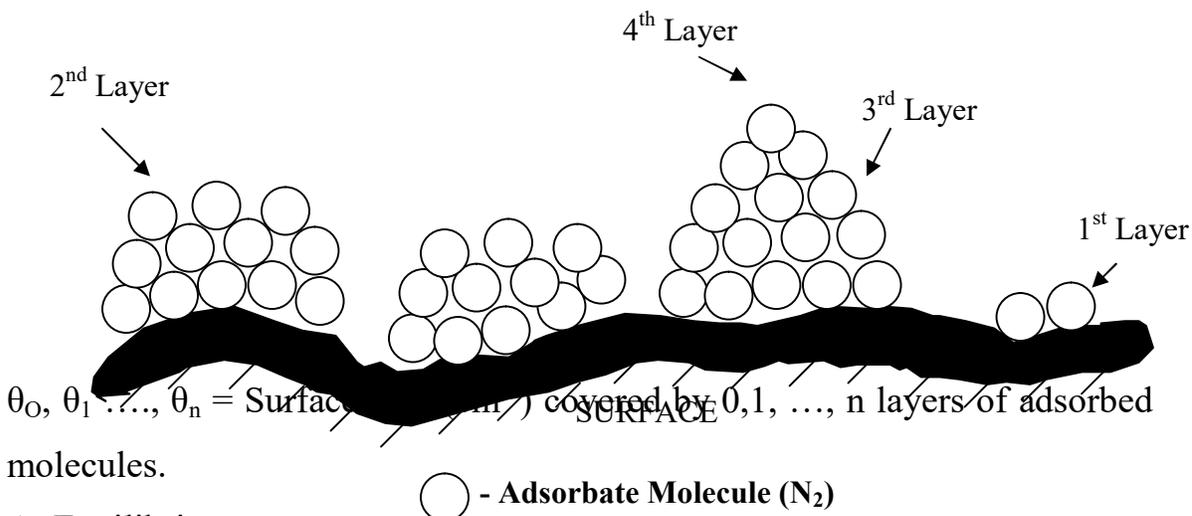
$V_m$  = volume adsorbed to give a monolayer

The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for adsorbates. The linear form of the Temkin isotherm is expressed as;

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \text{ -----3.29}$$

where the  $1/b_T$  indicates the adsorption potential of the adsorbent and  $K_T$  is the Temkin isotherm constant.

### 3.9 Derivation of the BET Isotherm



At Equilibrium:

$\theta_0$  must remain constant.

$\therefore$  rate of evaporation from first layer = rate of condensation onto bare surface.

$$K_{-1}\theta_1 = K_1P\theta_0 \text{ ..... 3.30}$$

Similarly, at equilibrium  $\theta_1$  must remain constant.

Therefore,

Rate of condensation on the bare surface + Rate of Evaporation from the second layer

= Rate of Condensation on the 1<sup>st</sup> layer + Rate of Evaporation from the second layer

$$\therefore K_1 P \theta_0 + K_2 \theta_2 = K_2 P \theta_1 + K_{-1} \theta_1$$

Substituting into (3.30) gives

$$K_2 \theta_2 = K_2 P \theta_1$$

Extending this argument to other layers;

$$K_i \theta_i = K_i P \theta_{i-1} \dots\dots\dots 3.31$$

Definitions;

Total surface area of the catalyst,

$$A = \sum_{i=0}^{\infty} \theta_i \dots\dots\dots 3.32$$

Total volume of gas adsorbed on surface

$$= V_0 \sum_{i=0}^{\infty} i \theta_i \dots\dots\dots 3.32$$

where  $V_0$  is the volume of gas adsorbed on one square centimeter of surface when it is covered with a complete layer.

$$\therefore \frac{v}{Av_0} = \frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} i \theta_i}{\sum_{i=0}^{\infty} \theta_i} \dots\dots\dots 3.33$$

where  $V_m$  is the volume of gas adsorbed when the entire surface is covered with a complete monolayer.

From (3.30),

$$\begin{aligned} \theta_1 &= \left( \frac{K_1}{K_{-1}} \right) P \theta_0 \\ &= y \theta_0 \left\{ y = \left( \frac{k_1}{k_{-1}} \right) P \right\} \end{aligned}$$

If we assumed that the properties of the 1<sup>st</sup>, 2<sup>nd</sup>, ... layers are equivalent, then,

$$\frac{k_{-2}}{k_2} \dots \frac{k_{-i}}{k_i} = g \dots\dots\dots 3.34$$

Similarly;

$$\begin{aligned} \theta_2 &= \left( \frac{k_2}{k_{-2}} \right) P \theta_1 \\ &= x \theta_1 \left\{ x = \frac{P}{g} \right\} \end{aligned}$$

$$\theta_3 = x \theta_2 = x^2 \theta_1$$

Generally,

$$\theta_i = x \theta_{i-1} = x^{i-1} \theta_1 x^{i-1} y \theta_0 c x^i \theta_0 \left( c = x/y \right)$$

Substituting into (3.33),

$$\frac{v}{v_m} = \frac{\sum_{i=0}^{\infty} i \theta_i}{\sum_{i=0}^{\infty} \theta_i} = \frac{c \theta_0 \sum_{i=1}^{\infty} i x_i}{(\theta_0 + \theta_1 + \theta_2 + \dots)} = \frac{c \theta_0 \sum_{i=1}^{\infty} i x_i}{\theta_0 (1 + c \sum_{i=1}^{\infty} x_i)} = \frac{c \sum_{i=1}^{\infty} i x_i}{(1 + c \sum_{i=1}^{\infty} x_i)}$$

Now,

$$\sum_{i=1}^{\infty} x_i = \frac{x}{1-x} \text{ [sum of an inf initegeometric progression]}$$

Also,

$$\begin{aligned} \sum_{i=1}^{\infty} i x_i &= x^1 + 2x^2 + 3x^3 + \dots \\ &= x \sum_{i=1}^{\infty} 1 + 2x + 3x^2 + \dots \\ &= x \frac{d}{dx} \sum_{i=1}^{\infty} x^i \end{aligned}$$

$$\begin{aligned}
 &= x \frac{d}{dx} \left( \frac{x}{1-x} \right) = \frac{x}{(1-x)^2} \\
 \therefore \frac{v}{V_m} &= \frac{cx}{(1-x)^2} \times \frac{1}{\left(1 + \frac{cx}{1-x}\right)} = \frac{cx}{(1-x)^2} \frac{(1-x+cx)}{(1-x)} \\
 &= \frac{cx}{(1-x)(1-x+cx)} \dots\dots\dots 3.35
 \end{aligned}$$

At saturation pressure of gas  $P_o$ , an infinite numbers of adsorbate layers build up on the surface. From equation 3.35 for this to be possible,

$$\frac{CX}{(1-X)(1-X+CX)}$$

Must be infinite. This means that at  $P_o$ ,  $x$  must equal 1.

$$\therefore g = P_o \quad (\text{From definition of } X)$$

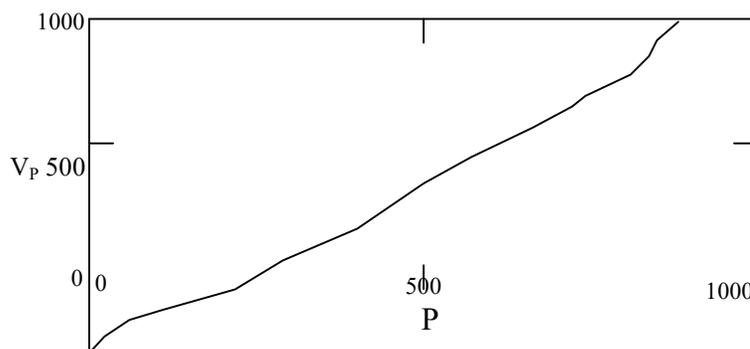
$$\therefore X = P/P_o$$

Substituting into 3.35, we arrive at the recognized form of the BET isotherm,

$$V = \frac{V_m CX}{(1-X)(1+(C-1)X)}$$

This can be rearranged to give,

$$\frac{X}{V(1-X)} = \frac{1}{VmC} + \frac{X(C-1)}{VmC} \dots\dots\dots 3.36$$



**Fig.3.3: Graphical form of the BET Isotherm**

**Table 3.2: ADSORPTION ISOTHERM EQUATIONS**

S/NO	Isotherm Model	Equation
1	Langmuir	$q_e = \frac{K_L b C_e}{(1 + K_L C_e)}$
2	Freundlich	$q_e = K_f C_e^{1/n}$
3	Radke-Prausnitz	$q = \frac{K_{RP} C_i}{(1 + K_{RP} C_i)^m}$
4	Temkin	$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e$
5	BET	$q = \frac{X}{V(1-X)} = \frac{1}{VmC} + \frac{X(C-1)}{VmC}$
6	Redlich-Peterson	$q_e = \frac{AC_e}{1 + BC_e^n}$

Source: Yu and Neretnicks(1999)

### 3.10 ADSORPTION KINETICS

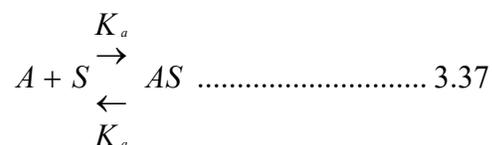
Generally adsorption proceeds through varied mechanisms such as external mass transfer to solute onto sorbent followed by intraparticle diffusion. Unless extensive experimental data are available concerning the specific adsorption application, determining the rate-controlling step is impossible. Therefore, empirical design procedures based on adsorption equilibrium conditions are the most common method to predict adsorber size and performance (Sekar Et al, 1998). Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb onto surface is

equal to the rate at which they desorb. The physical chemistry involved may be complex and no single theory of adsorption has been put forward to explain all the systems. Fortunately, engineer requires only the data at equilibrium conditions. Still not the oldest theories were used to predict the sorption process even though the assumption on which those models lie were found to be not entire valid in later years. Also most of the adsorption theories have been developed for gas solid systems because the gaseous state is better understood than the liquid. Till now the statistical theories developed for gas solid systems were applied for liquid solid with little confidence for designing of the equipment. The most commonly used equilibrium models to understand the adsorption was Freundlich and Langmuir isotherm equation (**Ismadji, et al; 2000**).

In general rate equation for a heterogeneous reaction (adsorption) accounts for more than one process. Two main process that occur in heterogeneous systems are physical (heat and mass transfer) and reaction steps. For example reactions catalyzed by solid catalyst, the process first is proceeded by the rupture of a bond of a molecules, followed by the formation of a new bond, but in this case the molecules are previously chemisorbed onto the catalyst surface. This physical transfer process (chemisorptions) depends on the reaction occurring between the molecules and the co-ordinative unsaturated atoms called 'active sites' existing on the solid surface which can be considered elementary steps of the reaction mechanism. Such rates are called global or overall rates and their use allows us to the most of design equations. The global rate involved in such systems was predicted by formulating the rate constants corresponding to each step that occurs in the overall process. The sequence of steps involved in converting reacting to product is:

1. Transport of reactants from the bulk fluid to the fluid-solid interface (external surface catalyst particle).
2. Intraparticle transport of reactants into the catalyst particle (if it is porous).
3. Adsorption of reactants at interior sites of the catalyst particle.
4. Chemical reaction of adsorbed reactants to adsorbed products (surface reaction – the intrinsic chemical step).
5. Transport of products from the interior sites to the outer surface of the particle.
6. Transport of products from the fluid interface into the bulk fluid stream.

At steady state all these rate steps will be the same. The quality can be used to develop a global rate equation in terms of the concentration and temperature of the bulk fluid. If there exists any unsteady state behavior then the slowest step contributes the global rate equation in order to apply in design equations. In the present communication the theory of heterogeneous reactions are explained based on the theory behind adsorption reactions. Consider the reversible adsorption of single species A, which remains intact (undissociated) on adsorption, can be represented by



The rate of adsorption of A is proportional to the rate at which molecules of A strike the surface, which in turn is proportional to the concentration in the bulk gas, and to the fraction of unoccupied sites.

$$r_A = K_a C_A (1 - \theta_A) \dots\dots\dots 3.38$$

Where  $K_a$  is the adsorption rate constant. Equation (3.38) gets more meaningful if only one molecules of solute gets transferred onto the solid surface particle till time,  $t = 0$  to  $t = t_e$ . Similarly the rate of desorption,  $r_d$  is proportional to the fraction of surface of surface covered,  $\theta_A$ :

$$r_d = K_d \theta_A \quad \dots \dots \dots 3.39$$

Where  $K_d$  is the desorption constant.

At equilibrium the rate of adsorption is equal to rate of desorption, with  $r_a = r_d$ . Therefore,

$$K_a C_A (1 - \theta) = K_d \theta_A \quad \dots \dots \dots 3.40$$

Rearranging equation (3.40), the fraction of solid particles covered by solute, which is proportional to the amount of gas adsorbed, is:

$$\theta_A = (K_a C_A) / (K_d + K_a C_A) = (K_a C_A) / (1 + K_a C_A) \quad \dots \dots \dots 3.41$$

Where  $K_A = K_a / K_d$ , is the equilibrium constant and  $K_a$  values are given by:

$K_a > 1$ ; domination of adsorption process

$K_a < 1$ ; domination of desorption process

$K_a = \infty$ ; irreversible process

The equation expressing the amount of A adsorbed on the surface as a function of temperature is called Langmuir adsorption isotherm.

In case of multicomponent adsorption, say solute species A and B striking the solid surface, then for species A the rate of adsorption is:

$$r_{aA} = K_{aA} C_A (1 - \theta_A - \theta_B) \dots \dots \dots 3.42$$

for the expression (3.42) it is assumed that a molecule of A from the bulk gas striking a site occupied by a B molecules is reflected, and does not displace the adsorbed molecule. The rate of desorption, as for a single species is:

$$r_{dA} = K_{dA} \theta_A \quad \dots \dots \dots 3.43$$

at equilibrium,  $r_a = r_d$ , thus

$$K_{aA}C_A(1-\theta_A-\theta_B) = K_{dA}\theta_A \quad \dots\dots\dots 3.44$$

Or, if  $K_A = (K_{aA}/K_{dA})$ , then for component A

$$\theta_A = K_A C_A (1-\theta_A-\theta_B) \quad \dots\dots\dots 3.45$$

Similarly for component B,

$$\theta_B = K_B C_B (1 - \theta_A - \theta_B) = \theta_B \quad \dots\dots\dots 3.46$$

where,  $K_B$  in equation (3.45) is given by ( $K_B = K_{aB}/K_{dB}$ )

Applying equation (3.44) in equation (3.45) and equation (3.46), we get

$$\theta_B = (K_B C_B)/(1 + K_A C_A + K_B C_B) \quad \dots\dots\dots 3.47$$

The term  $K_A C_A$  and  $K_B C_B$  in equation (3.46) and (3.47) indicates the inhibition of one component over another. Based on equation (3.45) and (3.46), the general equation of Langmuir Kinetic model for the adsorption of species 'i' from a multiphase gas mixture is:

$$\theta_i = (K_i C_i)^{1/n_i} / (1 + \sum (K_j C_j)^{1/n_j}); I, j = 1, 2, 3, \dots n \quad \dots\dots\dots 3.48$$

where the term 'n' in equation (3.48) indicates the no of fragments that the solute particles gets splitted, the significance of 'n' are explained in the following example:

consider the solute particles get dissociated into two fragments as follows:



Thus, the rate of adsorption is given by

$$r_a = K_a (1 - \theta_B)^2 \quad \dots\dots\dots 3.50$$

Similarly the rate of desorption with respect to  $B_2$  is given by:

$$r_d = K_d (\theta_B)^2 \quad \dots\dots\dots 3.51$$

Thus the solute coverage rate can be calculated equating equation (3.50) and (3.51) at equilibrium conditions:

$$\theta_B = (K_B C_B)^{1/2} / 1 + (K_B C_B)^{1/2} \quad \dots\dots\dots 3.52$$

Where  $K_B$  in equation (3.52) is the equilibrium rate constant and equal to  $K_a/K_d$  and the denominator of power term in equation (3.52) indicates the no of fragments that the solute components is dissociated.

All these equations from (3.37) to (3.51) are derived based on the assumption that the surface of solid are uniform and also only one molecule occupies one vacant site and also this assumption holds for catalytic reactions. i.e., the enthalpy change for the adsorption of molecule is same to all active sites. But true homogeneous surface particles are nowhere used in chemical systems (whether with or without reaction), as even a polished surface shows a rough surface in a microscopic scale. This shows the imitation of Langmuir model. This model also suffers from the background that reaction mechanism occurs only due to solid liquid reactions and doesn't consider the liquid interactions at solid liquid interface. However previous investigations in literature and textbooks confirm the Langmuir type model is the best model to analyze the gas solid reactions.

Also the rate of adsorption,  $R_{ads}$ , of a molecule onto a surface can be expressed in the same manner as any kinetic expression: i.e.

$$R_{ads} = kC^x \quad \dots\dots\dots 3.53$$

$$R_{ads} = k^1P^x \quad \dots\dots\dots 3.54$$

Where  $x$  = Kinetic order,  $K$  = Rate constant,  $C$  = Gas phase concentration, and

$P$  = Partial pressure of the molecule.

If the rate constant in either of the above expression is expressed in an Arrhenius form, then we obtain kinetic equations of the form:

$$R_{\text{ads}} = AC^x_{\text{exp}} (-E_a / RT) \dots\dots\dots 3.55$$

Where  $E_a$  is the activation energy for adsorption, and  $A$  the preexponential (frequency) factor. It is much more informative, however, to consider the factors controlling this process at the molecular level . . .

The rate of adsorption is governed by

1. the rate of arrival of molecules at the surface
2. the proportion of incident molecules which undergo adsorption i.e.

we can express the rate of adsorption (per unit area of surface) as a product of the incident molecular flux,  $F$ , and the sticking probability,  $S$ .

$$R_{\text{ads}} = S \cdot F \quad [\text{molecules m}^{-2}\text{s}^{-1}]$$

The flux of incident molecules is given by the Hertz-Kundsen equation

$$\text{Flux, } F = P / (2\pi mkT)^{1/2} \quad [\text{molecules m}^{-2}\text{s}^{-1}] \dots\dots\dots 3.56$$

Where  $P$ -gas pressure [ $\text{Nm}^{-2}$ ],  $m$ -mass of one molecules [ $\text{kg}$ ],

$T$ - Temperature [ $\text{K}$ ]

The sticking probability is clearly a property of the adsorbate/substrate system under consideration but must lie in the range  $0 < S < 1$ ; it may depend upon various factors – foremost amongst these being the existing coverage of adsorbed specie ( $\theta$ ) and the presence of any activation barrier to adsorption. In general, therefore,

$$S = f(\theta) \cdot \text{Exp}(-E_a / RT) \dots\dots\dots 3.57$$

Where, once again,  $E_a$  is the activation energy for adsorption and  $f(\theta)$  is some, as yet undetermined, function of the existing surface coverage of adsorption species.

Combining the equations for  $S$  and  $F$  yields the following expression for the rate of adsorption:

$$R = \frac{f(\theta) \cdot P}{\sqrt{2\pi mkT}} \exp(-E_a/RT) \dots\dots\dots 3.58$$

Note:

1. It should be recognized that the activation energy for adsorption may itself be dependent upon the surface coverage, i.e.  $E_a = E(\theta)$ .
2. If it is further assumed that the sticking probability is directly proportional to the concentration of vacant surface sites (which would be a reasonable first assumption for non-dissociative adsorption) then  $f(\theta) = (1-\theta)$ ; where, in this instance,  $\theta$  is the fraction of sites which are occupied (i.e. the Langmuir definition of surface coverage).

### 3.11 EQUILIBRIUM AND KINETIC MODELLING

#### 3.11.1 Pseudo First – Order and Pseudo Second – Order Kinetic models

The pseudo-first order and pseudo – second order kinetic models assumed that adsorption is a pseudo-chemical reaction process and the adsorption rate can be determined respectively by the first – order and second – order reaction rate equations.

The first order rate equation is expressed as;

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \text{ -----} 3.59$$

separating the variables;

$$\frac{dq_t}{q_e - q_t} = K_1 dt$$

Integrating;

$$-\ln (q_e - q_t) = K_1 t + C \text{ -----} 3.60$$

$$\ln (q_e - q_t) = K_1 t + C$$

Initial condition,  $t = 0, q_t = 0$

$$\ln q_e = C$$

Substituting the value of C into the above equation, gives

$$\ln (q_e - q_t) = \ln q_e - k_1 t \text{ -----} 3.61$$

$$\text{or } \log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \text{ -----} 3.62$$

where  $q_e$  ( $\text{mgg}^{-1}$ ) is the solid phase concentration at equilibrium,  $q_t$  ( $\text{mgg}^{-1}$ ) at time  $t$ (min), and  $K_1$  is the pseudo-first-order rate constant.

It has been established recently chiou and Li, (2002) that a pseudo – second order reaction can be used to describe a multicomponent system.

The pseudo – second order adsorption kinetic rate equation is expanded as

$$\frac{dq_t}{dt} = (q_e - q_t)^2 \text{ -----} 3.63$$

Where

$K_2$  = the rate constant of pseudo – second order adsorption ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ )

$q_e$  and  $q_t$  = sorption capacity at equilibrium and at time,  $t$  respectively ( $\text{mgg}^{-1}$ )

For the boundary conditions;

$t = 0$  to  $t = t$

and  $q_t = 0$  to  $q_t = q_t$ ,

The integrated form of the above equation becomes

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt$$

Which is the integrated rate law for a pseudo – second order reaction. The rate equation can be rearranged to obtain:

$$q_t = \frac{1}{\frac{1}{kq_e^2} + \frac{1}{q_e}} \text{-----} 3.64$$

Which has a linear form;

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \text{-----} 3.65$$

### 3.11.2 Modified Pseudo-First-Order Kinetic Model

In this work, a modified pseudo-first-order kinetic model is proposed which may prove to be especially useful when the other two kinetic models fail to generate good agreement with the experiment. To set up the new model, the pseudo-first-order equation represented by equation (3.59) is modified through the modification of its rate constant.

Denote the rate constant in the modified pseudo-first-order rate equation by  $K_1$ , the following equation is proposed;

$$k_1 = K_1 \frac{q_e}{q_t} \text{.....} 3.66$$

As  $q_t < q_e$ , the above equation implies that the rate constant  $K_1$  is minimum when equilibrium is reached. The modified pseudo-first-order rate equation can be derived as follows:

$$\frac{dq_e}{dt} = K_1 \frac{q_e}{q_t} (q_e - q_t) \text{.....} 3.67$$

Equation (3.66) can be rearranged into;

$$-dq_t + \frac{q_e dq_t}{(q_e - q_t)} = K_1 q_e dt \text{.....} 3.68$$

Integrate equation (3.68) over time  $t \in (0, t)$ , during which the solid phase concentration increases from zero to  $q_t$ , the following algebraic equation can be obtained:

$$\frac{q}{q_e} + L_n(q_e - q_t) = L_n(q_e) - K_1 t \dots\dots\dots 3.69$$

If the adsorption process follows the modified pseudo-first-order kinetic model represented by equation (3.69), a plot of  $q_t/q_e + \ln(q_e - q_t)$  against  $t$  should be a straight line.

### 3.12 Adsorption Thermodynamics (Thermodynamic Parameter)

For designing adsorption columns or batch adsorption systems, the designer should be able to answer the following two questions (**Levenspiel, 1995**).

- (a) What changes can be expect to occur
- (b) How fast will they take place

The reaction rate can be calculated from the knowledge of kinetic studies, but the changes in reaction that can be expected during the sorption process require the brief idea of thermodynamic parameters. The three main thermodynamic parameters includes enthalpy of adsorption ( $\Delta H$ ), free energy ( $\Delta G$ ) due to transfer of unit mole of solute from solution to the solid-liquid interference and entropy ( $\Delta S$ ) of adsorption.

The thermodynamic function which is most commonly used due to its practical significance is enthalpy of adsorption or heat change in adsorption. The apparent heat change or net enthalpy,  $\Delta H$  of adsorption is related to the Langmuir constant,  $K_L$  as follows:

$$K_L = K e^{-\Delta H/RT} \dots\dots\dots 3.70$$

or

$$\ln K_L = \ln K - \Delta H/RT \dots\dots\dots 3.71$$

where  $K$  is a constant. The function  $\Delta H$  is very useful wherever a differential change occurs in the system. Enthalpy is an extensive property that is its value is additive. The  $\Delta H$  value in equations (3.70) and (3.71) can be calculated from the plot of  $\ln K_L$  versus  $1/T$ . The negative value of  $\Delta H$  will indicate the process is exothermic and the sorption behaviour may be physical in nature and can be reversed by supplying the heat equal to calculated  $\Delta H$  value to the adsorption system. The positive value of  $\Delta H$  indicates the process is endothermic, also the process may be due to chemical bonding or chemisorption. Also positive  $\Delta H$  indicates process is irreversible. Negative values of  $\Delta H$  indicates the free diffusion of molecules through bulk solution and boundary layer is less than compensated by bulky groups and the stereotactic arrangements of adsorbates on the surface and in the pores of adsorbents. Another important thermodynamic parameter is the free energy change  $\Delta G$  can be calculated using the relation as follows:

$$\Delta G = RT \ln K_x \quad \text{3.72}$$

$$\text{Where } K_x = C_o/C_e \quad \text{3.73}$$

From the calculated  $\Delta H$  and  $\Delta G$ , the change in entropy  $\Delta S$  can be calculated as follows (**Myers, 2002**).

$$\Delta S = \Delta G - \Delta H/T \quad \text{3.74}$$

Increase in negative value of  $\Delta S$  will indicate the spontaneity in the adsorption process with reduction in molecular size and increased randomness at solid-interface. Also, value of  $\Delta S$  less than 1 indicates that the process is highly reversible.

The values of thermodynamic function  $\Delta S$  and  $\Delta H$  can also be evaluated using VanHoff's equation, which is given by:

$$\frac{d \ln K}{dt} = \frac{\Delta H}{RT^2} \quad \text{3.75}$$

If the heat of reaction is assumed to be constant with temperature, this differential equation can be solved to yield the following:

$$\ln\left(\frac{k_2}{K_1}\right) = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \text{-----3.76}$$

In this equation  $K_1$  is the equilibrium constant at absolute temperature  $T_1$  and  $K_2$  is the equilibrium constant at absolute temperature  $T_2$ .  $\Delta H$  is the enthalpy and  $R$  is the gas constant.

Taking advantage of the relationships between the Gibbs energy and the equilibrium constant,

One can also write the equation in the following form;

$$\ln(k) = \frac{-\Delta H}{R} \left(\frac{1}{T}\right) + \frac{\Delta S}{R} \text{-----3.77}$$

$$\text{Or } \log K_x = (\Delta S/2.303R) - (\Delta H/2.303RT) \text{-----3.78}$$

Thus the value of  $\Delta S$  and  $\Delta H$  can be calculated from the intercept and slope of plot between  $\log K_x$  versus  $1/T$ .

## CHAPTER FOUR

### EXPERIMENTAL METHODOLOGY

#### 4.1 Materials and Equipments

The materials used in this study were;

- (a) Commercial DPK
- (b) Animal bone (Bone Char) purchased from an abattoir in Port Harcourt.
- (c) Dolomitic limestone obtained from Ukpilla cement factory, Edo State
- (d) Bentonitic clay collected from Abonemma water side in Rivers State.
- (e) Silical gel (XPO 2113) obtained from NNPC

The equipment lists are as follows;

- (a) Magnetic stirrer
- (b) Hot plate
- (c) Thermometer
- (d) Stopwatch
- (e) Separating funnel
- (f) Weighing balance
- (g) Crucible
- (h) Carbolite furnace
- (i) Atomic Absorption spectrophotometer
- (j) Fluorescent indicator adsorption column
- (k) Oxford lab x – 3000 analyser
- (l) pH meter
- (m) Filter paper
- (n) Oven
- (o) Beakers, conical flask

- (p) Horiba-sulphur analyzer
- (q) Analytical grade reagents
- (r) Sample bottles
- (s) Porosimeter
- (t) Density bottle
- (u) Aniline point tester
- (v) Cloud point electronic machine
- (w) Displacement can
- (x) Conductivity meter
- (y) Fluorescent Indicator dye gel
- (z) Column syringe

## **4.2 Preparation of Samples**

### **4.2.1 Preparation of Clay Sample**

A known mass of clay was stirred into distilled water (2 liters) and allowed to stand for 30 minutes. The supernatant liquid was decanted and the process repeated 5 times. The clay samples was obtained by filtration, oven- dried at 80<sup>0</sup>C for 5 hours. The dried sample was finally ground and sieved using laboratory test sieve 250 mesh size.

Clay samples were put into different beakers and about 100ml of the conc. were added to each beaker. The resulting suspension was stirred and allowed to equilibrate for 6 hours. The clay samples were then washed thoroughly with large quantities of distilled water (to remove excess acid) before finally drying the acid treated clay samples in air.

To activate clays thermally, each of the acid dried material was ground to a fine powder, put in a crucible and heated in a furnace at a temperature of 900<sup>0</sup>C for three hours. The clay body progressively loses moisture, chemically bonded water, organic matter, sulphur and CO<sub>2</sub>.

#### **4.2.2 Preparation of Bone Char (Carbonized bone)**

The animal bones were washed to remove the debris and cut into very small bits. About 700g of the animal bone pieces were destructively distilled at 900<sup>0</sup>C using carbolite furnace (Bamford, Sheffield, L<sub>m</sub>F<sub>4</sub> + PD/IND model).

The carbonized and oxidized bones were washed with dilute hydrochloride acid (HCl) solution until a pH of about 7.0 was obtained before being exposed to ambient air.

The dried char was ground to a fine powder put in a crucible and heated in a furnace maintained at temperature of 750 – 900<sup>0</sup>C for three hours. On cooling the material was milled again and then sieved.

#### **4.2.3 Preparation of Limestone**

Limestone was thoroughly washed. The sample was ground and sieve into different particle sizes.

#### **4.2.4 Clay / Limestone**

The solid clay and limestone samples were thoroughly mixed. The mixture was charged into furnace maintained at the desired temperature of activation for 3 hours and then allowed to cool.

### **4.3 Determination of Physiochemical properties of the Adsorbents**

#### **4.3.1 Moisture Content**

The hygroscopic moisture content was determined using the ASTM method, D280 – 33. A clean empty nickel porcelain was oven-dried (105<sup>0</sup>C), cooled in a desiccator and then weighed. Clay sample (1.0g) was measured into the porcelain and the weight recorded. The porcelain and its contents were then oven-dried at 105<sup>0</sup>C to a constant weight for 3 hours. The percentage moisture content was calculated using the formular.

$$\% \text{ moisture content} = \frac{\text{loss in weight of sample}}{\text{original weight}} \times 100\%$$

#### **4.3.2 Specific Surface Area determination**

The specific surface area of the adsorbents were determined using the European spot method used by Kandhal and Parker (1998) and Santamarina et al (2002). This method is an offshoot of the technique used in determining the cation exchange capacity of drilled formation shale. In this method, methylene blue solution was prepared by mixing 1.0 gram of dry powder with 200ml of deionized water. 10g of air-dried adsorbent was suspended in 30ml of deionized water. The methylene blue solution was added to the suspension of adsorbent in 0.5ml increments. For each addition of methylene blue, the adsorbent suspension was mixed for 1 minute and a small drop of the suspension removed and placed on a filter paper. When the unabsorbed methylene blue forms a permanent light blue halo around the adsorbent aggregate, the “end point” is reached (i.e. the methylene blue has replaced cations on the adsorbent surface).

The specific area was calculated from the optimum amount of methylene blue absorbed.

$$\text{Specific surface area (SSA)} = \frac{(N)A_v A_{MB}}{1.280 \times 10^6}$$

Where N = the number of MB increments added to the adsorbent suspension.

$$A_v = \text{Avogadro's number } 6.02 \times 10^{23}$$

$A_{MB}$  = Area covered by one methylene blue (MB) molecule (typically assumed to be  $130 \text{ \AA}^2$ ).

### 4.3.3 Cation Exchange Capacity

To a suspension of clay samples (1.0g) in water (10ml), contained in an Erlenmeyer flask, was added, 30% hydrogen peroxide (15ml) and 98%  $\text{H}_2\text{SO}_4$  (0.5ml). The contents of the flask were mixed by swirling and then gently heated ( $100^\circ\text{C}$ ) for 10 mins. before diluting the contents to 50ml with distilled water. Methylene blue solution (0.01ml) was added drop wise from a burette to the flask. After each addition of 0.5ml a rubber stopper was inserted and the contents were shaken for about 30 second, during which period a particle of clay sample was introduced onto a filter paper. On appearance of the greenish blue tint spreading around the drop, the flask was further shaken (2 mins) and titration resumed until the greenish blue colour persisted. The volume of methylene blue was then recorded.

$$\text{Cation exchange capacity} = \frac{\text{ml.ofmethylene blue}}{\text{ml.of sample}}$$

#### 4.3.4 Specific Gravity (Relative Density)

The method utilized here is that applicable to the determination of the relative density of a granular solid insoluble in water with the aid of a relative density bottle. The clean, dry, relative density bottle was weighed empty with the stopper ( $W_1$ ).

It was then partly filled with the clay sample and re-weighed ( $W_2$ ). The remaining space in the bottle was finally filled with water and shaken gently to remove air bubbles. The stopper was inserted and the bottle cleaned, dried and weighed ( $W_3$ ). After emptying the contents of the bottle, it was washed thoroughly with water and filled with water. The stopper was next inserted, excess water wiped off and the bottle was then weighed ( $W_4$ ). The relative density of the sample was calculated using the relationship;

$$\text{R.D} = \frac{\text{Mass of Substance}}{\text{Mass of equal volume of water}}$$

#### 4.3.5 pH Measurement

The pH of a 10% suspension of the clay sample in water was determined using Philips PW 9409 digital pH meter at 28<sup>0</sup>C. The pH meter was first standardized using a buffer tablet dissolved in 100ml/g distilled water to a pH of 4.

#### 4.4 Chemical Analysis

The sample were air dried for a minimum of 12 hours. About 2g of the sample was digested with 100mls of distilled water, 10 mls of con. HCl and 1 ml of con HNO<sub>3</sub>. The resulting mixture was heated in an electrothermal heater, but it must not boil. When the mixture gets to 15mls, it was allowed to cool, and filtered to a flask. The filtrate was made up to 100mls with distilled water and then subjected to atomic absorption spectrophotometer, model 200A for analysis.

## 4.5 Determination of Structural Parameter

### 4.5.1 Pore Volume Measurement

The pore volume of adsorbent may be determined gravimetrically by totally saturating a sample with a liquid of known density and noting the weight increase using porosimeter.

#### Procedure

- (a) Place a clean dry previously weighed sample inside the saturation flask.
- (b) Create a high vacuum inside the flask using a vacuum pump.
- (c) Introduce kerosene (or any other liquid of known density) into the vessel until it completely covers the sample.
- (d) Remove the saturated sample from the flask using forceps. Dry the sample of excess liquid and immediately reweigh the sample.

#### Calculation

The pore volume of the sample is given by;

$$V_p = \frac{W_s - W_d}{\rho_L}$$

where;

$V_p$  = Pore volume

$W_s$  = Saturated sample weight

$W_d$  = Dry sample weight,

$\rho_L$  Density of saturated liquid.

### 4.5.2 Bulk Volume Measurement

The bulk volume of the samples (adsorbents) were determined by measuring the volume of liquid displaced. Other methods employed include

application of Archimede's principle, that is, sample weighed in air and weighed again, suspended in a wetting liquid such as water.

### 4.5.3 Porosity

Porosity was determined as a ratio between the pore volume and the bulk volume as determined from 4.5.1 and 4.5.2.

$$\text{Porosity } (\phi) = \frac{V_p}{V_b}$$

$V_p$ =pore volume

### 4.5.4 Tortuosity

Tortuosity of the samples were determined as inverse of porosity.

$$\tau = \frac{1}{\phi}$$

## 4.6 Determination of Sulphur content of DPK before and after adsorption by x-ray method (Oxford lab X-3000)

Instructions / Activities of the Oxford Lab x-3000 machine

- (a) Prepare mould with film and disposal kits
- (b) Add sample to mould to mark
- (c) Start from main menu
- (d) Choose calibration name and enter
- (e) Press analyse when sample is inserted to the secondary window.
- (f) Confirm that the required sample is in the chamber
- (g) Obtain reading at the of the scanning
- (h) Remove sample from the chamber

- (i) Record your result
- (j) Use fresh sample for analysis
- (k) Remove sample from the chamber when you finish

#### **4.6.1 Determination of Sulphur content of DPK before and after adsorption using Horiba sulphur analyzer**

This machine measures the amount of reduction adsorbed by compounds within the x-ray region of electromagnetic spectrum. This Horiba sulphur in oil analyser is an electronic detector which uses 10ml. of the test solution in determining the total sulphur contained in it. It has the provision of disposable containers where the 10ml. of disposable liquid is poured and placed in a special compartment made available by the machine. The electronic detector automatically records the total sulphur contained in the test liquids 30 seconds for each interval and the average taken. This average is the total sulphur contained in the kerosene.

#### **4.70 Determination of Aromatic content of DPK before and after adsorption using Fluorescent indicator Adsorption method (ASTM D1379)**

This method covers a procedure for the determination of saturates, non-aromatic Olefins, and aromatics in petroleum fractions that distill below 315°C.

Approximately 0.75ml of sample of kerosene is introduced into a special glass adsorption column packed with activated silica gel. A small layer of the silica gel contains a mixture of fluorescent dyes. When all the sample has been adsorbed on the gel, propan – 2 – 01 is added to desorb the sample and force it down the column. The hydrocarbons are separated according to their adsorption affinities into aromatics / including some diolefins and aromatics with olefinic side chains plus any sulphur, nitrogen, and oxygen compounds), Olefins, and Paraffins (saturates). The fluorescent

dyes are also separated selectively, with the hydrocarbon types, and make the boundaries of the aromatic, olefin, and paraffin zones visible under ultraviolet light. The volume of each hydrocarbon type is calculated from the length of each zone in the column.

#### Calculation

For each set of observations, calculate to the nearest 0.1% the volume percent of the hydrocarbon types as follows;

$$\text{Aromatics, \% Volume} = (L_a/L) \times 100$$

$$\text{Olefins, \% Volume} = (L_o/L) \times 100$$

$$\text{Saturates, \% Volume} = (L_s/L) \times 100$$

Where;

$L_a$  = Length of the aromatic zone, mm

$L_o$  = length of the Olefin zone, mm

$L_s$  = Length of Saturate zone, mm

$L$  = Sum of  $L_a + L_o + L_s$

#### 4.8 Adsorption Equilibrium Studies

All the experiments were carried out at ambient temperature of  $29 \pm 1^\circ\text{C}$  in batch mode. Batch mode was selected because of its relative simplicity. The batch experiments were run in different glass flask of 250ml capacity using average speed rotary shaker machine (150 rpm). Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The stirring was kept constant for each run throughout the experiment ensuring equal mixing. The desired pH was maintained using dilute NaOH/HNO<sub>3</sub> solutions. Each flask was filled with a known volume of sample having desired pH commenced the stirring. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered through Whatman No. 44 filter paper. The fraction  $F(t)$  of adsorbed

solution or adsorbed at each time was calculated according to relation **(Quaker and Hanif, 1994)**.

$$F(t) = \frac{C_1 - C_2}{C_1}$$

Where  $F(t)$  is the fraction or volume of adsorbed solution or adsorbate at time  $t$  on the solid

$C_1$  - initial concentration of bulk fluid

$C_2$  - Final concentration of adsorbate

The concentrations of the solution before and after adsorption were measured using fluorescent indicator adsorption (FIA) method – ASTM D1388.

#### **4.8.1 Experimental Conditions**

##### **(a) Effect of contact time:**

These studies were conducted by agitating 100ml sample with a known amount of adsorbent agitated it for different time period 60-240 minutes. After the predetermined time intervals, the sample were withdrawn, filtered and determined residual kerosene concentration using FIA method.

##### **(b) Effect of Adsorbent Mass:**

The studies were conducted by varying the amount of adsorbent. A known volume of sample was treated with different doses of different adsorbents 5.00 – 20.00g/100ml. The samples were agitated for specified time, filtered and then analysed for residual kerosene concentration.

##### **(c) Effect of pH:**

The pH of the aqueous solution is a controlling factor in the adsorption process. Thus, the role of hydrogen ion concentration was

examined at pH values of 2,4,8 and 10. This was adjusted by adding 0.5N HNO<sub>3</sub> or 0.1M NaOH with 100ml of solution for a contact time of 120 min. with a dose of 10g/L of adsorbent (Bergaoni, 1995) from preliminary kinetic studies, it was found that an equilibrium time of a few minutes was presumed to be sufficient for adsorption to reach equilibrium. For consistency, a time of 2hrs was chosen to stop the experiment. So in all cases, the equilibrium was reached within 2 hrs.

**(d) Effect of adsorbent particle size:**

Experiments were conducted to evaluate the influence of adsorbent particle size for a constant weight on the removal of adsorbates. Studies for adsorbent particle size were performed by keeping all conditions constant and varying particle size. The residual adsorbate concentration were determined after each run.

**(e) Effect of Temperature:**

Similarly, studies for effect of temperature on adsorbents were also conducted by varying the temperature. The samples were heated in a thermostatic bath or hot plate apparatus for a specific time, filtered and then analysed for aromatic and sulphur removal.

## **4.9 Determination of Kerosene Properties before and after adsorption**

### **4.9.1 Doctor Test**

Shake vigorously together in a test tube 10ml of the solvent being tested and 5ml of sodium plumbite solution for about 15 seconds. Add a small amount of sulphur so that practically all of it floats on the surface between the solvent and the sodium plumbite solution after shaking for 15 seconds. Allow to settle and observe within 2 minutes. If the solution is discoloured or if the yellow colour of the sulphur film is noticeably marked, consider the test positive and report the solvent as sour. If the sample remains unchanged in colour and the sulphur is bright yellow or only slightly discoloured with grey or black, consider the test negative and report the solvent as sweet. If the Doctor test is positive, mercaptan content may be determined using test method D 3227 (potentiometric method).

4.9.2 Determination of Aniline Point using Aniline point Tester (TY 714 No. 209, ROGOSHI and Co. Ltd)

Equal volumes of kerosene sample and aniline (10 ml) are heated or cooled with stirring in a jacketed tube until there is a homogenous mixture of aniline and kerosene. The temperature at which complete miscibility occurs was noted and recorded as aniline point.

### **4.9.3 Determination of Cloud Point of Kerosene using Cloud Point Electronic Tester**

About 1 ml of sample was injected into the cup lid with the aid of a syringe, and then placed inside inner chamber of the electronic tester. The machine will automatically detect, stabilize and verify the cloud point of the sample.

#### **4.9.4 Determination of electrical conductivity of Kerosene sample**

##### Procedure

- (1) Attach probe to connector
- (2) Clean probe with isopropyl alcohol and dry
- (3) Press (M) button to read zero
- (4) Press (C) button to read 390
- (5) Shake sample
- (6) Insert probe to sample
- (7) Press (M) after 3 seconds
- (8) Record your reading in Ps/m

## CHAPTER FIVE

### RESULTS AND DISCUSSION

The results of the various experiment and analysis performed in this work are presented in this section.

#### 5.1 Physio-chemical Properties / Structural Parameters of Adsorbents

The important physico-chemical properties / structural parameters use in this work are presented in Tables 5.1 – 5.4. Adsorbents can be characterized according to size, shape, porosity and surface area. From the table, it was observed that silica gel has the highest surface area when compared with other adsorbents. This is due to its microporous internal structure and a vast network of interconnected microscopic pores. An increase in surface areas increases or greatly enhance the adsorbents capacity and efficiency because it provides a larger surface area thereby increasing the number of available adsorption or active sites. Also, the larger the surface area, the higher the porosity and this structural property lowers tortuosity of the adsorbent. It is also observed that Bone char has the highest porosity (83%) followed by clay (78%). Studies have shown that increase in surface area of adsorbents increases the rate of adsorption of the adsorbate due to the creation of more pores and micro-capillaries as sites for adsorption.

**Table 5.1 Silical gel (XPO-2113) – (standard)****Chemical**

Composition	Percentage %
Silica SiO <sub>2</sub>	99.80
Alumina Al <sub>2</sub> O <sub>3</sub>	0.11
Sodium Na <sub>2</sub> O	0.04
Sulphate SO <sub>4</sub>	0.01
Iron Fe <sub>2</sub> O <sub>3</sub>	0.01
Calcium CaO	0.00
Magnesium MgO	0.01

**Physical**

Parameter	Value
<b>Surface area</b>	506 m <sup>2</sup> /g
Pore volume (N <sub>2</sub> )	1.54 CC/g
Average pore diameter	122 Å

**Table 5.2: Limestone:****Chemical**

Composition	Percentage %
CaO	51.29
MgO	2.23
SiO <sub>2</sub>	3.47
Al <sub>2</sub> O <sub>3</sub>	1.00
Fe <sub>2</sub> O <sub>3</sub>	0.21

**Physical Properties**

Nature	-	Crystalline
Calcinations behaviour	-	Decrepitating
Moisture content	-	0.82%
Specific gravity	-	2.04

Specific surface area - 100m<sup>2</sup>/g

### Structural

Pore volume - 0.15 cc/g

Bulk volume - 0.60 cc/g

Porosity - 25%

Tortuosity - 4.0

**Table 5.3: Summary of Characteristics of Clay sample**

Clay

Chemical

Oxide	Percentage composition
SiO <sub>2</sub>	47.38
Al <sub>2</sub> O <sub>3</sub>	31.46
Fe <sub>2</sub> O <sub>3</sub>	9.87
CaO	0.0237
MgO	0.001

Physical

**Moisture content (%) - 16.48**

Specific surface area (m<sup>2</sup>/g) - 331

Specific gravity - 2.45

pH - 6.20

Cation – Exchange capacity (ml.eq/100g) 45

### Structural

Pore volume - 0.88cc/g

Bulk volume	-	1.12 cc/g
Porosity	-	78%
Tortuosity	-	1.27

Table 5.4: Bone Char

**Chemical**

<b>Composition</b>	<b>Percentage (%)</b>
CaCO <sub>3</sub>	7.00
CaSO <sub>4</sub>	0.15
Fe	0.25

**Physical**

<b>Characteristics</b>	<b>Value</b>
Moisture content	4.5%
Specific gravity	2.4
Specific surface area	204

**Structural**

<b>Pore volume</b>	-	<b>0.20 cm<sup>3</sup>/g</b>
<b>Bulk volume</b>	-	<b>0.24</b>
<b>Porosity</b>	-	<b>83%</b>
<b>Tortuosity</b>	-	<b>1.2</b>

## 5.2 EFFECT OF CONTACT TIME

The amount of adsorbate adsorbed by an adsorbent at a particular time is one of the important factors governing the efficiency of adsorption. Figure 5.1 and Appendix 1 represent the effect of contact time with the various adsorbents. The time variation curves for aromatic removal are smooth and continuous, except for few variations indicating the formation of monolayer coverage on the surface of the adsorbent. From the figure, the rate of adsorption of aromatic removal was very rapid in the first 10 minutes and increases linearly for up to another 20 minutes followed by a continuous relatively slower rate up to a maximum at 50 minutes. The sharp increase for limestone was not linear up to about 30 minutes but gradually increased till 50 mins. contact time and all the adsorbents display a similar characteristics till equilibrium is attained. From the figure, the rate of aromatic removal by the six adsorbents varied with oxidized bone being the most efficient adsorbents while limestone was the least. The increase may be due to the increased surface area and the number of binding sites. The differences in the amount of aromatics adsorbed may be due to the chemical properties of the adsorbents.

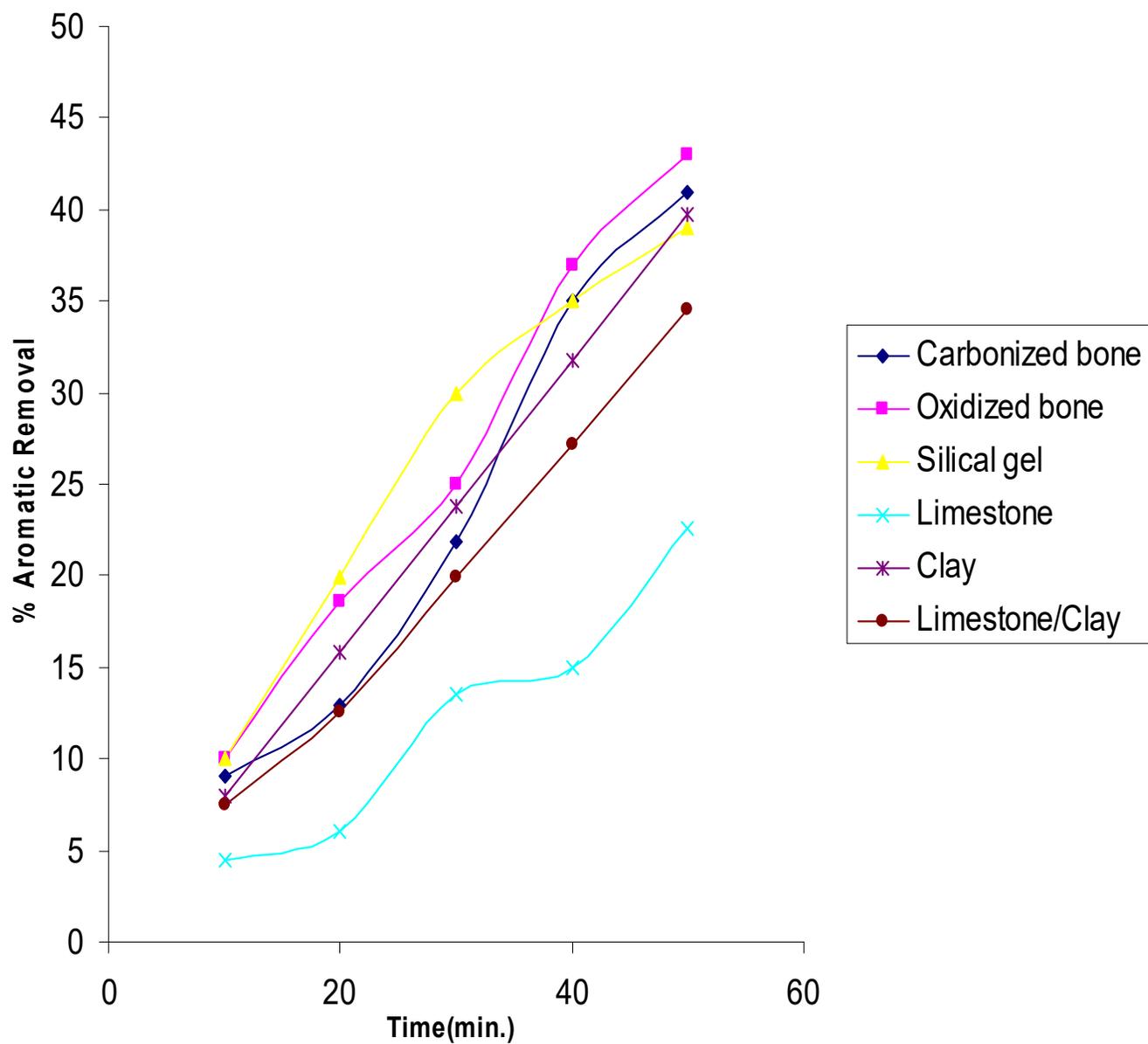
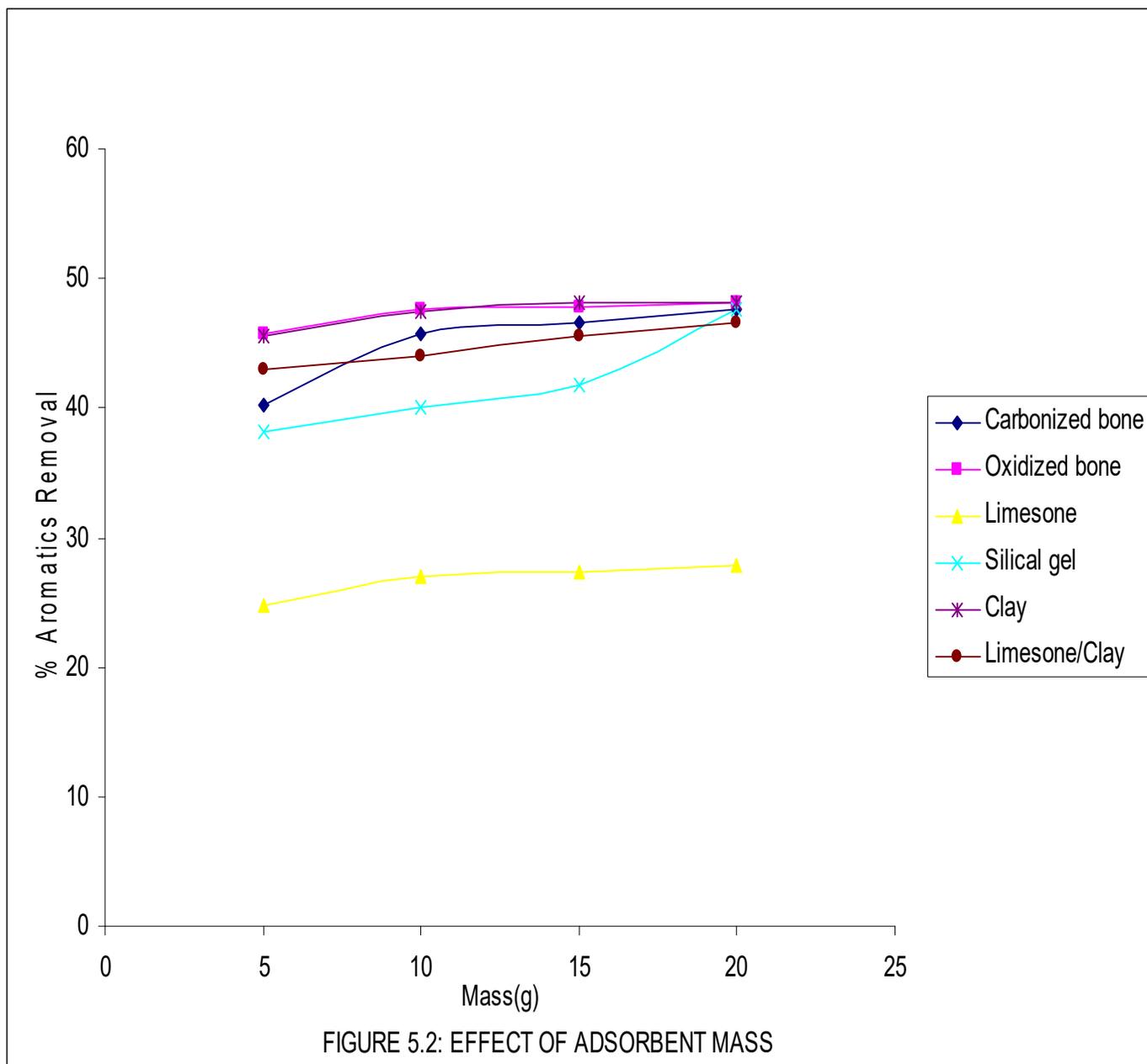


FIGURE 5.1; EFFECT OF CONTACT TIME

### 5.3 EFFECT OF ADSORBENT MASS

The plot of the rate of aromatic removal against mass of adsorbents used is presented in figure 5.2. It is observed that the removal of aromatics and sulphur increased with an increase in the amount of adsorbent. The percentage aromatic removal of the maximum dose of 20g were 47.59%, 48.10%, 27.28%, 47.70%, 48.10% and 46.55% for carbonized bone, oxidized bone, limestone, silica gel, clay and limestone / clay respectively. The results reveal that increase in adsorbent mass increased the number of binding sites, adsorbent porosity and surface area thereby enhancing the adsorption capacity due to the number of available adsorption sites. The size of the pores( micropores, mesopores and macropores), nature of their structures , surfaces and chemical composition of each adsorbent greatly influenced the degree of solubility and diffusion of the aromatics in the adsorbate solution. This lead to increased number of sorption sites due to the electrostatic interaction that might have result from this property.



## 5.4 EFFECT OF TEMPERATURE

The effect of temperature on the rate of aromatic removal for various adsorbent is shown in figure 5.3. In all cases, there is a considerable effect of temperature and the rate of removal becomes more linear as temperature is increased. The results indicated that adsorptive capacity of adsorbents decreased with increase in the adsorption temperature. The decrease in adsorptive capacity may be due to chemical and structural modifications that have taken place following the treatment of the adsorbents with hydrochloric acid and subsequent thermal activation resulting in increased porosity and creation of more active sites. Silica gel is extremely efficient at temperature below 25<sup>0</sup>C, but will loose some of its adsorbing capacity as temperature begin to rise due to decreasing velocity and molecular movement of the adsorbate at high temperatures. The lower the temperature, the faster the adsorption rate (Myers, 2002). At high temperature, the free energy of the molecules is not sufficient to effect spontaneous adsorption. The rate of adsorption depends on the rate of collision between adsorbent and adsorbate molecules, which in turn depends on the free energy of the latter.

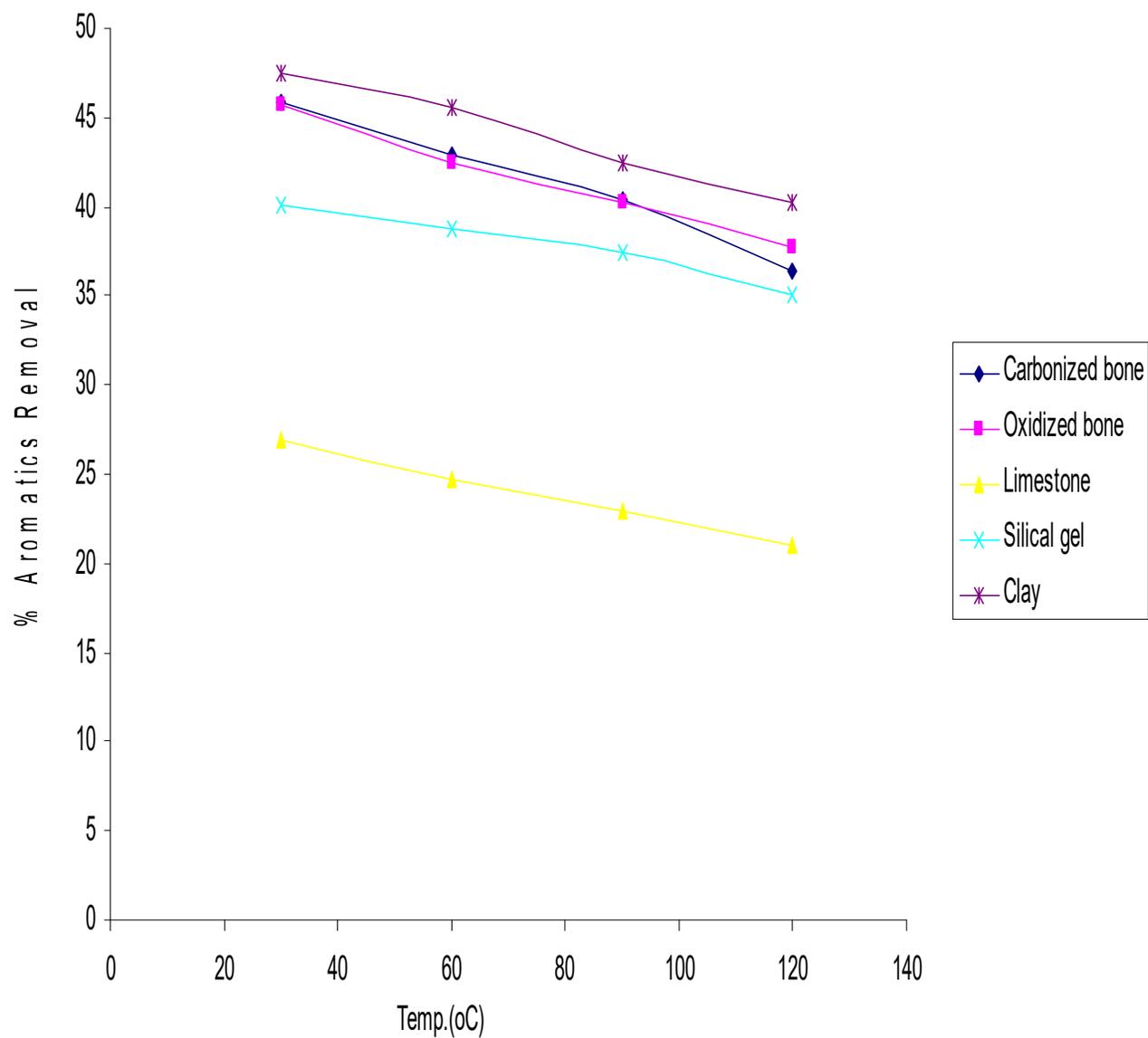


FIGURE: 5.3 EFFECT OF TEMPERATURE

## 5.5 EFFECT OF pH

The adsorption of adsorbate from aqueous solution is highly dependent on the pH of the solution. The pH of the adsorbate affects the surface charge of the adsorbent and level of dissociation of functional groups on the adsorbent surface. Figure 5.4 depicts the effect of pH on percent aromatic removal by oxidized bone, clay, limestone and silica gel. The results indicate that at all pH levels below 5.0, the oxidized bone has consistently higher adsorption capacity for aromatics. The pH of the aqueous solution is a controlling factor in the adsorption process. The influence of pH on the adsorption rate have shown a decrease in the extent of removal of aromatics with increase in pH of the solution. The reason for the better adsorption capacity observed at low pH levels may be attributed to the larger number of H ions present, which in turn neutralize the negatively charged adsorbent surface, thereby reducing hindrance to the diffusion of organics at higher PH. The reduction in adsorption may be possible due to the abundance of OH<sup>-</sup> ions, causing increased hindrance to diffusion of organics. Similar observations have been reported by the workers (Mott et al, 1992), (Liskowitz et al, 1980) and (Mall et al,1998).

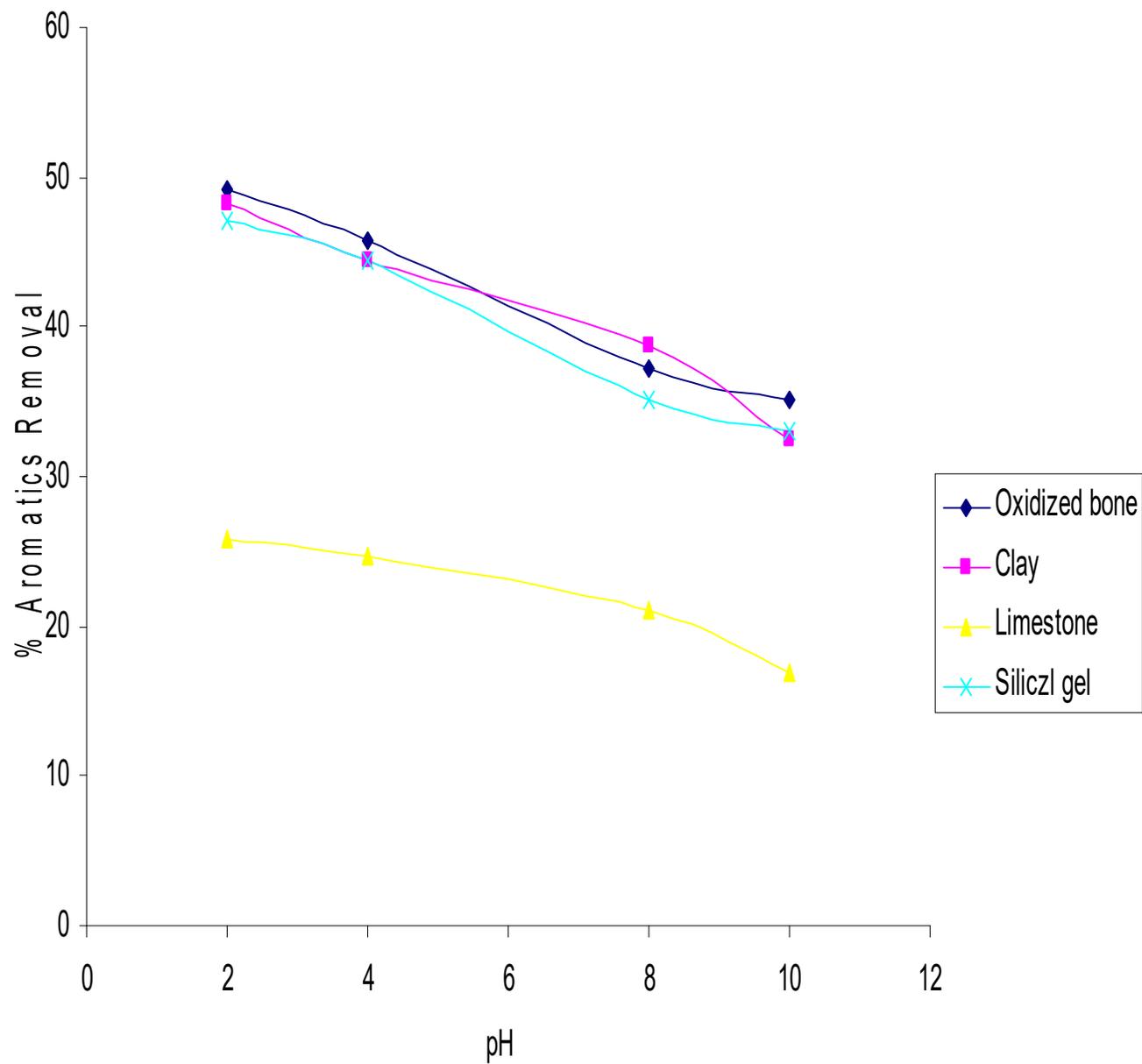


FIGURE 5.4 : EFFECT OF pH

## 5.6 EFFECT OF PARTICLE SIZE

Since adsorption is a surface phenomenon, it is evident that the greater the surface area per unit mass of the adsorbent, the greater is its capacity for adsorption. Figure 5.5 represent the effect of particle size on aromatic and sulphur reduction. It was observed that the extent of adsorption decreased with increasing particle size. From the result, Oxidized bone has the highest percentage aromatic removal while limestone is the least. This is due to the microporous structure and wide size distribution formed within both the carbon and hydroxyapatite compounds. Each of the above components in bone play a distinct role in the adsorption process. Also, the oxidized bone has a firm physical structure, high porosity and white ash upon ignition, In general, the intra-particle mass transfer effect will increase with the increasing particle size. However, the surface area per unit mass of adsorbent as well as diffusional transport, might be larger in case of smaller particles, which increases the adsorption rate. (Rao et al, 2000) observed similar characteristics for the adsorption of COD on activated carbon. Also, the time required for 50% of total adsorption is less with the particle of smaller size. This also gives some idea of rate-limiting step of the adsorption process.

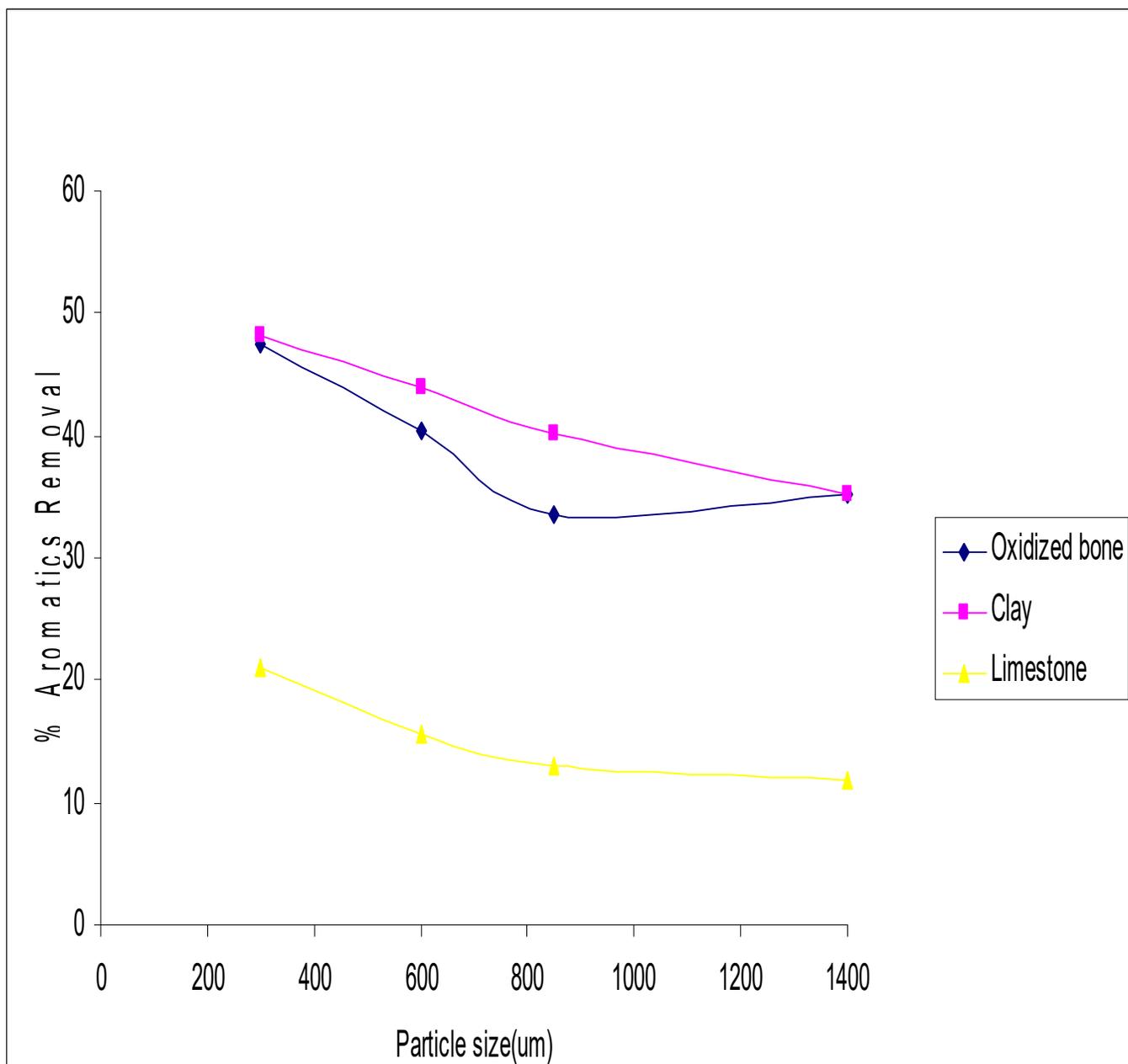
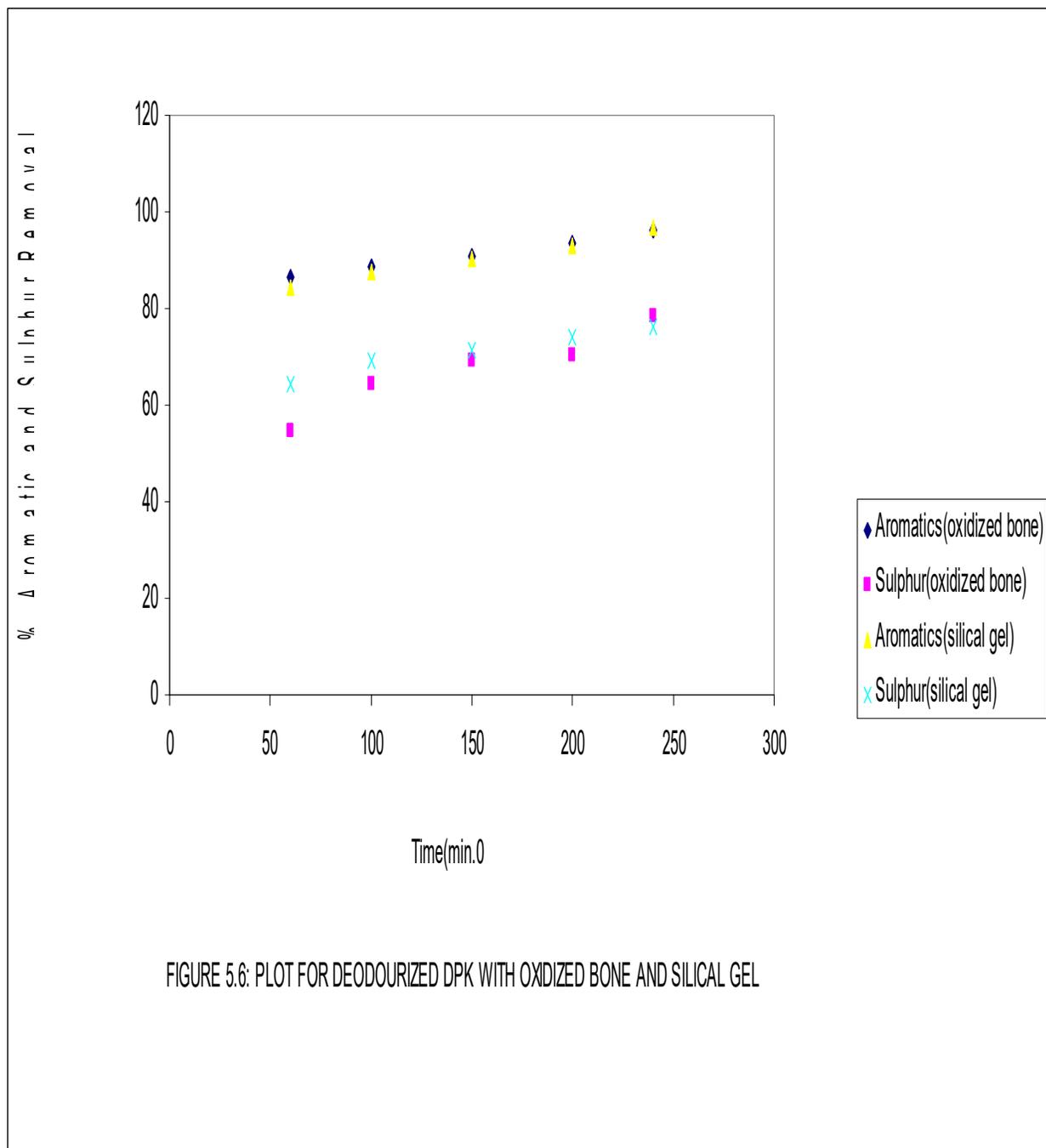


FIGURE 5.5 EFFECT OF PARTICLE SIZE

## 5.7 VARIATION OF TIME WITH MASS

Figure 5.6 and represent the effect of variation of time, while figure 5.7 illustrates the effect of mass of adsorbents on the removal of aromatics and sulphur. The result shows that increase in mass of adsorbent and time decreases the aromatic and sulphur contents of DPK. This is due to greater pore space per unit surface area exposed as well as molecular attraction or chemical forces that provide an interface of larger area on the surface of the solid adsorbent. Adsorption increases with increase in time because a larger number of vacant surface sites are available for adsorption. At lower mass, the significant small adsorption is possibly due to the saturation of surface active sites with the adsorbate molecules. From the results, it was also observed that aromatic and sulphur reduction has been achieved to the extent of more than 0.74 vol.% and 0.009% wts by oxidized bone at a maximum period of 240mins and 30<sup>0</sup>C and the trend of percent aromatic and sulphur reduction with oxidized bone was comparable to that of commercial silica gel. The carbon surface of the oxidized bone adsorbs weakly anionic molecules while the hydroxyapatite adsorbs strongly charged molecules with many inorganic ions. Also, the oxidized bone has a firm physical structure, high porosity and white ash upon ignition.



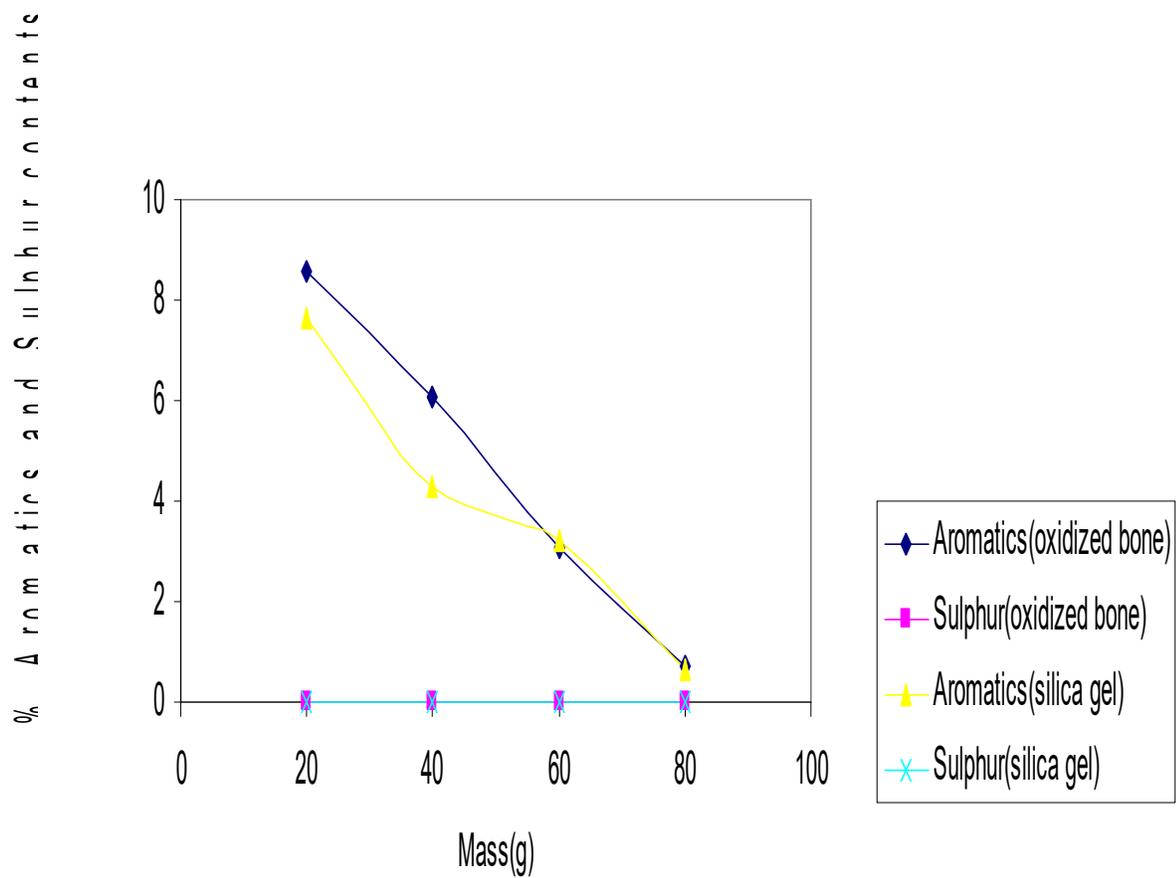


FIGURE 5.7: PLOT FOR AROMATICS AND SULPHUR CONTENTS IN DPK DEODOURIZED WITH OXIDIZED BONE AND SILICA GEL

## 5.8 EQUILIBRIUM ADSORPTION ISOTHERM MODELS

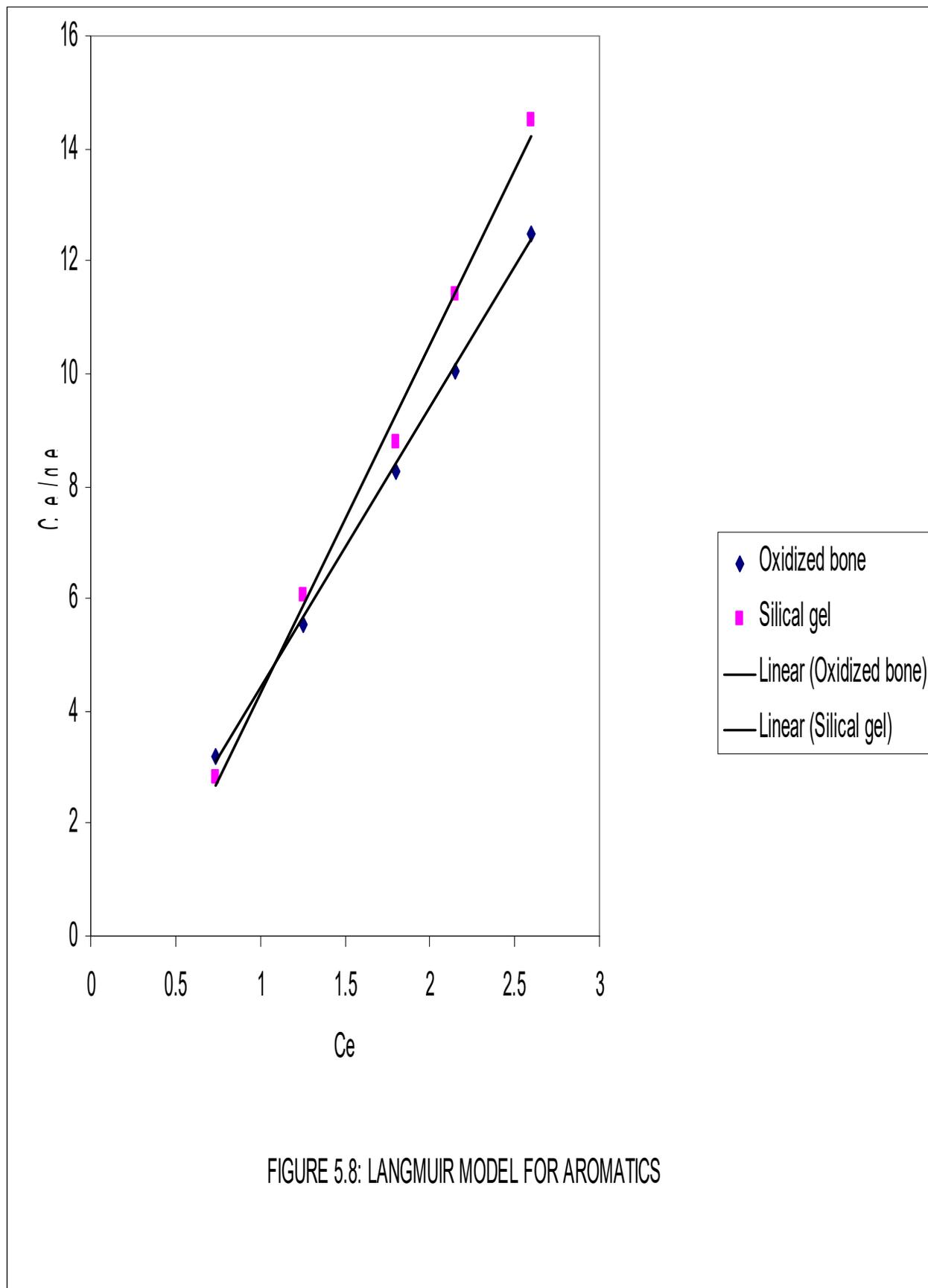
The analysis of experimental results by equilibrium sorption isotherms are important in developing accurate data that could be used for adsorption design purposes. The adsorption equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the adsorption mechanism and surface properties and affinity of the adsorbent. Figures 5.8-5.9 shows the linear plot of Langmuir isotherm model which gives a straight line of slope  $1/K_L$  and intercept  $1/bK_L$ . The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding monolayer coverage on the adsorbent surface. The values of the Langmuir constants  $K_L$  and  $b$  are presented in Appendix 4 for Aromatics and Sulphur using oxidized bone and silica gel. The values of the correlation coefficients indicate that there is a strong positive relationship for the data and that the aromatic sulphur data follows the Langmuir isotherm model. The monolayer saturation capacities are 0.196 and 0.000225 for aromatic and sulphur using oxidized bone, 0.20 and 0.00022 using silica gel.

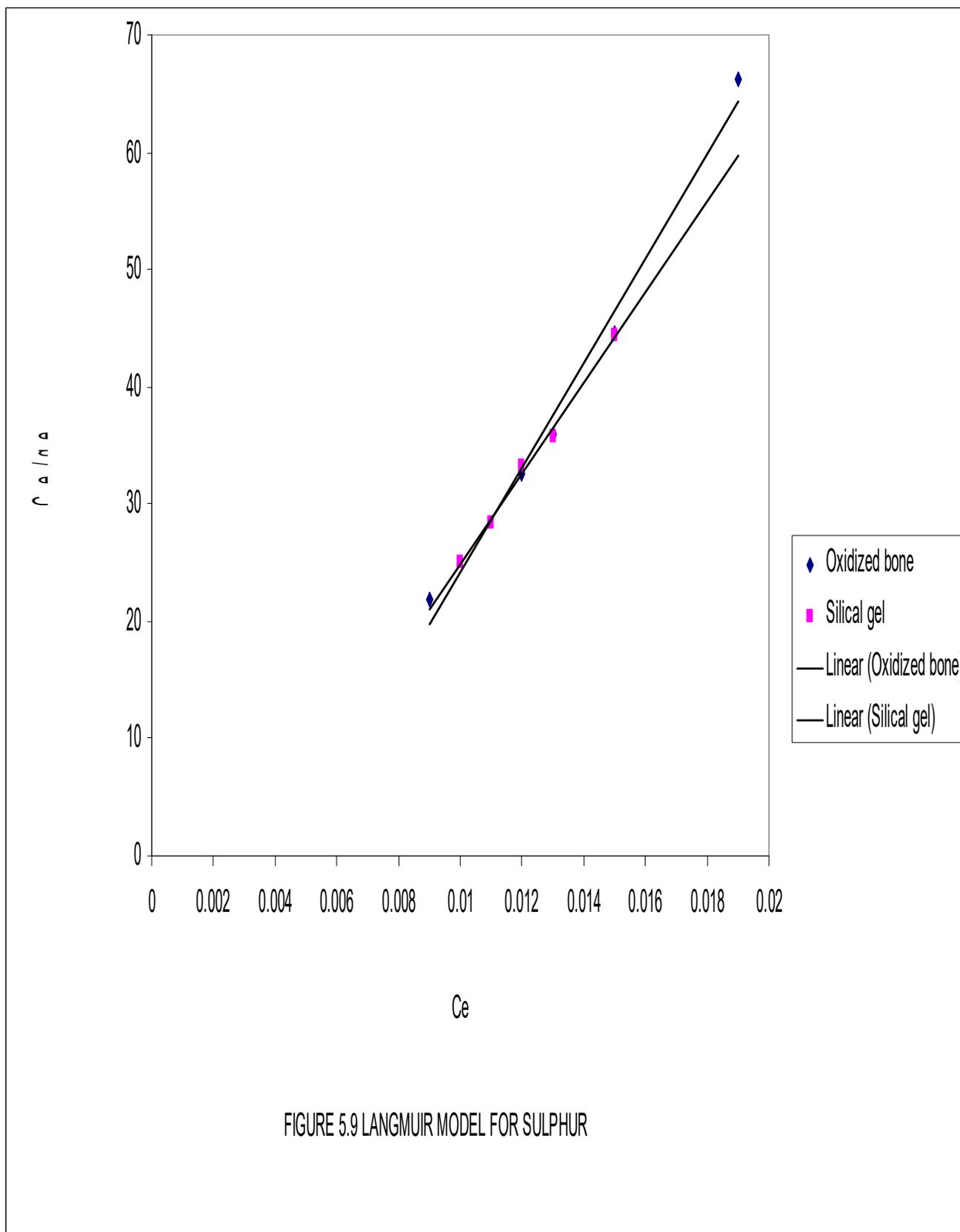
The applicability of the Freundlich sorption isotherm is also analysed by plotting  $\log(q_e)$  versus  $\log(C_e)$  as shown in figures 5.10 – 5.11, but data

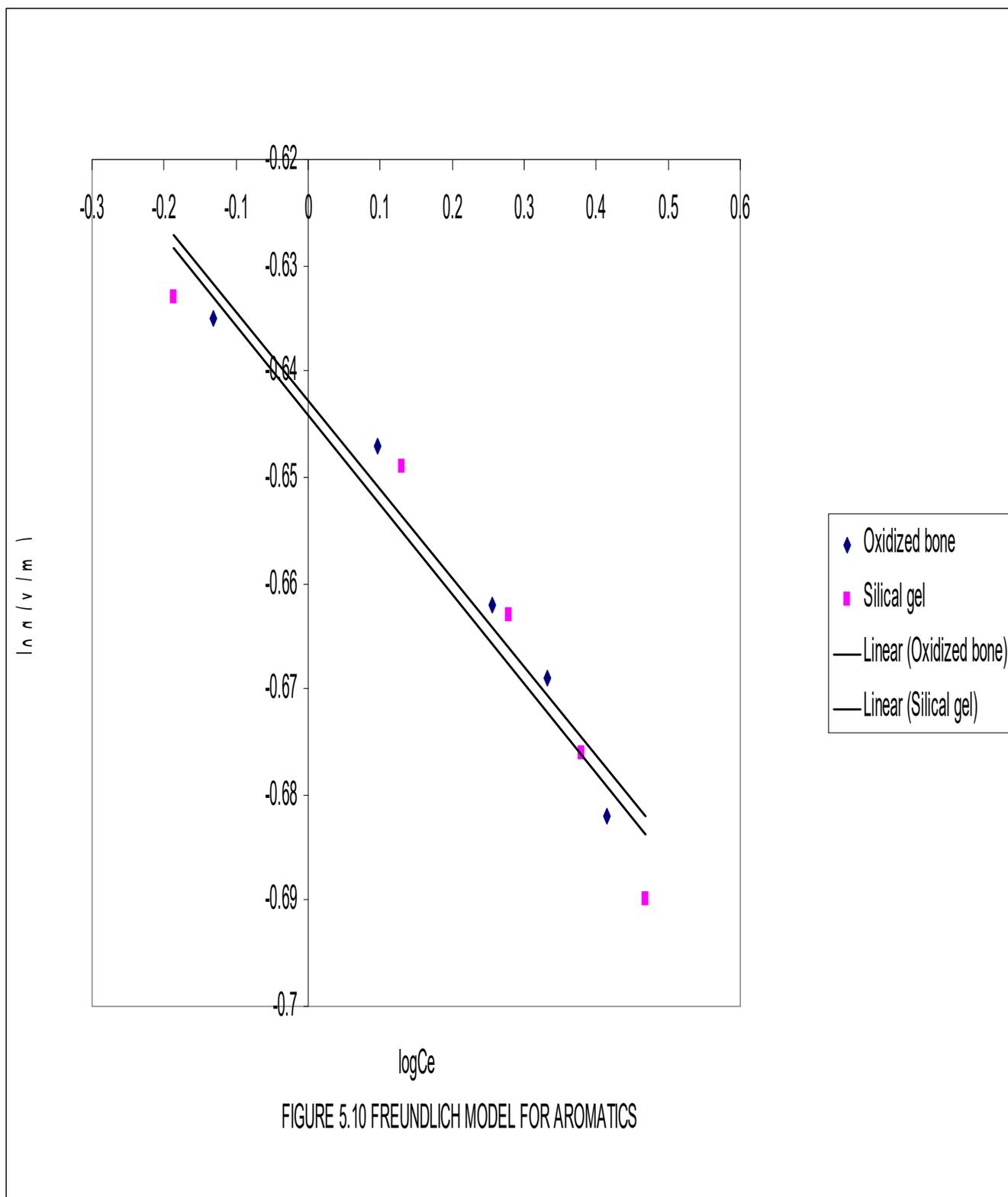
are not found in good agreement as in the case of the Langmuir. The Freundlich sorption isotherm constants and the correlation coefficients are presented in Appendix 6. The Freundlich model was chosen to estimate the adsorption intensity of the adsorbate on the adsorbent surface. Experimental analysis of the result showed that the values of  $1/n$  were found to be less than unity indicating that bond energies increase with surface density. It also indicates that the isotherm cannot be characterized by a convex Freundlich isotherms. The adsorption behavior of the adsorbents can also be described by the Redlich – Peterson description of the data for Aromatic and sulphur over the concentration ranges studied (figures 5.12- 5.13). In all cases, the Redlich – Peterson isotherm exhibits a high correlation coefficient as the case of the Langmuir, which is considerably better when compared with the Freundlich isotherm. The equation shows an excellent fit with the experimental data for the Redlich – Peterson and the Langmuir isotherms.

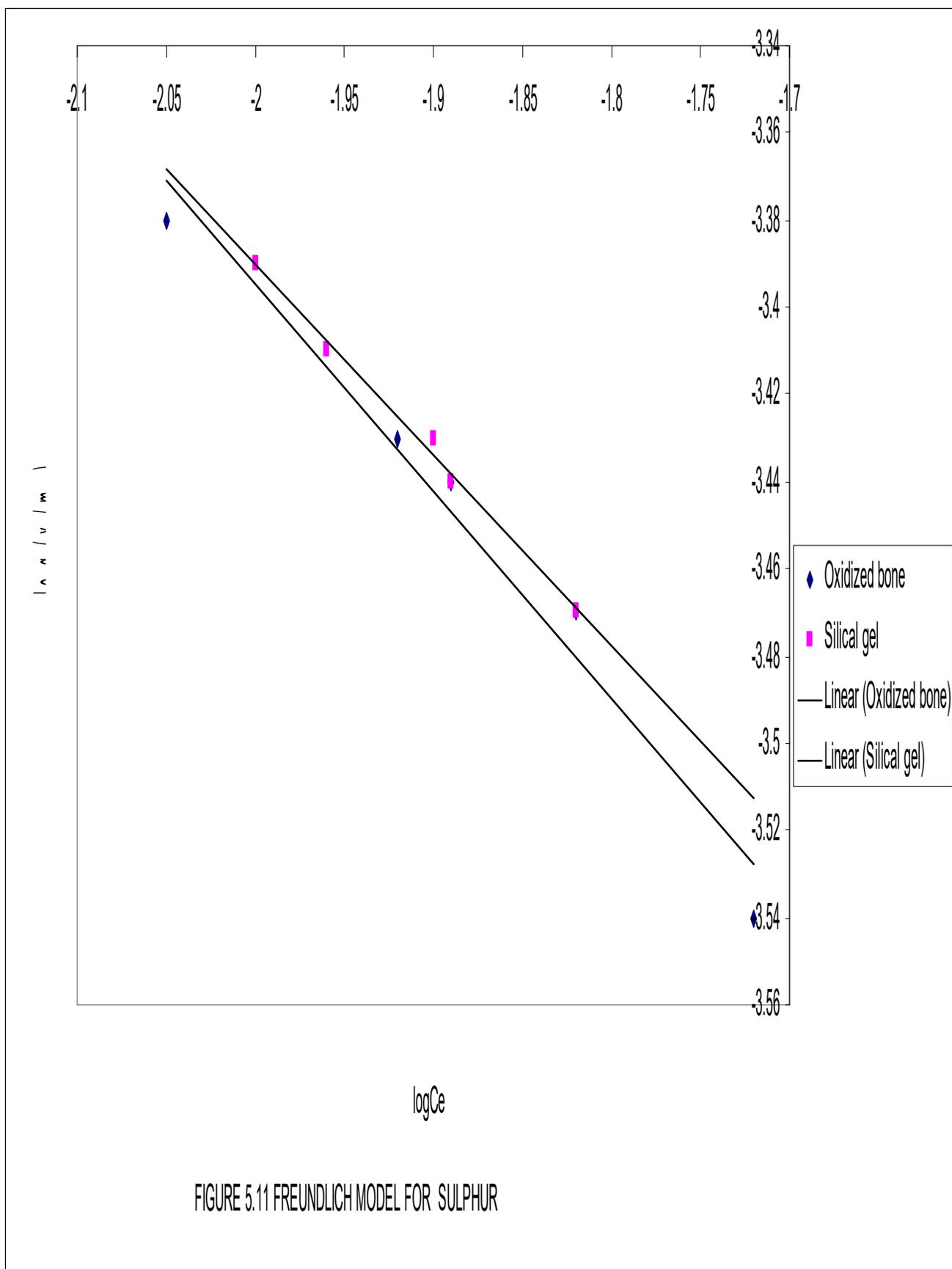
The Radke-Prutniz, and Temkin Models (figures 5.14- 5.17) clearly does not fit the data. It is evident that these models, originally developed for gas adsorption on surfaces, could be employed for adsorption on complex homogenous surfaces in aqueous solution. Clearly, it must therefore be cautioned that the application of these models should be limited to the mathematical representation of the data and the mechanistic inferences be

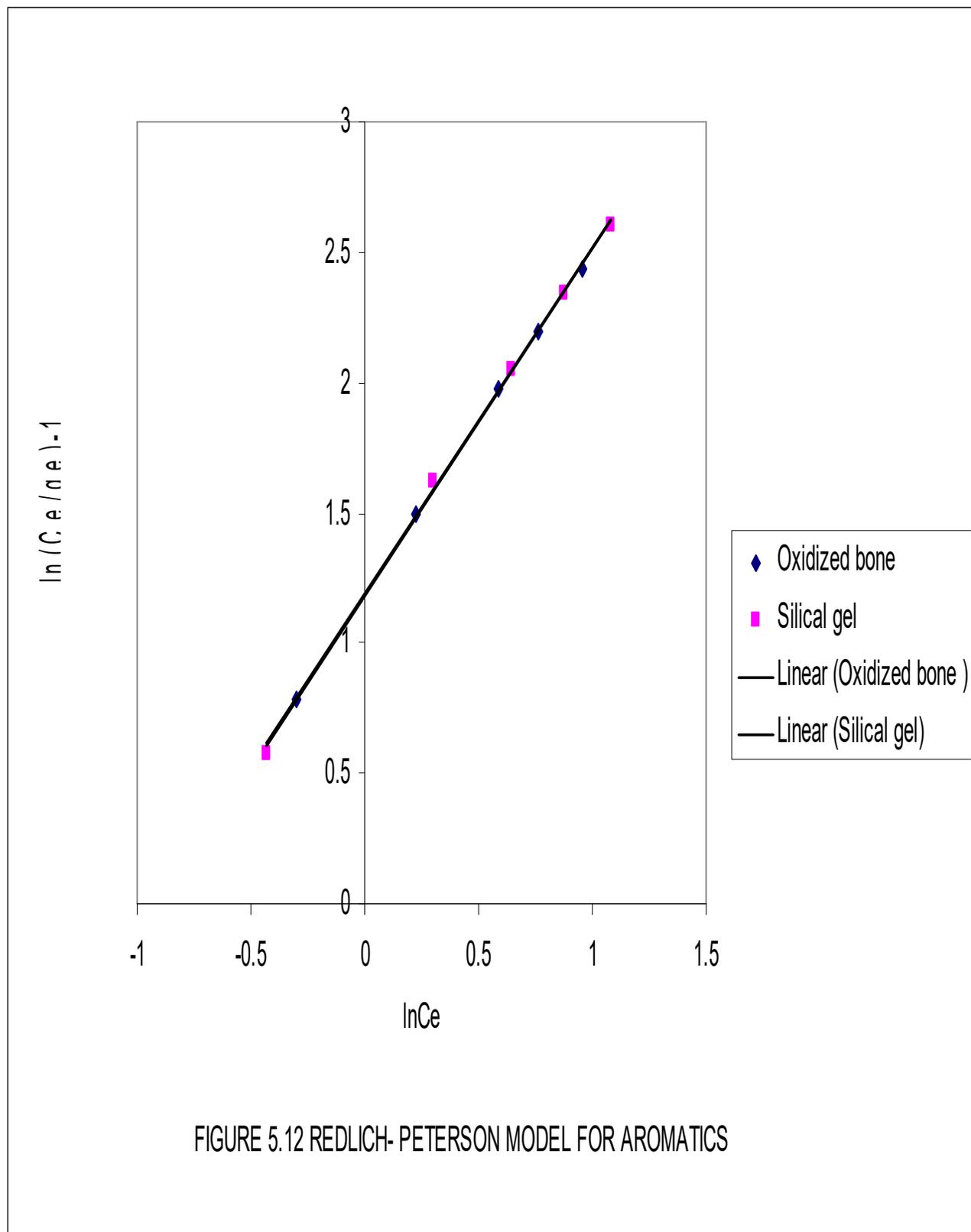
drawn very carefully. Furthermore, favourability, of adsorption Aromatic and Sulphur using oxidized bone and silica gel was tested using the essential features of the Langmuir isotherm model, expressed in terms of a dimensionless constant called separation factor as presented in Appendix 6. The separation factor is less than unity indicating that the sorption is favourable aromatic and sulphur using oxidized bone and silica gel and the shape is concave downward. Concave isotherms are favourable because high fluid concentrations are necessary for low adsorbate concentrations in the solid.

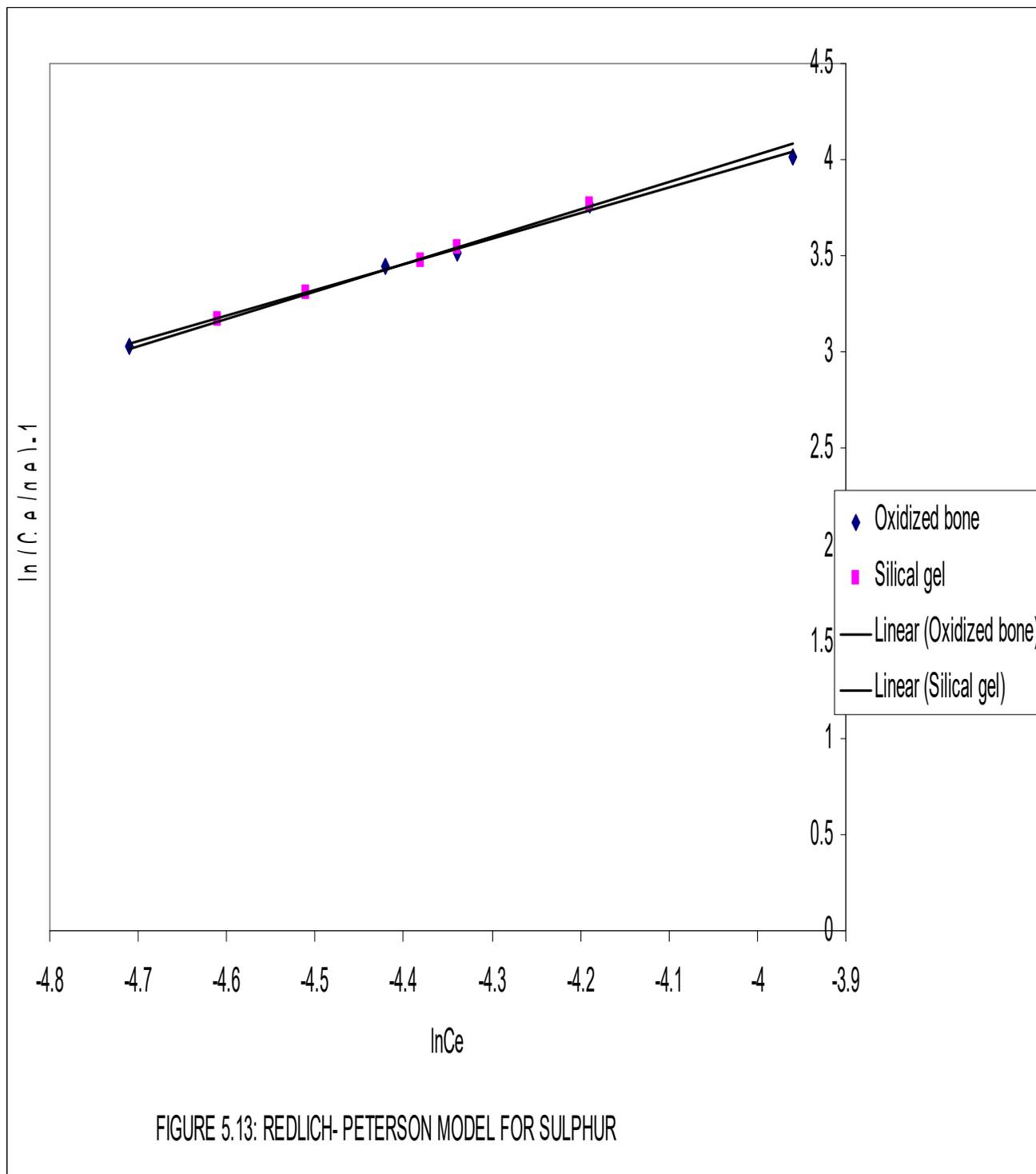


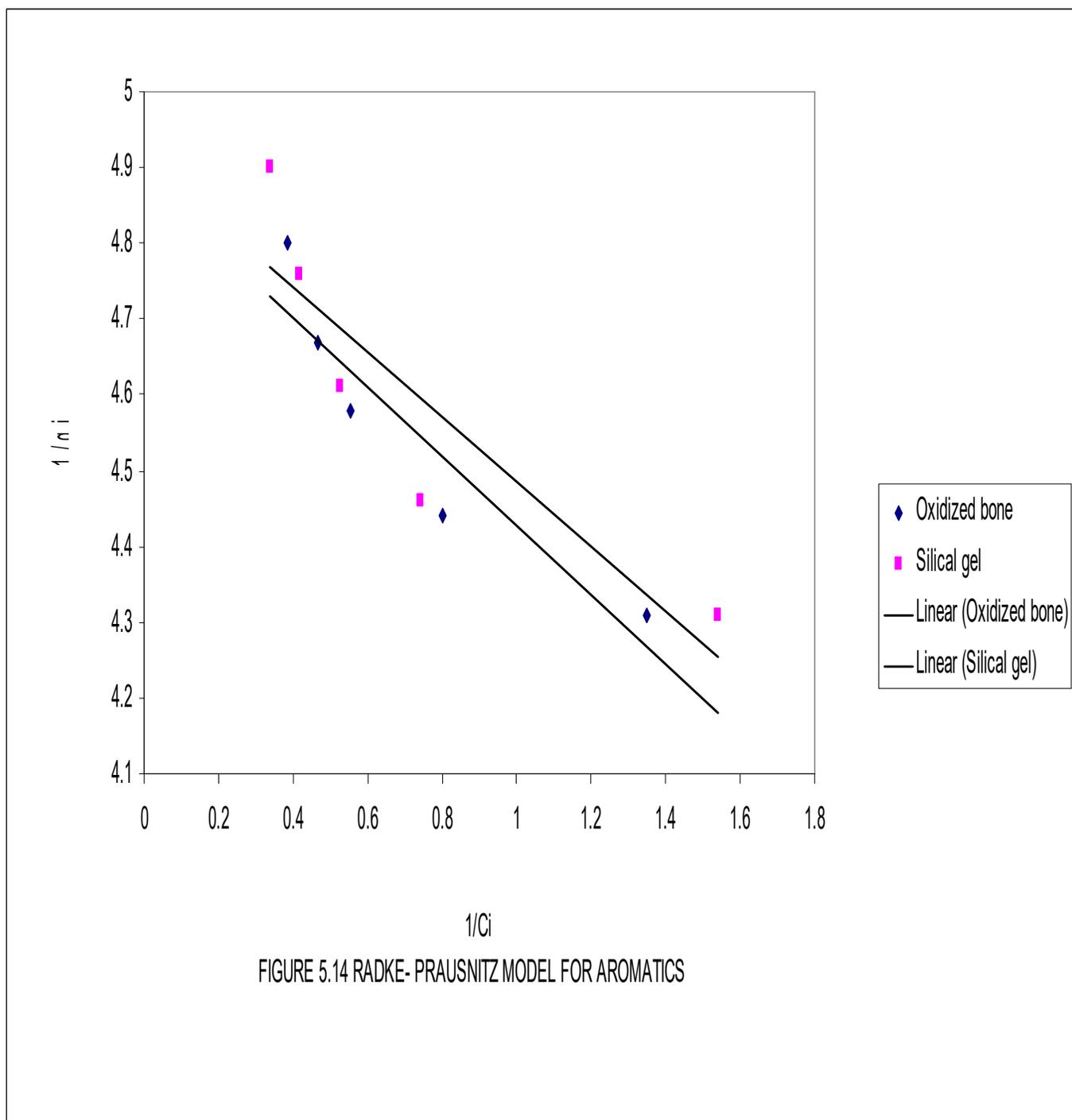












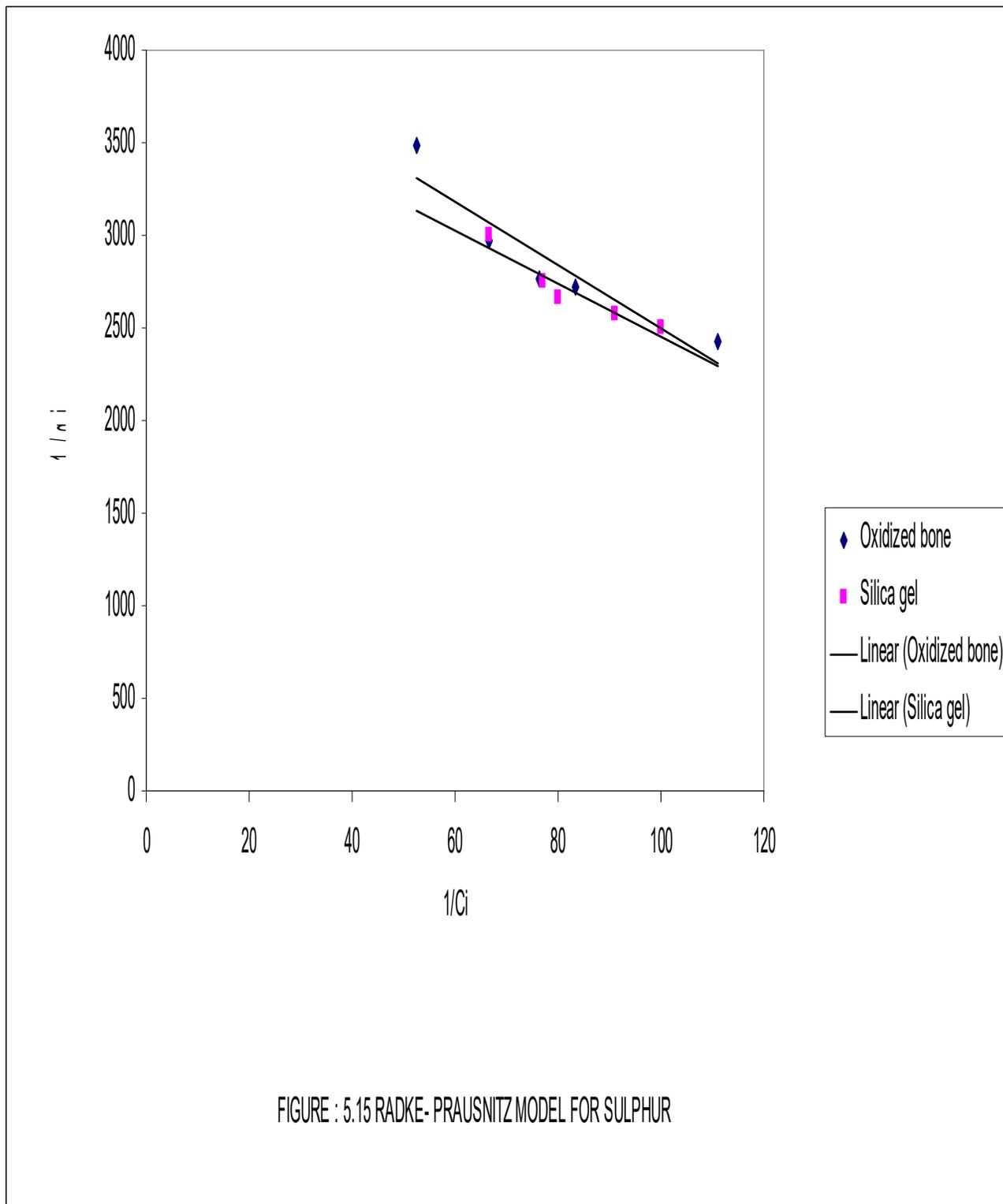


FIGURE : 5.15 RADKE- PRAUSNITZ MODEL FOR SULPHUR

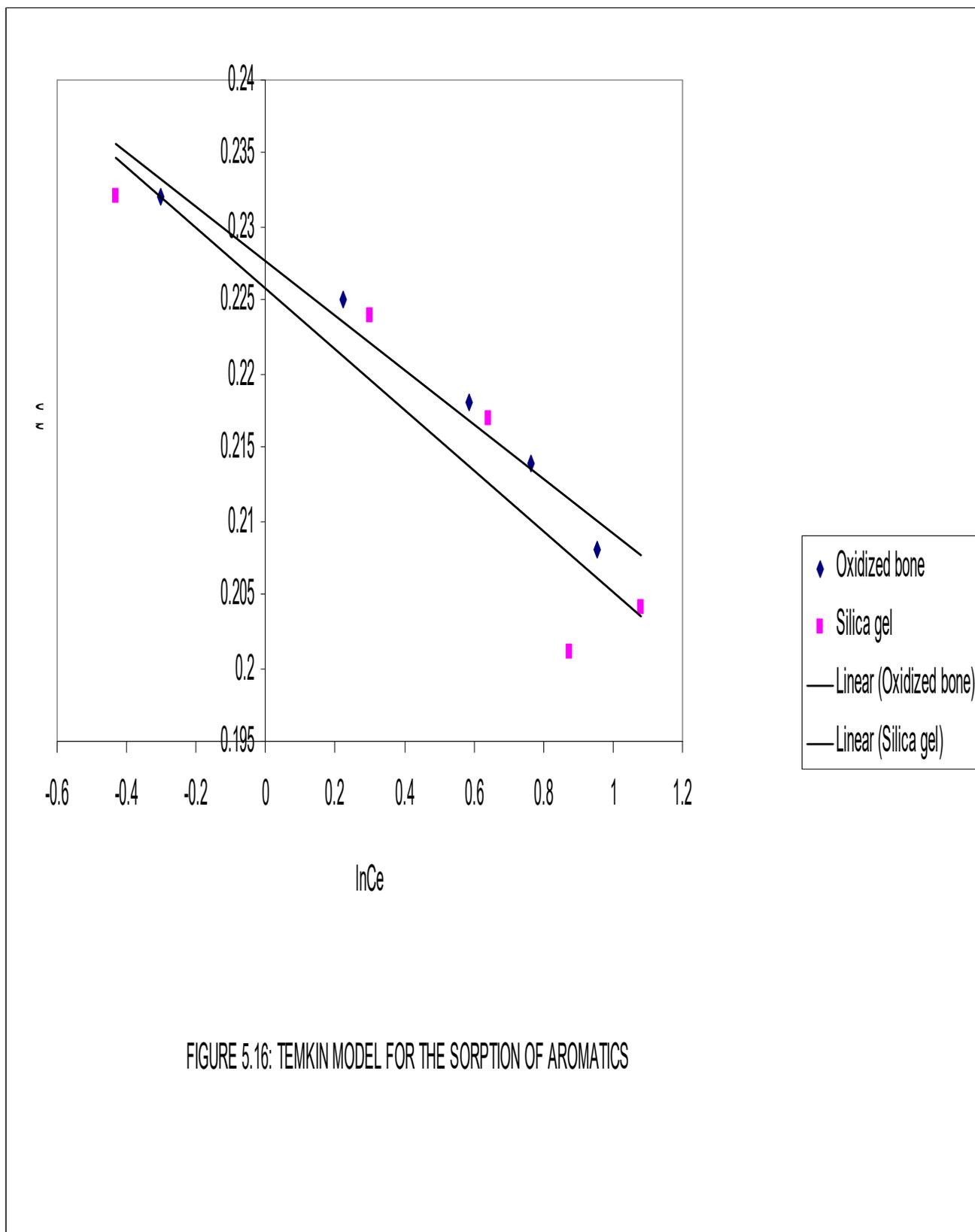


FIGURE 5.16: TEMKIN MODEL FOR THE SORPTION OF AROMATICS

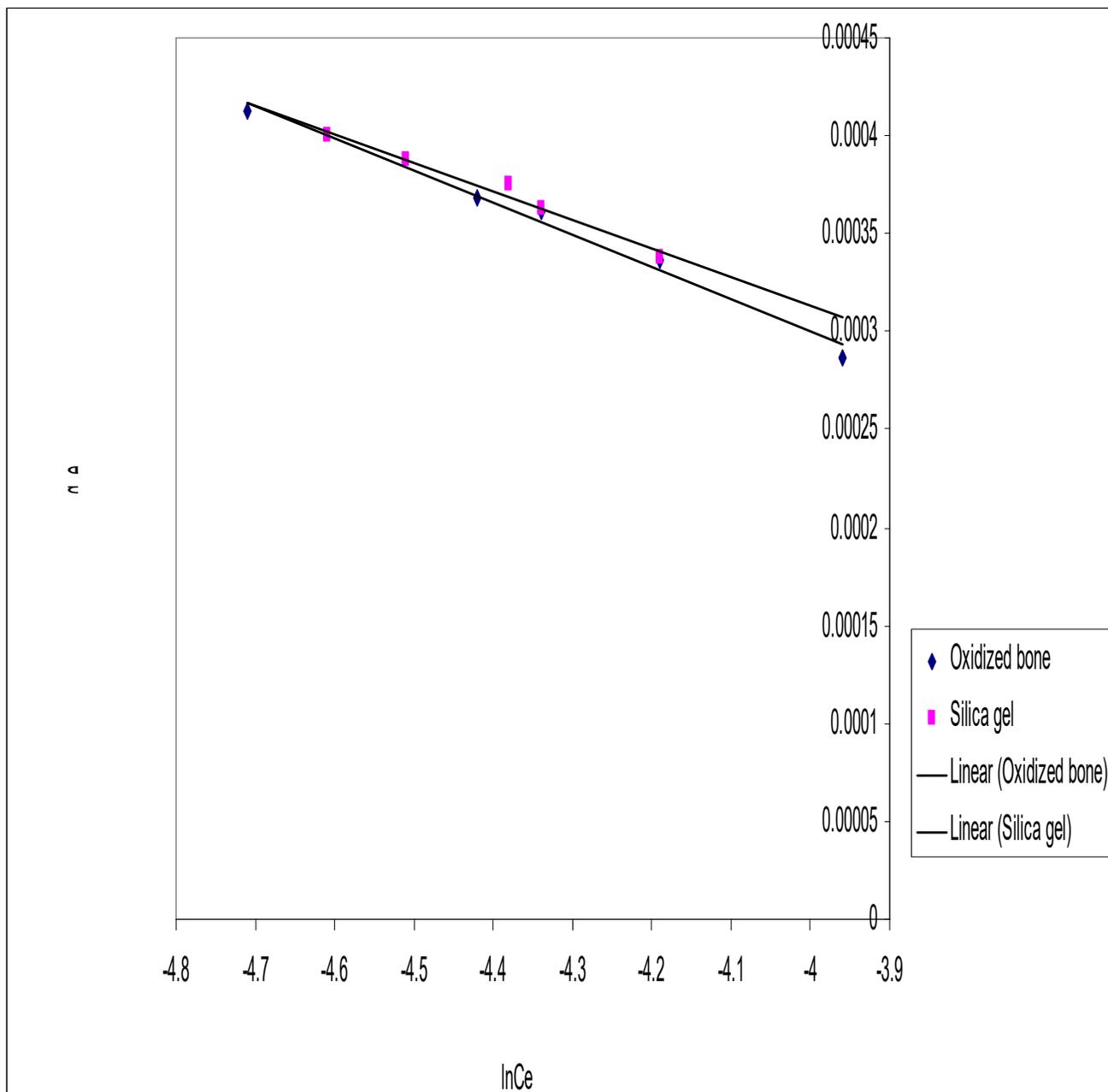


FIGURE 5.17: TEMKIN MODEL FOR THE SORPTION OF SULPHUR

## 5.9 Thermodynamic Model

Figure 5.18 depict the thermodynamic parameters, namely entropy, enthalpy and free energy. The negative value of entropy indicates the process is exothermic, sorption behaviour is physical and reversible. Also, negative values of enthalpy indicates the free diffusion of molecules through bulk solution and the stereotactic arrangements of adsorbates on the surface and in the pores of the adsorbents. The magnitude of enthalpy as shown in Appendix 5 for oxidized bone is higher than that of silica gel. This suggests that Van der Waals forces involved in the interaction of the molecules is stronger than the those involved with their interaction with the surface of the silica gel. This is not unexpected since the surface of the bone is likely to possess some hydrophilic character. The Van't Hoff plots showed that the entropy is negative for the two adsorbents indicating that this process is highly entropy driven. As would be anticipated, the Gibbs free energy is found to be positive, suggest that the sorption is spontaneous and that the process is thermodynamically favourable overall. However, silica gel has greater energy when compared with oxidized bone. This is attributed to the number of molecules that can accumulate on the surface due to physical adsorption. A low amount of the adsorbent in the fluid will cover

the surface of the adsorbent only up to the point when the pressure exerted by the adsorbent phase is equal that in the fluid. Furthermore, the molecules in the bone are not attached to all points on the surface of the solid, the chemical attraction between the solid and molecules in the fluid are saturated when each active centre are occupied. Increase in negative value of entropy indicates the spontaneity in the adsorption process with reduction in molecular size and increased randomness at solid-interface.

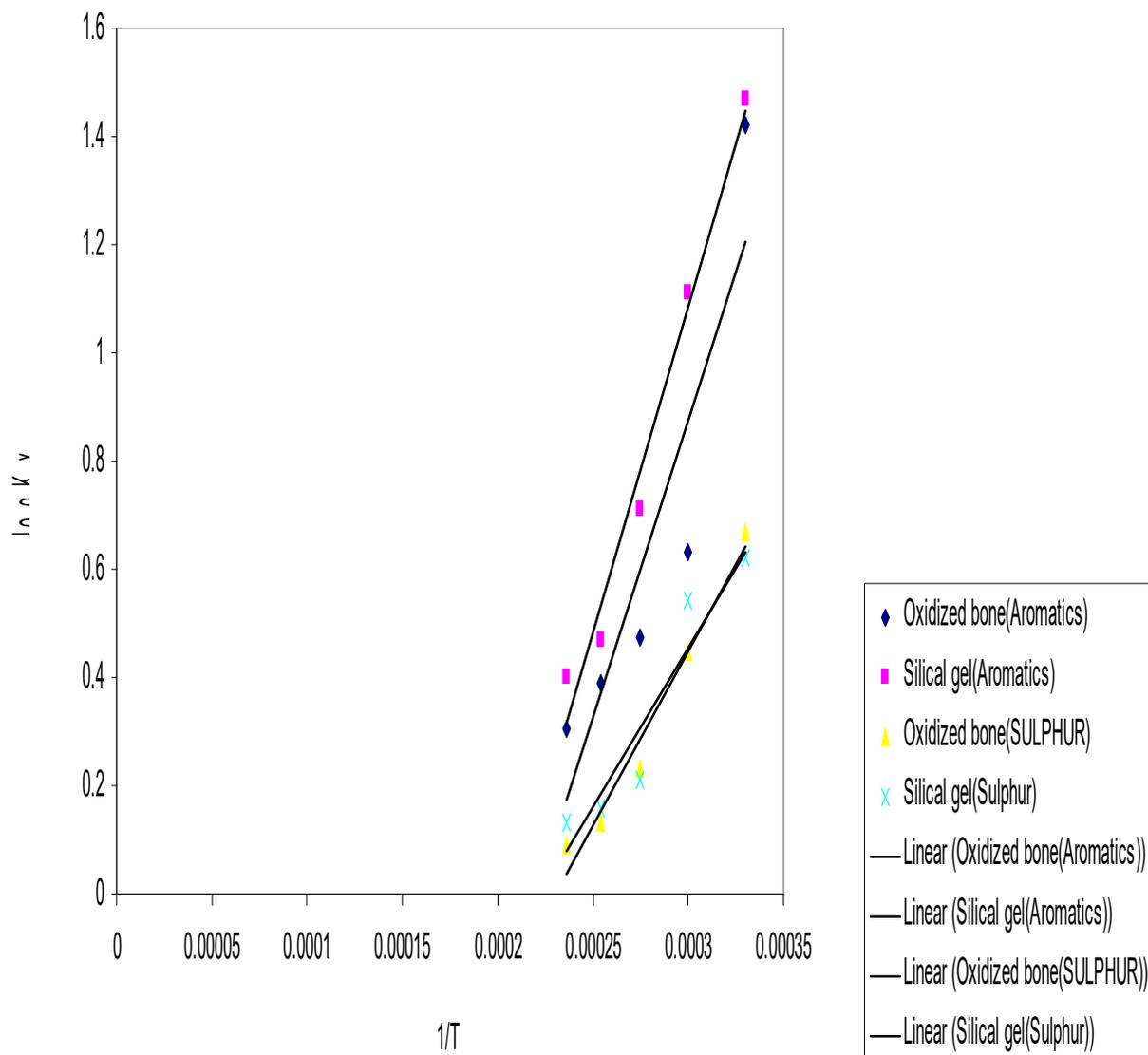


FIGURE 5.18: VAN'T HOFF PLOT OF  $\text{LOG}K_x$  AGAINST  $1/T$  FOR AROMATICS AND SULPHUR

## 5.10 KINETIC MODEL

Numerous kinetic models and mathematical correlation have been derived to determine the various sorption rate parameters. It is well recognized that the topography and roughness of a sorbent are critical factors that affect the sorption rate parameters, and that both particle diffusion and film diffusion play an important role in the overall transport of the sorbate (Okimen, et al, 1991 and Chanda, et al 1983). In order to investigate the mechanism of adsorption the pseudo first –order and second – order equations were used to test the experimental data. Figures 5.19 – 5.21 represents the plot of  $\log (q_e - q)$  and  $(t/q)$  versus time for first and second order kinetics. The correlation coefficient for the second order kinetic model obtained for aromatic and sulphur were higher than the first order kinetic model. Thus a high degree of correlation coefficient was obtained for the second order kinetic model. The results suggest that the adsorption system follows the second order kinetics which indicates that the rate controlling step is the film-diffusion (external mass transfer).

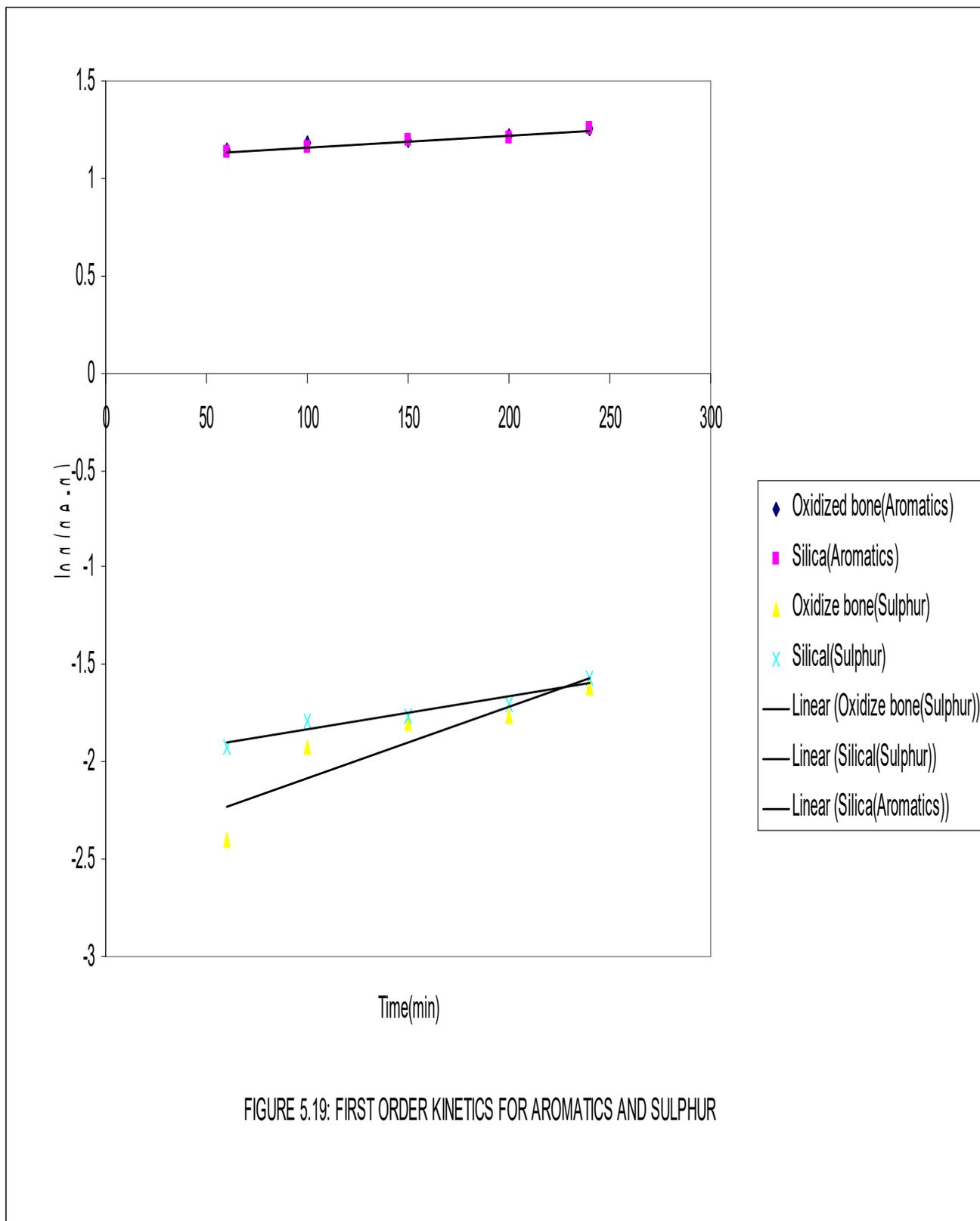


FIGURE 5.19: FIRST ORDER KINETICS FOR AROMATICS AND SULPHUR

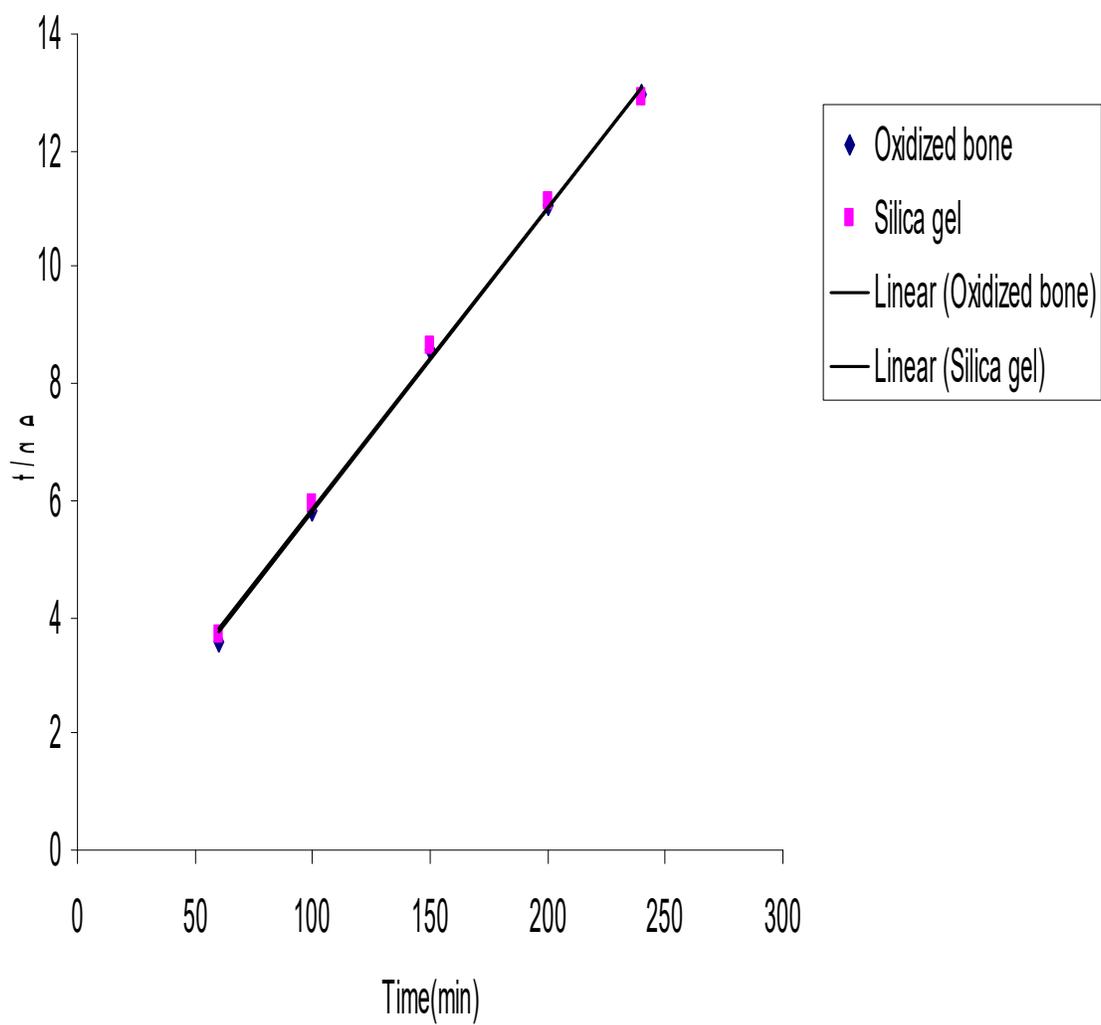
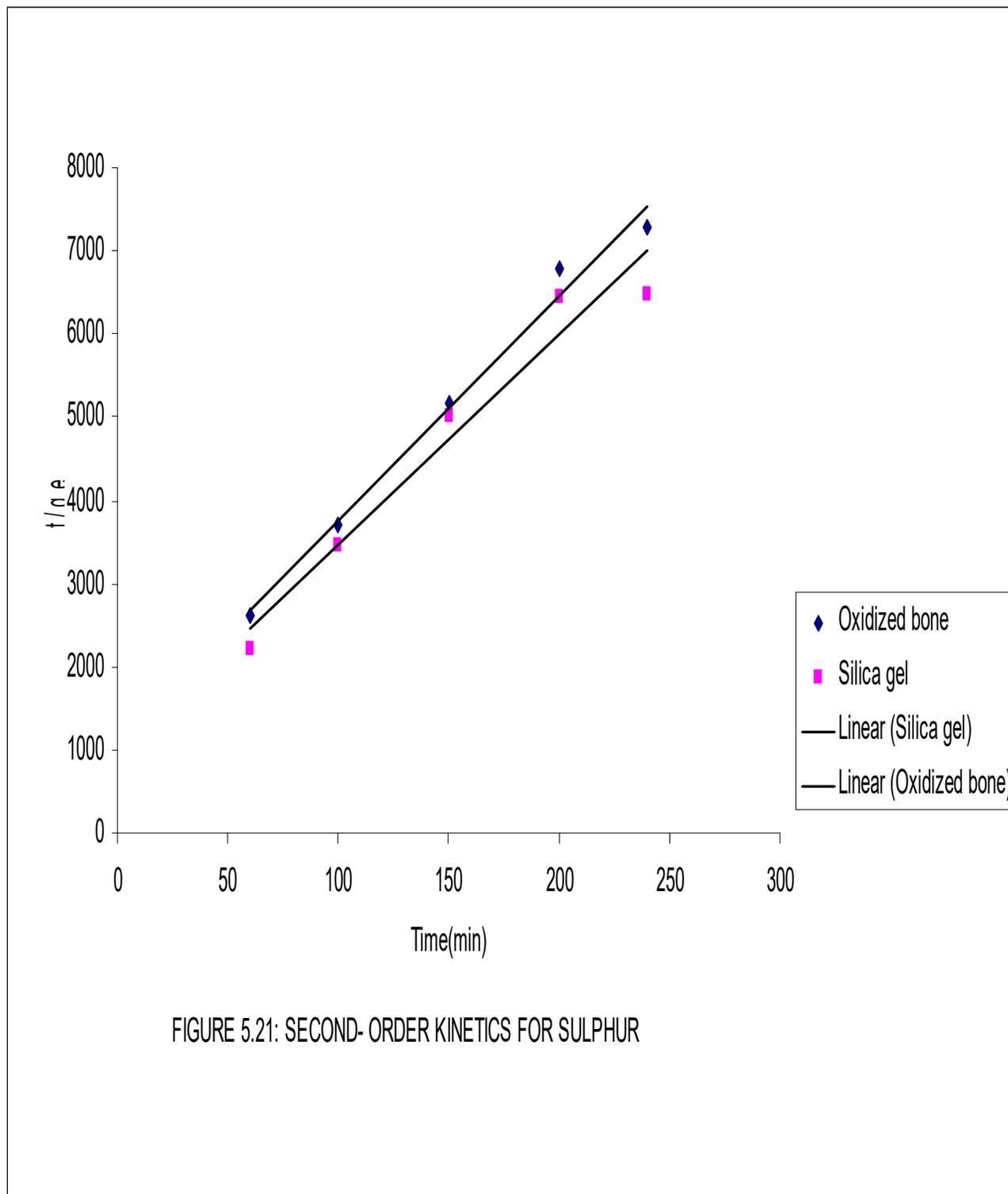


FIGURE 5.20: SECOND- ORDER KINETICS FOR AROMATICS



## CHAPTER SIX

### CONCLUSION AND RECOMMENDATION

#### 6.1 CONCLUSION

DPK remains a very important petroleum product and still continuous to play an important part in the life and well being of people. The essence of the treatment of DPK is to remove the sulphur group as well as the aromatics inherent in kerosene and which cause the characteristic odour.

The study of low-cost adsorbent (non-conventional adsorbent) viz: bone char, clay, limestone limestone/clay mixture and silica gel to remove aromatic and sulphur has been investigated. Results show that these low-cost adsorbents could be fruitfully used for the removal of aromatic and sulphur over a wide range of concentrations. Equilibrium studies showed that oxidized bone has the maximum capacity. Diffusion studies showed that initial part of the adsorption is attributed to external mass transfer effects followed by intra-particle diffusion.

The percentage of aromatic and sulphur removal was found to be a function of adsorbent dose and time at a given initial solute concentration. The shape of the adsorption isotherm was “favourable” as the curve was concave downward throughout representing Type 1 isotherm. The

experimental results were analysed by using the Langmuir, Freundlich, Redlich – Peterson, Temkin, Radke-Praustniz equations. Correlation 251 coefficients for fitting the Langmuir and Redlich-Peterson models were significantly better than the coefficients for other models. The results from this study are extremely well described by the theoretical Langmuir isotherm and the Redlich-Peterson isotherm.

In order to know the equilibrium constants that represents the adsorption process, the modeling of the process was done using the first-order and second-order models. Only the second-order model adequately provided good agreement with experimental data. This means that the models are highly dependent on the operational conditions. The thermodynamic parameters from this study revealed that the deodourisation of commercial DPK is highly exothermic, sorption behavior is physical and the process is reversible.

The study has shown that it is possible to prepare a good adsorbent with high sorption properties from conventional and non-conventional low cost adsorbents. The results from this study can provide a basis for the understanding of adsorbate sorption mechanism. In addition, the data obtained from the Kinetic behaviour of the sorption process would be useful

in the design of a semi-batch sorption system, which can be used in small scale industries.

Finally, adsorption technology is important for the separation and purification of products, which often is the value adding step in process industry. Together with the development of new materials, like micro-porous membranes, this stresses the need to gain understanding in adsorption process. This study therefore contribute to the understanding and modeling of the equilibria and kinetics of adsorption processes.

## **6.2 RECOMMENDATIONS**

Adsorption of adsorbate from aqueous solutions is a broad area. The following are hereby recommended for further studies:

- (a) Considerable research should be undertaken to utilize agricultural residues as low cost non-conventional adsorbents.
- (b) The rate of attainment of equilibrium should be extended to determine whether both film resistance and pore diffusion play an important role in the overall transport of the sorbate. On the basis of these resistances, more approaches should be proposed to determine the overall mass transfer in an adsorption system.

(c) The applicability of other models such as Competitive Langmuir – like, Modified Competitive Langmuir – like, Ideal Adsorbed solution, Levan-Vermeulen, and BET models for adsorption analysis should be tested for the deodourization of DPK.

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## APPENDIX 1

### 5.2 ANALYSIS OF DPK FOR AROMATIC CONTENT BEFORE ADSORPTION

As stated in chapter 4, the initial vol. % of aromatic content of DPK was analysed before adsorption studies. The result obtained are presented below:

Paraffin	-	80.07 vol. %
Aromatic	-	19.27 vol. %
Olefin	-	0.66 vol. %

#### 5.2.1 Adsorption Equilibria experiments with DPK at various experimental conditions

All the experiments were carried out at ambient temperature (30<sup>0</sup>C) in batch mode.

**Table 5.5 Effect of contact Time:**

(a)	Adsorbent	-	Carbonized bone
	Mass	-	10g
	Volume of DPK	-	100ml

Time (min)	Aromatics contents % vol.	Amount Adsorbed % vol.	% Aromatics Removal
10	17.53	1.74	9.03
20	16.79	2.48	12.87
30	15.05	4.22	21.90
40	12.53	6.74	35.00
50	11.37	7.90	41.00

**Oxidized bone**

<b>Time (min)</b>	<b>Aromatic content % vol.</b>	<b>Aromatic Adsorbed %vol</b>	<b>Aromatic Removal (%)</b>
10	17.35	1.92	10.00
20	15.79	3.48	18.60
30	14.40	4.87	25.00
40	12.14	7.13	37.00
50	10.98	8.29	43.00

**Silical Gel (control)**

<b>Time (min)</b>	<b>Aromatic content % vol.</b>	<b>Aromatics Adsorbed %Vol.</b>	<b>Aromatic removal (%)</b>
10	17.34	1.93	10.02
20	15.42	3.85	19.98
30	13.49	5.78	30.00
40	12.43	6.74	34.98
50	11.57	7.70	39.96

**Limestone**

<b>Time (min)</b>	<b>Aromatic content % vol.</b>	<b>Aromatics Adsorbed %vol</b>	<b>Aromatic removal (%)</b>
10	18.40	0.87	4.5
20	18.11	1.16	6.02
30	16.67	2.60	13.50
40	16.38	2.89	15.00
50	14.92	4.35	22.57

**CLAY**

<b>Time (min)</b>	<b>Aromatic content % vol.</b>	<b>Aromatics Adsorbed % vol</b>	<b>Aromatic removal (%)</b>
10	17.74	1.53	7.94
20	16.21	3.06	15.88
30	14.68	4.59	23.82
40	13.15	6.12	31.76
50	11.62	7.65	39.70

**Limestone / Clay Mixture**

<b>Time (min)</b>	<b>Aromatic content % vol.</b>	<b>Aromatics adsorbed % vol.</b>	<b>Aromatic removal (%)</b>
10	17.86	1.41	7.32
20	16.85	2.42	12.56
30	15.44	3.83	19.88
40	14.03	5.24	27.19
50	12.62	6.65	34.51

**Table 5.6: Effect of Temperature****Carbonized Bone**

Mass = 10g

Vol. of DPK = 100ml

<b>Temp °C</b>	<b>Aromatic content % vol.</b>	<b>Aromatic adsorbed % vol.</b>	<b>Aromatic removal %</b>
30	10.44	8.83	45.80
60	11.27	8.00	42.91
90	11.50	7.77	40.32
120	12.27	7.00	36.32

**Oxidized Bone**

<b>Temp °C</b>	<b>Aromatic content %vol.</b>	<b>Aromatic adsorbed % vol.</b>	<b>Aromatic removal %</b>
30	10.45	8.82	45.77
60	11.10	8.17	42.39
90	11.52	7.75	40.22
120	12.00	7.27	37.72

**Limestone**

<b>Temp <sup>0</sup>C</b>	<b>Aromatic content %vol.</b>	<b>Aromatic adsorbed % vol.</b>	<b>Aromatic removal %</b>
30	14.27	5.00	26.95
60	14.50	4.77	24.75
90	14.85	4.42	22.93
120	15.21	4.06	21.06

**Silica Gel**

<b>Temp <sup>0</sup>C</b>	<b>Aromatic content % vol.</b>	<b>Aromatic adsorbed % vol.</b>	<b>Aromatic removal %</b>
30	11.55	7.72	40.10
60	11.80	7.47	38.76
90	12.05	7.22	37.46
120	12.50	6.77	35.13

**Clay**

<b>Temp <sup>0</sup>C</b>	<b>Aromatic content. %vol.</b>	<b>Aromatic adsorbed % vol.</b>	<b>Aromatic removal %</b>
30	10.12	9.15	47.50
60	10.51	8.76	45.50
90	11.10	8.17	42.40
120	11.52	7.75	40.22

**Table 5.7: Effect of Adsorbent Mass at 30<sup>0</sup>C using Remi agitator machine at 120rpm for 1 hour**

**Carbonized Bone**

<b>Mass (g)</b>	<b>Aromatic content. % vol</b>	<b>Aromatic adsorbed %vol.</b>	<b>Aromatic removal (%)</b>
5	11.51	7.76	40.26
10	10.44	8.83	45.80
15	10.30	8.97	46.55
20	10.10	9.17	47.59

**Oxidized Bone**

<b>Mass (g)</b>	<b>Aromatic content. %vol.</b>	<b>Aromatic adsorbed %vol.</b>	<b>Aromatic removal (%)</b>
5	10.45	8.82	45.80
10	10.08	9.19	47.70
15	10.07	9.20	47.80
20	10.00	9.27	48.10

**Limestone**

<b>Mass (g)</b>	<b>Aromatic content. % vol</b>	<b>Aromatic adsorbed vol (%)</b>	<b>Aromatic removal (%)</b>
5	14.51	4.76	24.71
10	14.07	5.20	26.98
15	14.01	5.26	27.30
20	13.91	5.36	27.80

**Silica Gel**

<b>Mass (g)</b>	<b>Aromatic content . %vol</b>	<b>Aromatic adsorbed vol (%)</b>	<b>Aromatic removal (%)</b>
5	11.91	7.36	38.20
10	11.54	7.73	40.10
15	11.22	8.05	41.80
20	10.08	9.19	47.70

**Activated Clay**

<b>Mass (g)</b>	<b>Aromatic content % vol.</b>	<b>Aromatic adsorbed %vol.</b>	<b>Aromatic removal (%)</b>
5	10.50	8.72	45.50
10	10.12	9.15	47.50
15	10.00	9.27	48.11
20	10.01	9.26	48.10

**Limestone / Clay**

Mass (g)	Aromatic content . % vol	Aromatic adsorbed vol	(%)	Aromatic removal (%)
5	11.00	8.27		42.91
10	10.08	8.47		43.95
15	10.49	8.78		45.55
20	10.30	8.97		46.55

## APPENDIX II

### 5.3 ANALYSIS OF DPK FOR SULPHUR CONTENT BEFORE ADSORPTION

The analysis for sulphur content was before adsorption studies using oxford Lab X-3000 (x-ray method).

<b>Runs</b>	<b>Sulphur content % WTS</b>
1	0.041
2	0.042
Mean	0.042

5.3.1 Adsorption equilibria experiments for Sulphur contents of DPK at various experimental conditions

**Table 5.8: Effect of contact Time**

Mass = 10g, vol. of DPK = 100ml

#### **Oxidized Bone**

<b>Time (min)</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% sulphur removal</b>
60	0.038	0.004	9.5
100	0.034	0.008	19.0
150	0.033	0.009	21.4
200	0.031	0.011	26.2
240	0.030	0.012	28.6

#### **Carbonized Bone**

<b>Time (min)</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
60	0.041	0.001	2.4
100	0.040	0.002	4.8
150	0.039	0.003	7.1
200	0.0385	0.0035	8.3
240	0.0380	0.004	9.52

**Silica Gel (Control)**

<b>Time (min)</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
60	0.041	0.001	2.4
100	0.040	0.002	4.8
150	0.039	0.003	7.1
200	0.039	0.003	7.1

**Clay**

<b>Time (min)</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
60	0.035	0.007	16.6
100	0.033	0.009	21.4
150	0.0331	0.0089	21.2
200	0.033	0.009	21.4

**Limestone**

<b>Time (min)</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
60	0.390	0.003	7.1
100	0.041	0.001	2.4
150	0.040	0.002	4.8
200	0.043	-0.001	-2.4

**Limestone / Clay**

<b>Time (min)</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
60	0.039	0.003	7.10
100	0.038	0.004	9.52
150	0.039	0.003	7.10
200	0.0386	0.0034	8.10

**Table 5.9 EFFECT OF TEMPERATURE****Carbonized Bone**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
30	0.032	0.01	23.8
60	0.031	0.011	26.2
90	0.033	0.009	21.4
120	0.036	0.006	14.3

**Oxidized Bone**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
30	0.032	0.01	23.8
60	0.033	0.009	21.4
90	0.035	0.007	16.7
120	0.037	0.005	11.9

**Silica Gel**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
30	0.031	0.011	26.2
60	0.032	0.010	23.8
90	0.033	0.009	21.4
120	0.039	0.003	7.1

**Clay**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
30	0.033	0.009	21.4
60	0.036	0.006	14.3
90	0.037	0.007	11.9
120	0.039	0.003	7.1

**Limestone**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
30	0.041	0.001	2.4
60	0.0415	0.0005	1.2
90	0.0411	0.0009	2.1
120	0.042	0.00	0.0

**Limestone/Clay**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
30	0.035	0.007	16.7
60	0.033	0.009	21.4
90	0.0332	0.0088	20.90
120	0.0331	0.0089	21.2

**Table 5.10: Effect of Adsorbent Mass**

Vol. of DPK 100ml, Time = 1hr.

**Carbonized Bone**

<b>mass (g)</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
5	0.039	0.003	7.1
10	0.040	0.002	4.8
15	0.041	0.001	2.4
20	0.038	0.004	9.5

**Oxidized Bone**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
5	0.041	0.001	2.4
10	0.040	0.002	4.8
15	0.039	0.003	7.1
20	0.037	0.005	11.9

**Silica Gel**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
5	0.041	0.001	2.4
10	0.040	0.002	4.8
15	0.038	0.004	9.5
20	0.035	0.006	14.3

**Clay**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
5	0.040	0.002	4.8
10	0.0394	0.0026	6.2
15	0.039	0.003	7.1
20	0.0384	0.004	9.5

**Limestone**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
5	0.042	0.00	0.00
10	0.043	-0.011	-2.3
15	0.041	0.001	2.3
20	0.039	0.003	7.1

**Limestone / Clay**

<b>Temp °C</b>	<b>Sulphur content % wtS</b>	<b>Sulphur adsorbed % wtS</b>	<b>% Sulphur removal</b>
5	0.043	-0.001	-2.4
10	0.042	0.00	0.00
15	0.041	0.001	2.3
20	0.0415	0.005	1.2

**Table 5.11: Effect of pH using 0.5N HNO<sub>3</sub> and 0.1MNaOH for adjustment**

**Oxidized bone**

<b>pH</b>	<b>Aromatic content %vol.</b>	<b>Aromatic Adsorbed % vol.</b>	<b>% Aromatic Removal</b>
2	9.80	9.47	49.14
4	10.44	8.83	45.82
8	12.10	7.17	37.20
10	12.50	6.77	35.13

**Clay**

<b>pH</b>	<b>Aromatic content % vol.</b>	<b>Aromatic Adsorbed % vol.</b>	<b>% Aromatic Removal</b>
2	9.98	9.29	48.20
4	10.70	8.57	44.47
8	11.80	7.47	38.76
10	13.00	6.27	32.53

**Lime Stone**

<b>pH</b>	<b>Aromatic content % vol.</b>	<b>Aromatic Adsorbed % vol.</b>	<b>% Aromatic Removal</b>
2	14.29	4.98	25.80
4	14.50	4.77	24.75
8	15.21	4.06	21.1
10	16.00	3.27	16.96

**Silica gel**

<b>pH</b>	<b>Aromatic content % vol.</b>	<b>Aromatic Adsorbed % vol.</b>	<b>% Aromatic Removal</b>
2	10.20	9.07	47.06
4	10.70	8.57	44.50
8	12.50	6.77	35.13
10	12.90	6.37	33.05

**Table 5.12: Effect of Particle Size****Oxidized bone**

<b>Size</b>	<b>Aromatic contents vol. %</b>	<b>Aromatic adsorbed % vol.</b>	<b>% Aromatic Removal</b>
300 $\mu$ m	10.12	9.15	47.48
600 $\mu$ m	11.50	7.77	40.32
850 $\mu$ m	12.80	6.47	33.57
1.4mm	12.50	6.77	35.13

**Clay**

<b>Size</b>	<b>Aromatic contents % vol</b>	<b>Aromatic adsorbed % vol.</b>	<b>% Aromatic Removal</b>
300 $\mu$ m	10.00	9.27	48.10
600 $\mu$ m	10.80	8.47	43.95
850 $\mu$ m	11.55	7.72	40.10
1.40mm	12.50	6.77	35.13

**Limestone**

<b>Mass (g)</b>	<b>Aromatic contents %vol.</b>	<b>Aromatic adsorbed % vol.</b>	<b>% Aromatic Removal</b>
300 $\mu$ m	15.21	4.06	21.06
600 $\mu$ m	16.27	3.00	15.56
850 $\mu$ m	16.75	2.52	13.07
1.40 mm	17.00	2.27	11.77

## APPENDIX III

## 5.4 ANALYSIS OF VARIANCE (ANOVA)

ANOVA technique has been used to rank the adsorbents in the order of highest selectivity for aromatics and sulphur as follows: (see statistical analysis of adsorbents in Appendix 7)

- (a) Oxidized bone
- (b) Carbonized bone
- (c) Activated clay
- (d) Silica gel (control)
- (e) Limestone / clay mixture
- (f) Limestone

Further experiments were carried out using oxidized bone (which has the highest performance) and silica gel (as control).

**Table 5.14 AROMATIC AND SULPHUR ANALYSIS USING OXIDIZED BONE**

Mass = 20g, Vol. of DPK = 100ml

<b>Time (Min)</b>	<b>Aromatic content. % vol.</b>	<b>Sulphur content % wtS</b>
60	9.19	0.037
100	9.07	0.034
150	8.97	0.033
200	8.76	0.033
240	8.57	0.032

Mass = 40g

<b>Time (Min)</b>	<b>Aromatic content. % vol.</b>	<b>Sulphur content. % wtS</b>
60	7.00	0.0290
100	7.18	0.028
150	6.90	0.028
200	6.53	0.0279
240	6.10	0.0275

Mass = 60g

<b>Time (Min)</b>	<b>Aromatic content. % vol.</b>	<b>Sulphur content. % wtS</b>
60	4.80	0.026
100	4.30	0.025
150	4.00	0.024
200	3.80	0.021
240	3.10	0.020

Mass = 80g

<b>Time (Min)</b>	<b>Aromatic content. vol. %</b>	<b>Sulphur content. % wtS</b>
60	2.60	0.019
100	2.15	0.015
150	1.80	0.013
200	1.25	0.012
240	0.74	0.009

**Table 5.15 AROMATIC AND SULPHUR ANALYSIS USING SILICA GEL**

Mass = 20g

<b>Time (Min)</b>	<b>Aromatic content. vol. %</b>	<b>Sulphur content. % wtS</b>
60	9.00	0.038
100	8.85	0.037
150	8.30	0.032
200	8.00	0.031
240	7.65	0.029

Mass = 40g

<b>Time (Min)</b>	<b>Aromatic content. % vol</b>	<b>Sulphur content. % wtS</b>
60	7.40	0.027
100	6.85	0.026
150	5.75	0.024
200	4.85	0.0235
240	4.30	0.0231

Mass = 60g

<b>Time (Min)</b>	<b>Aromatic content. % vol</b>	<b>Sulphur content. % wtS</b>
60	4.15	0.021
100	4.00	0.020
150	3.95	0.0195
200	3.80	0.018
240	3.20	0.016

Mass = 80g

<b>Time (Min)</b>	<b>Aromatic content. % vol</b>	<b>Sulphur content. % wtS</b>
60	2.95	0.015
100	2.40	0.013
150	1.90	0.012
200	1.35	0.014
240	0.65	0.01

**Table 5.16: SUMMARY OF THE DEODOURIZED DATA FOR AROMATIC ANALYSIS**

Adsorbent – oxidized bone

Mass – 80g

Vol. of DPK – 100ml

Temperature – 30<sup>0</sup>C

<b>Time (min)</b>	<b>Aromatic content %vol</b>	<b>Amount adsorbed %vol.</b>	<b>% Aromatic removal</b>
60	2.60	16.67	86.50
100	2.15	17.12	88.50
150	1.80	17.47	90.70
200	1.25	18.02	93.40
240	0.74	18.53	96.16

Adsorbent – Silica Gel

<b>Time (min)</b>	<b>Aromatic content vol. %</b>	<b>Amount adsorbed vol. %</b>	<b>% Aromatic removal</b>
60	2.95	16.32	84.50
100	2.40	16.87	87.50
150	1.90	17.37	90.10
200	1.55	17.92	92.90
240	0.65	18.62	96.63

**Table 5.17: SUMMARY OF THE DEODOURIZED DATA FOR  
SULPHUR ANALYSIS**

Adsorbent – Oxidized bone

Mass – 80g

Vol. of DPK – 100ml

Temperature – 30<sup>0</sup>C

<b>Time (min)</b>	<b>Sulphur content % wtS</b>	<b>Amount Adsorbed % wtS</b>	<b>% Sulphur removal</b>
60	0.019	0.023	54.8
100	0.015	0.027	64.3
150	0.013	0.029	69.04
200	0.012	0.0295	70.2
240	0.009	0.033	78.6

**SILICA GEL**

<b>Time (min)</b>	<b>Sulphur content % wtS</b>	<b>Amount Adsorbed % wtS</b>	<b>% Sulphur removal</b>
60	0.015	0.027	64.3
100	0.013	0.029	69.0
150	0.0125	0.030	71.4
200	0.011	0.031	73.8
240	0.001	0.037	76.2

**Table 5.18: Kerosene properties before and after adsorption**

Properties	Before	After	
	Initial	Oxidized bone	Silical gel
Cloud point <sup>0</sup> C	-43	-47	-49
Aniline point <sup>0</sup> C	60	58.2	56
Smoke point ( mm)	22	20	19
Electrical conductivity ps/meter	340	335	326
Doctor test	-Ve	-Ve	-Ve

## APPENDIX IV

### 5.5 FITTING EXPERIMENTAL DATA TO ADSORPTION

#### MODELS

##### 5.5.1 Freundlich Adsorption Isotherm Model

It has the form;

$$q_e = K_f C_e^{1/n}$$

where  $q_e$  = amount of aromatic adsorbed per unit mass of adsorbent

$$q_e = \frac{x}{m}$$

$x$  = amount of aromatic adsorbed

$m$  = mass of adsorbent

$C_e$  = concentration of the aromatic adsorbed

$K_f, 1/n$  = Freundlich constants

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\text{or } \log \frac{x}{m} = \log k_f + \frac{1}{n} \log C_e$$

Thus, if  $\log \left( \frac{x}{m} \right)$  is plotted against  $\log C_e$ , a straight line of slope  $1/n$  and intercept  $\log K$  is obtained.

**Table 5.19: Freundlich Calculations for Aromatic and Sulphur using Oxidized Bone and Silica Gel**

**Oxidized Bone – Aromatic**

$q = \frac{x}{m}$	$C_e$	$\log \left( \frac{x}{m} \right)$	$\log C_e$
0.208	2.60	-0.682	0.415
0.214	2.15	-0.669	0.332
0.218	1.80	-0.662	0.255
0.225	1.125	-0.647	0.096
0.232	0.74	-0.635	-0.131

**Oxidized Bone – Sulphur**

$q = \frac{x}{m}$	$C_e$	$\text{Log } (x/m)$	$\text{Log } C_e$
$2.87 \times 10^{-4}$	0.019	-3.54	-1.72
$3.37 \times 10^{-4}$	0.015	-3.47	-1.82
$3.62 \times 10^{-4}$	0.013	-3.44	-1.89
$3.68 \times 10^{-4}$	0.012	-3.43	-1.92
$4.13 \times 10^{-4}$	0.009	-3.38	-2.05

**Silica Gel – Aromatics**

$q = (x/m)$	$C_e$	$\log (x/m)$	$\log C_e$
0.204	2.95	-0.69	0.469
0.201	2.40	-0.676	0.380
0.217	1.90	-0.663	0.278
0.224	1.35	-0.649	0.130

0.232	0.65	-0.633	-0.187
<b>Silica Gel – Sulphur</b>			
<b>q = x/m</b>	<b>C<sub>e</sub></b>	<b>log (x/m)</b>	<b>log C<sub>e</sub></b>
3.38 x 10 <sup>-4</sup>	0.015	-3.47	-1.82
3.63 x 10 <sup>-4</sup>	0.013	-3.44	-1.89
3.75 x 10 <sup>-4</sup>	0.0125	-3.43	-1.9
3.88 x 10 <sup>-4</sup>	0.011	-3.41	-1.96
4.0 x 10 <sup>-4</sup>	0.01	-3.39	-2.0

### 5.5.2 Langmuir Adsorption Isotherm model

$$q_e = \frac{K_L b C_e}{(1 + K_L C_e)}$$

where;

C<sub>e</sub> = equilibrium concentration

q<sub>e</sub> = amount adsorbed per unit mass of adsorbent

K<sub>L</sub> = Langmuir constant

b = Langmuir monolayer maximum sorption capacity

A plot of C<sub>e</sub>/q<sub>e</sub> versus C<sub>e</sub> indicate a straight line of the slope 1/b and an intercept of 1/K<sub>L</sub>b.

**Table 5.20: Calculations for Langmuir Model using Oxidized Bone and Silica Gel**

<b>Oxidized bone</b>		<b>Silica Gel</b>	
C <sub>e</sub> /q <sub>e</sub>	C <sub>e</sub>	C <sub>e</sub> /q <sub>e</sub>	C <sub>e</sub>
12.50	2.60	14.50	2.95
10.05	2.15	11.40	2.40
8.26	1.80	8.76	1.90
5.56	1.25	6.03	1.35

3.19	0.74	2.80	0.65
<b>Sulphur</b>			
<b>Oxidized bone</b>		<b>Silica Gel</b>	
$C_e/q_e$	$C_e$	$C_e/q_e$	$C_e$
66.2	0.019	44.4	0.015
44.5	0.15	35.8	0.013
35.9	0.013	33.3	0.0125
32.6	0.012	28.4	0.011
21.80	0.009	25	0.01

### 5.5.3 RADKE-PRAUSNITZ ISOTHERM MODEL

Radke and Prausnitz isotherm model (1972) equation is

$$q = \frac{nK_{RP}C_i}{(1 + K_{RP}C_i)^M}$$

$K_{RP}$ , is the model parameter.

At low concentration, it reduces to a linear isotherm. At high concentration, it becomes the Freundlich isotherm and for the special case of  $M = 1$ , it becomes the Langmuir isotherm.

The parameters are often determined by plotting  $\frac{1}{q}$  versus  $\frac{1}{C_i}$

**Table 5.21: Calculation for Radke-Prausnitz Model**

#### **Aromatics**

<b>Bone</b>		<b>Silica</b>	
$1/q_i$	$1/C_i$	$1/q_i$	$1/C_i$
4.8	0.385	4.90	0.338
4.67	0.465	4.76	0.416
4.58	0.555	4.61	0.526
4.44	0.800	4.46	0.741
4.31	1.35	4.31	1.54

**Sulphur**

<b>Bone</b>		<b>Silica</b>	
<b>1/q<sub>i</sub></b>	<b>1/C<sub>i</sub></b>	<b>1/q<sub>i</sub></b>	<b>1/C<sub>i</sub></b>
3,484	52.63	2,996	66.67
2,967	66.67	2,755	76.92
2,762	76.48	2,667	80
2,717	83.33	2,577	91
2,421	111	2,500	100

**5.5.4 Temkin Isotherm Model**

The linear form of the temkin isotherm model is expressed as

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln l_e$$

$$\frac{1}{b_T} = \text{adsorption potential of the adsorbent}$$

$K_T$  = Temkin constan

**Table 5.22: Calculation for Temkin Model**

**Aromatics**

<b>Oxidized Bone</b>		<b>Silica</b>	
<b>q<sub>e</sub></b>	<b>ln C<sub>e</sub></b>	<b>q<sub>e</sub></b>	<b>ln C<sub>e</sub></b>
0.208	0.955	0.204	1.08
0.214	0.765	0.201	0.875
0.218	0.587	0.217	0.641
0.225	0.223	0.224	0.300
0.232	-0.301	0.232	-0.430

**Sulphur**

<b>Oxidized Bone</b>	<b>Silica</b>
----------------------	---------------

$q_e$	$\ln C_e$	$q_e$	$\ln C_e$
0.000287	-3.96	0.000338	-4.19
0.000337	-4.19	0.000363	-4.34
0.000362	-4.34	0.000375	-4.38
0.000368	-4.42	0.000388	-4.51
0.000413	-4.71	-0.0004	-4.61

### 5.5.6 Linearized Redlich-Peterson Model for Aromatics and Sulphur

$$q_e = \frac{AC_e}{1+BC_e^n}$$

$$\ln\left[\left(\frac{C_{eq}}{q_{eq}}\right)^{-1}\right] \text{ vs } \ln C_{eq}$$

**Table 5.23: Calculation for Redlich Peterson Model**

#### Aromatics

Oxidized Bone		Silica Gel	
$\ln\left[\left(\frac{C_{eq}}{q_{eq}}\right)^{-1}\right]$	$\ln C_{eq}$	$\ln\left[\left(\frac{C_{eq}}{q_{eq}}\right)^{-1}\right]$	$\ln C_{eq}$
2.44	0.955	2.60	1.08
2.20	0.765	2.34	0.875
1.98	0.587	2.05	0.641
1.495	0.223	1.62	0.300
0.78	-0.301	0.58	-0.43

#### Sulphur

Oxidized bone		Silica Gel	
$\ln\left[\left(\frac{C_{eq}}{q_{eq}}\right)^{-1}\right]$	$\ln C_{eq}$	$\ln\left[\left(\frac{C_{eq}}{q_{eq}}\right)^{-1}\right]$	$\ln C_{eq}$
4.01	-3.96	3.77	-4.19
3.77	-4.19	3.55	-4.34

3.52	-4.34	3.47	-4.38
3.45	-4.42	3.31	-4.51
3.03	-4.71	3.17	-4.61

## APPENDIX V

### 5.5.7 Thermodynamic Model

The values of thermodynamic function  $\Delta S$  and  $\Delta H$  can be evaluated using VanHoff's equation, which is given by:

$$\text{Log } K_x = (\Delta S/2.303R) - (\Delta H/2.303RT).$$

Thus value of  $\Delta S$  and  $\Delta H$  can be calculated from the intercept and slope of plot between  $K_x$  versus  $1/T$ . Another important thermodynamic parameter is the free energy change  $\Delta G$  and can be calculated using the relation as follow:

$$\Delta G = RT \ln K_x$$

where  $K_x = C_o/C_e$

**Table 5.24: Experimental data for thermodynamic parameters**

#### Oxidized bone (Aromatics)

$C_o$	$C_e$	$K_x = C_o/C_e$	$\log k_x$	$T^\circ K$	$1/T$
19.27	0.74	26.04	1.42	303	$3.3 \times 10^{-4}$
	4.50	4.28	0.631	333	$3.0 \times 10^{-4}$
	6.49	2.96	0.473	363	$2.75 \times 10^{-4}$
	7.80	2.47	0.392	393	$2.54 \times 10^{-4}$
	9.50	2.03	0.307	423	$2.36 \times 10^{-4}$

**Silica Gel (Aromatic)**

$C_o$	$C_e$	$K_x = C_o/C_e$	$\log k_x$	$T^\circ K$	$I/T$
19.27	0.65	29.64	1.47	303	$3.3 \times 10^{-4}$
	1.50	12.84	1.11	333	$3.0 \times 10^{-4}$
	3.80	5.07	0.71	363	$2.75 \times 10^{-4}$
	6.50	2.96	0.47	393	$2.54 \times 10^{-4}$
	7.65	2.52	0.40	423	$2.36 \times 10^{-4}$

**Oxidized Bone (Sulphur)**

$C_o$	$C_e$	$K_x = C_o/C_e$	$\log k_x$	$T^\circ K$	$I/T$
0.042	0.009	4.66	0.67	303	$3.3 \times 10^{-3}$
	0.015	2.80	0.45	333	$3.0 \times 10^{-3}$
	0.025	1.68	0.23	363	$2.75 \times 10^{-3}$
	0.031	1.35	0.13	393	$2.54 \times 10^{-3}$
	0.034	1.23	0.09	423	$2.36 \times 10^{-3}$

**Silica Gel (Sulphur)**

$C_o$	$C_e$	$K_x = C_o/C_e$	$\log k_x$	$T^\circ K$	$I/T$
0.042	0.01	4.2	0.62	303	$3.3 \times 10^{-3}$
	0.012	3.5	0.54	333	$3.0 \times 10^{-3}$
	0.026	1.62	0.21	363	$2.75 \times 10^{-3}$
	0.029	1.45	0.16	393	$2.54 \times 10^{-3}$
	0.03.1	1.35	0.13	423	$2.36 \times 10^{-3}$

**Table 5.25: Entropy, Enthalpy and Free energy calculations**

Parameter	Oxidized Bone		Silical gel	
	Aromatic	Sulphur	Aromatic	Sulphur
$\Delta S$ (J/g $^\circ K$ )	-46.35	-34.50	-48.30	-25.10
$\Delta H$ (J/g $^\circ K$ )	-1,118	-12,315	-23,009	-11,259
$\Delta G$ (J/g $^\circ K$ )	5851	2,465	6832	2,562
$R^2$	0.857	0.9683	0.9783	0.9045

## APPENDIX VI

### 5.5.8 Kinetic Model

#### (a) Chiou and Li Model

First order equation is expressed as:

$$\log (q_e - q) = \log (q_e) - \frac{K_1 t}{2.303}$$

The second order model has the same principle as the first order model, although it was expressed as a function of  $q_e$ .

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

**Table 5.26: Experimental data using the first and second Kinetic model**

#### **Oxidized Bone – Aromatics**

$q_e$	$q$	Time (min)	First-order $\log (q_e - q)$	Second- order $t/q$
16.67	2.60	60	1.15	23.08
17.12	2.15	100	1.18	46.51
17.47	1.80	150	1.195	83.33
18.02	1.25	200	1.22	160
18.53	0.74	240	1.25	324

**Oxidized Bone – Sulphur**

<b>q<sub>e</sub></b>	<b>q</b>	<b>Time (min)</b>	<b>First-order log (q<sub>e</sub>-q)</b>	<b>Second- order t/q</b>
0.023	0.019	60	-2.4	3158
0.027	0.015	100	-1.92	6667
0.029	0.013	150	-1.80	11538
0.0295	0.012	200	-1.76	16667
0.033	0.009	240	-1.62	26667

**Silica Gel – Aromatic**

<b>q<sub>e</sub></b>	<b>q</b>	<b>Time (min)</b>	<b>First-order log (q<sub>e</sub>-q)</b>	<b>Second- order t/q</b>
16.32	2.95	60	1.13	20.34
16.87	2.40	100	1.16	41.67
17.37	1.9	150	1.19	78958
17.92	1.55	200	1.21	129.03
18.62	0.65	240	1.25	369.23

**Silica Gel – Sulphur**

<b>q<sub>e</sub></b>	<b>q</b>	<b>Time (min)</b>	<b>First-order log (q<sub>e</sub>-q)</b>	<b>Second- order t/q</b>
0.027	0.015	60	-1.92	4000
0.029	0.013	100	-1.795	7692
0.030	0.0125	150	-1.76	12000
0.031	0.011	200	-1.698	18182
0.037	0.01	240	-1.57	24000

**Table 5.27 First and second rate constants and comparison of coefficients**

Parameter	Oxidized bone		Silica gel	
	Aromatic	Sulphur	Aromatic	Sulphur
$K_1$	-0.0012	-0.0085	-0.0014	-0.0039
$K_2$	0.0045	0.697	0.00358	0.672
$R_{K1}^2$	0.9807	0.8048	0.9839	0.9426
$R_{K2}^2$	0.9986	0.9882	0.9981	0.9569

**Table 5.28: Langmuir isotherm parameters for aromatics and sulphur from Oxidized Bone and Silica gel**

Parameter	Oxidized bone		Silica gel	
	Aromatic	Sulphur	Aromatic	Sulphur
$K_1$	-7.25	-272.2	-8.1	-219
b	0.196	0.00025	0.20	0.00022
$R^2$	0.9982	0.9936	0.9990	0.9867

**Table 5.39: Freundlich isotherm parameter or constants for Aromatics and sulphur**

Parameter	Oxidized bone		Silica gel	
	Aromatic	Sulphur	Aromatic	Sulphur
$K_f$	0.227	$4.52 \times 10^{-5}$	0.227	$5.6 \times 10^{-5}$
1/n	-0.0843	-0.4749	-0.0851	-0.4309
$R^2$	0.9662	0.9717	0.9540	0.9933

**Table 5.31: Parameter for shape of the isotherm**

$$K_R = 1/1 + K_1 C_0$$

where  $K_R$  is a dimensionless separation factor,  $C_0$  is initial concentration and  $K_1$  is Langmuir constant. The parameter  $K_R$  indicates the shape of the isotherm accordingly.

Value of $K_R$	Type of Isotherm
$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

The value of  $K_R$  for Aromatics and Sulphur are given in the table

below:

Parameter	Oxidized bone		Silica gel	
	Aromatic	Sulphur	Aromatic	Sulphur
$K_R$	0.21	0.99	0.21	0.99

From table above,

$K_R < 1$ , showing that the isotherm shape is concave.



## APPENDIX VII

translate from = 'ben.wk1' /range a1..h30

Data written to the active file.  
11 variables and 30 cases written.  
11 of 603 storage units used.

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This procedure was completed at 22:35:42  
variable labels a 'contact time' b 'ct-group'  
c 'temperature' d 't-group' e 'absorbent mass'  
f 'am-group' g 'absortion equilibria' h 'ae-group'.  
oneway variables = a by b(1,6)  
/ranges = lsd  
/statistics = 1.

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----- O N E W A Y -----

Variable A contact time  
By Variable B ct-group

## Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	5	891.5191	178.3038	37.2927	.0000
Within Groups	24	114.7489	4.7812		
Total	29	1006.2680			

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----- O N E W A Y -----

Group Mean	Count	Mean	Standard Deviation	Standard Error	Minimum	Maximum	95 Pct Conf Int for
Grp 1 47.8725	5	46.8220	.8461	.3784	45.8000	47.8500	45.7715 To
Grp 2 48.5316	5	47.0060	1.2287	.5495	45.0500	48.0300	45.4804 To
Grp 3 47.6239	5	44.1600	2.7897	1.2476	40.0600	46.8100	40.6961 To
Grp 4 36.2637	5	31.4040	3.9140	1.7504	26.9800	36.3200	26.5443 To
Grp 5 47.1460	5	45.5060	1.3208	.5907	43.9500	47.0600	43.8660 To
Grp 6 47.1400	5	45.5620	1.2709	.5684	43.9500	47.0500	42.9840 To
Total 45.6096	30	42.4100	5.8906	1.0755	26.9800	48.0300	41.2104 To

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----- O N E W A Y -----

Variable A contact time  
By Variable B ct-group

Multiple Range Test

LSD Procedure

Ranges for the .050 level -

2.92 2.92 2.92 2.92 2.92

The ranges above are table ranges.

The value actually compared with Mean(J)-Mean(I) is..

$$1.5462 * \text{Range} * \text{Sqrt}(1/N(I) + 1/N(J))$$

(\*) Denotes pairs of groups significantly different at the .050 level

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----- O N E W A Y -----

Variable A contact time  
(Continued)

G G G G G G  
r r r r r r  
P P P P P P

Mean	Group	4	3	5	6	1	2
31.4040	Grp 4						
44.1600	Grp 3	*					
45.5060	Grp 5	*					
45.5620	Grp 6	*					
46.8220	Grp 1	*					
47.0060	Grp 2	*					

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Homogeneous Subsets (Subsets of groups, whose highest and lowest means do not differ by more than the shortest significant range for a subset of that size)

SUBSET 1

Group Grp 4  
Mean 31.4040

SUBSET 2

Group	Grp 3	Grp 5	Grp 6	Grp 1	Grp 2
Mean	44.1600	45.5060	45.5620	46.8220	47.0060

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This procedure was completed at 22:35:42  
 translate from = 'ben.wk1' /range al..h30.

Data written to the active file.  
 11 variables and 30 cases written.  
 11 of 603 storage units used.

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This procedure was completed at 22:35:42  
 variable labels a 'contact time' b 'ct-group'  
 c 'temperature' d 't-group' e 'absorbent mass'  
 f 'am-group' g 'absortion equilibria' h 'ae-group'.  
 oneway variables = c by d(1,5)  
 /ranges = lsd  
 /statistics = 1.

-----  
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----- O N E W A Y -----

Variable C temperature  
 By Variable D t-group

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	4	1028.1691	257.0423	26.0022	.0000
Within Groups	15	148.2813	9.8854		
Total	19	1176.4505			

-----  
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----- O N E W A Y -----

Group Mean	Count	Mean	Standard Deviation	Standard Error	Minimum	Maximum	95 Pct Conf Int for
Grp 1 47.7418	4	41.3375	4.0248	2.0124	36.3200	45.8000	34.9332 To
Grp 2 46.9560	4	41.5250	3.4132	1.7066	37.7200	45.7700	36.0940 To
Grp 3 27.9515	4	23.8800	2.5588	1.2794	21.0600	26.9800	19.8085 To
Grp 4 41.2305	4	37.8625	2.1166	1.0583	35.1300	40.1000	34.4945 To
Grp 5 49.0460	4	43.8775	3.2482	1.6241	40.2200	47.5000	38.7090 To
Total 41.3792	20	37.6965	7.8688	1.7595	21.0600	47.5000	34.0138 To

-----  
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----- O N E W A Y -----

Variable C temperature  
By Variable D t-group

Multiple Range Test

LSD Procedure  
Ranges for the .050 level -

3.01 3.01 3.01 3.01

The ranges above are table ranges.  
The value actually compared with Mean(J)-Mean(I) is..  
 $2.2232 * \text{Range} * \text{Sqrt}(1/N(I) + 1/N(J))$

(\*) Denotes pairs of groups significantly different at the .050 level

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----- O N E W A Y -----

Variable C temperature  
(Continued)

		G G G G G
		r r r r r
		p p p p p
Mean	Group	3 4 1 2 5
23.8800	Grp 3	
37.8625	Grp 4	*
41.3375	Grp 1	*
41.5250	Grp 2	*
43.8775	Grp 5	* *

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Homogeneous Subsets (Subsets of groups, whose highest and lowest means do not differ by more than the shortest significant range for a subset of that size)

SUBSET 1

Group	Grp 3
Mean	23.8800

-----

SUBSET 2

Group	Grp 4	Grp 1	Grp 2
Mean	37.8625	41.3375	41.5250

-----

SUBSET 3

Group	Grp 1	Grp 2	Grp 5
Mean	41.3375	41.5250	43.8775

-----

-----  
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 -----

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This procedure was completed at 22:35:42  
 translate from = 'ben.wk1' /range al..h30.

Data written to the active file.  
 11 variables and 30 cases written.  
 11 of 603 storage units used.

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This procedure was completed at 22:35:42  
 variable labels a 'contact time' b 'ct-group'  
 c 'temperature' d 't-group' e 'absorbent mass'  
 f 'am-group' g 'absortion equilibria' h 'ae-group'.  
 oneway variables = e by f(1,6)  
 /ranges = lsd  
 /statistics = 1.

-----  
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----- O N E W A Y -----

Variable E absorbent mass  
 By Variable F am-group

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	5	1230.0804	246.0161	42.5151	.0000
Within Groups	18	104.1579	5.7866		
Total	23	1334.2383			

-----  
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----- O N E W A Y -----

Group Mean	Count	Mean	Standard Deviation	Standard Error	Minimum	Maximum	95 Pct Conf Int for
Grp 1 50.2637	4	45.0500	3.2766	1.6383	40.2600	47.5900	39.8363 To
Grp 2 49.0163	4	47.3500	1.0472	.5236	45.8000	48.1000	45.6837 To
Grp 3 28.8731	4	26.6975	1.3673	.6836	24.7100	27.8000	24.5219 To
Grp 4 48.4830	4	41.9500	4.1057	2.0528	38.2000	47.7000	35.4170 To
Grp 5 49.2677	4	47.3025	1.2351	.6175	45.5000	48.1100	45.3373 To

Grp 6 47.3230	4	44.7400	1.6233	.8116	42.9100	46.5500	42.1570 To
Total 45.3978	24	42.1817	7.6165	1.5547	24.7100	48.1100	38.9655 To

-----  
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----- O N E W A Y -----

Variable E absorbent mass  
 By Variable F am-group

Multiple Range Test

LSD Procedure  
 Ranges for the .050 level -

2.97 2.97 2.97 2.97 2.97

The ranges above are table ranges.  
 The value actually compared with Mean(J)-Mean(I) is..  
 $1.7010 * \text{Range} * \text{Sqrt}(1/N(I) + 1/N(J))$

(\*) Denotes pairs of groups significantly different at the .050 level

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----- O N E W A Y -----

Variable E absorbent mass  
 (Continued)

G G G G G  
 r r r r r  
 p p p p p

Mean	Group	3	4	6	1	5	2
26.6975	Grp 3						
41.9500	Grp 4	*					
44.7400	Grp 6	*					
45.0500	Grp 1	*					
47.3025	Grp 5	*	*				
47.3500	Grp 2	*	*				

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Homogeneous Subsets (Subsets of groups, whose highest and lowest means do not differ by more than the shortest significant range for a subset of that size)

SUBSET 1

Group	Grp 3
Mean	26.6975

SUBSET 2

Group	Grp 4	Grp 6	Grp 1
Mean	41.9500	44.7400	45.0500

SUBSET 3

Group	Grp 6	Grp 1	Grp 5	Grp 2
Mean	44.7400	45.0500	47.3025	47.3500

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This procedure was completed at 22:35:42  
translate from = 'ben.wk1' /range a1..h30.

Data written to the active file.  
11 variables and 30 cases written.  
11 of 603 storage units used.

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This procedure was completed at 22:35:42  
variable labels a 'contact time' b 'ct-group'  
c 'temperature' d 't-group' e 'absorbent mass'  
f 'am-group' g 'absortion equilibria' h 'ae-group'.  
oneway variables = g by h(1,6)  
/ranges = lsd  
/statistics = 1.

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----- O N E W A Y -----

Variable G	absortion equilibria
By Variable H	ae-group

## Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	5	1355.5270	271.1054	15.9924	.0000
Within Groups	20	339.0433	16.9522		
Total	25	1694.5704			

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----- O N E W A Y -----

Group Mean	Count	Mean	Standard Deviation	Standard Error	Minimum	Maximum	95 Pct Conf Int for
------------	-------	------	--------------------	----------------	---------	---------	---------------------

Grp 1	5	20.9400	7.4363	3.3256	9.5000	28.6000	11.7068 To
30.1732							
Grp 2	5	6.4240	2.8457	1.2726	2.4000	9.5200	2.8907 To
9.9573							
Grp 3	4	5.3500	2.2457	1.1229	2.4000	7.1000	1.7766 To
8.9234							
Grp 4	4	20.1500	2.3685	1.1843	16.6000	21.4000	16.3812 To
23.9188							
Grp 5	4	2.9750	4.0648	2.0324	-2.4000	7.1000	-3.4929 To
9.4429							
Grp 6	4	7.9550	1.1449	.5724	7.1000	9.5200	6.1333 To
9.7767							
Total	26	10.8669	8.2330	1.6146	-2.4000	28.6000	7.5415 To
14.1923							

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ONEWAY

Variable G absortion equilibria  
By Variable H ae-group

Multiple Range Test

LSD Procedure

Ranges for the .050 level -

2.95 2.95 2.95 2.95 2.95

The ranges above are table ranges.

The value actually compared with Mean(J)-Mean(I) is..

$$2.9114 * \text{Range} * \text{Sqrt}(1/N(I) + 1/N(J))$$

(\*) Denotes pairs of groups significantly different at the .050 level

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ONEWAY

Variable G absortion equilibria  
(Continued)

G G G G G  
r r r r r  
P P P P P

Mean	Group	5 3 2 6 4 1
2.9750	Grp 5	
5.3500	Grp 3	
6.4240	Grp 2	
7.9550	Grp 6	
20.1500	Grp 4	* * * *
20.9400	Grp 1	* * * *

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 -----  
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SPSS/PC+

Homogeneous Subsets (Subsets of groups, whose highest and lowest means do not differ by more than the shortest significant range for a subset of that size)

SUBSET 1

Group	Grp 4
Mean	31.4040

-----

SUBSET 2

Group	Grp 2	Grp 3	Grp 1
Mean	46.6100	46.6100	48.0140

-----

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 -----  
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SPSS/PC+

This procedure was completed at 11:25:06  
 translate from = 'beno4.wk1' /range a1..f20.

Data written to the active file.  
 9 variables and 20 cases written.  
 9 of 603 storage units used.

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 -----  
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SPSS/PC+

This procedure was completed at 11:25:06  
 variable labels a 'score1' b 'group1'  
 c 'score2' d 'score3' e 'score4' f 'group2'.  
 value labels b 1 'clay' 2 'oxidized' 3 'silica gel'  
 4 'limestone'.  
 oneway variable = b c d by f(1,4)  
 /ranges = lsd  
 /statistics = 1.

-----  
 -----  
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-----  
 -----  
 O N E W A Y

Variable B group1  
By Variable F group2

## Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	11.2500	3.7500	18.0000	.0001
Within Groups	12	2.5000	.2083		
Total	15	13.7500			

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----- O N E W A Y -----

Group	Count	Mean	Standard Deviation	Standard Error	Minimum	Maximum
Grp 1	4	1.0000	.0000	.0000	1.0000	1.0000
1.0000 To	1.0000					
Grp 2	4	1.7500	.5000	.2500	1.0000	2.0000
.9544 To	2.5456					
Grp 3	4	2.5000	.5774	.2887	2.0000	3.0000
1.5813 To	3.4187					
Grp 4	4	3.2500	.5000	.2500	3.0000	4.0000
2.4544 To	4.0456					
Total	16	2.1250	.9574	.2394	1.0000	4.0000
1.6148 To	2.6352					

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SPSS/PC+

----- O N E W A Y -----

Variable B group1  
By Variable F group2

## Multiple Range Test

LSD Procedure  
Ranges for the .050 level -

3.08 3.08 3.08

The ranges above are table ranges.  
 The value actually compared with Mean(J)-Mean(I) is..  
 .3227 \* Range \* Sqrt(1/N(I) + 1/N(J))

(\*) Denotes pairs of groups significantly different at the .050 level

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----- O N E W A Y -----

Variable B (Continued)	group1				
		G	G	G	G
		r	r	r	r
		p	p	p	p
Mean	Group	1	2	3	4
1.0000	Grp 1				
1.7500	Grp 2	*			
2.5000	Grp 3	*	*		
3.2500	Grp 4	*	*	*	

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Homogeneous Subsets (Subsets of groups, whose highest and lowest means do not differ by more than the shortest significant range for a subset of that size)

SUBSET 1

Group Grp 1  
 Mean 1.0000

SUBSET 2

Group Grp 2  
 Mean 1.7500

SUBSET 3

Group Grp 3  
 Mean 2.5000

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SUBSET 4

Group Grp 4  
Mean 3.2500

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ONEWAY

Variable C score2  
By Variable F group2

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	1030.7796	343.5932	57.8336	.0000
Within Groups	12	71.2927	5.9411		
Total	15	1102.0723			

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ONEWAY

Group	Count	Mean	Standard Deviation	Standard Error	Minimum	Maximum
Grp 1	4	45.0500	3.2766	1.6383	40.2600	47.5900
95 Pct Conf Int for Mean						
39.8363 To		50.2637				
Grp 2	4	47.3025	1.2351	.6175	45.5000	48.1100
45.3373 To		49.2677				
Grp 3	4	41.4000	3.1038	1.5519	38.2000	45.5000
36.4613 To		46.3387				
Grp 4	4	26.6975	1.3673	.6836	24.7100	27.8000
24.5219 To		28.8731				
Total	16	40.1125	8.5716	2.1429	24.7100	48.1100
35.5450 To		44.6800				

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----- ONEWAY -----

Variable C score2  
By Variable F group2

Multiple Range Test

LSD Procedure

Ranges for the .050 level -

3.08 3.08 3.08

The ranges above are table ranges.

The value actually compared with Mean(J)-Mean(I) is..

$$1.7235 * \text{Range} * \text{Sqrt}(1/N(I) + 1/N(J))$$

(\*) Denotes pairs of groups significantly different at the .050 level

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----- ONEWAY -----

Variable C score2  
(Continued)

G G G G  
r r r r  
P P P P

Mean	Group	
26.6975	Grp 4	
41.4000	Grp 3	*
45.0500	Grp 1	*
47.3025	Grp 2	* *

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SPSS/PC+

Homogeneous Subsets (Subsets of groups, whose highest and lowest means

do not differ by more than the shortest significant range for a subset of that size)

SUBSET 1

Group Grp 4  
Mean 26.6975

SUBSET 2

Group Grp 3 Grp 1  
Mean 41.4000 45.0500

SUBSET 3

Group Grp 1 Grp 2  
Mean 45.0500 47.3025

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SPSS/PC+

----- O N E W A Y -----

Variable D score3  
By Variable F group2

Analysis of Variance

Source	D.F.	Sum of Squares	Mean Squares	F Ratio	F Prob.
Between Groups	3	1288.6294	429.5431	18.4549	.0001
Within Groups	12	279.3033	23.2753		
Total	15	1567.9328			

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----- O N E W A Y -----

Group	Count	Mean	Standard Deviation	Standard Error	Minimum	Maximum
Grp 1	4	43.3950	5.4069	2.7035	37.7200	49.7400
95 Pct Conf Int for Mean		34.7915 To 51.9985				

Grp 2	4	43.6925	4.0748	2.0374	38.7600	48.6200
37.2087 To		50.1763				
Grp 3	4	41.0950	5.5959	2.7980	35.1300	47.0600
32.1907 To		49.9993				
Grp 4	4	22.1325	3.9935	1.9968	16.9700	25.8000
15.7780 To		28.4870				
Total	16	37.5788	10.2239	2.5560	16.9700	49.7400
32.1308 To		43.0267				

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----- O N E W A Y -----

Variable D score3  
By Variable F group2

Multiple Range Test

LSD Procedure  
Ranges for the .050 level -

3.08 3.08 3.08

The ranges above are table ranges.  
The value actually compared with Mean(J)-Mean(I) is..  
 $3.4114 * \text{Range} * \sqrt{1/N(I) + 1/N(J)}$

(\*) Denotes pairs of groups significantly different at the .050 level

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----- O N E W A Y -----

Variable D score3  
(Continued)

G G G G  
r r r r  
P P P P

Mean	Group	4 3 1 2
22.1325	Grp 4	
41.0950	Grp 3	*

43.3950	Grp 1	*
43.6925	Grp 2	*

---

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Homogeneous Subsets (Subsets of groups, whose highest and lowest means do not differ by more than the shortest significant range for a subset of that size)

SUBSET 1

Group	Grp 4
Mean	22.1325

---

SUBSET 2

Group	Grp 3	Grp 1	Grp 2
Mean	41.0950	43.3950	43.6925

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This procedure was completed at 11:25:06

fin

End of Include file.

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